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This month's cover photograph shows workmen making final adjustments on the V-2 rocket launched May 10, 1946, at White Sands, N. Mex. Photo from a 35-mm. Kodachrome by J. M. Crowe.

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INDUSTRIAL AND ENGINEERING CHEMISTRY

REPORTS ON THE CHEMICAL WORLD TODAY

Jet Propulsion

Skin You Love to Touch. Ten-mile-a-minute fighter speeds now, 1000 mile-per-hour military planes in the future—this is what Army Air Force engineers at the Wright Field Air Matériel Command Headquarters predict as the "jet age" zooms across our horizon. In a few years, when jet planes hurtle through space at supersonic speeds, one of the factors taken into consideration will be the surface of the plane. It will have to be supersmooth in order to minimize drag.

At ordinary cruising speeds the advantage of a supersmooth surface over the conventional surface is negligible. However, at speeds approximating 600 miles per hour, a smooth skin may account for an additional 15 to 30 miles per hour, and at higher envisioned speeds the importance of minimizing drag is increased.

In the present turbo-jet plane (P-80) the aluminum alloy skin is flush-riveted so that projecting rivet heads are eliminated. This construction leaves small cavities around rivets and seams which must be filled by an inert material. Zinc chromate primer is applied over the entire surface, and a puttylike filler is spread into the cavities and seams.

In addition to these surface irregularities, the thin aluminum alloy skin has a noticeable ripple surface because it is not continuously attached to the structural framework of the plane. These bulges are minimized by applying several coats of a lacquer-base surfacer and manually sanding to satisfactory smoothness. The surface is finished with lacquer and, for supersmoothness, a conventional automobile wax finish is finally applied.

Present materials used in building up the surface are not entirely satisfactory, however, since they tend to flake off under the stress of flying. The National Advisory Committee for Aeronautics is conducting research to develop a surfacing treatment that will reduce or eliminate this maintenance requirement.

The fuel, which is the lifeblood of the jet engine, also has come in for its fair share of attention. It is popularly imagined that ordinary kerosene is used to propel a jet plane. Although this may be true in a general sense, jet fuel is a tailor-made kerosene fraction. Ordinary kerosene may have good combustion properties, but it may also possess a high freezing point which would be a serious disadvantage in either cold climate or high altitude flight. Other disadvantages are poor stability, corrosiveness, etc.

The specifications for this refined kerosene include: freezing point, no higher than −60° C.; flash point, 110° F.; distillation range, 10% evaporated at 210° C. and 90% at 254° C.; sulfur content, less than 0.2% by weight; bromine number, not higher than 3.0; viscosity, not higher than 10 centistokes at −40° C.; and no corrosion of copper strip.

Storage stability of jet fuels is being studied under extremely severe conditions. When samples have been stored over a period of time, oxidation takes place with formation of a gum sludge. Oxidation inhibitors, to be added to the fuel for the purpose of decreasing gum formation, are being investigated. Jet fuel must be stable so that only a small amount of gum formation will take place when fuels have been exposed to desert storage conditions (at Blythe, Calif.) for two years.

The higher the aromatic hydrocarbon content of the fuel, the greater the power developed in a jet engine. High heat of combustion of aromatics is the contributing factor. However, fuels of high aromaticity tend to produce more carbon and smoke upon ignition. This carbon deposit fouls the fuel injection nozzles and other parts of the jet engine combustion chamber, with resulting loss of efficiency. To achieve the proper balance between these two factors, methods for determining the aromatic components are being studied. Eventually, with the progress of jet engine research, critical fuel factors will be evaluated so that a highly efficient jet fuel will be developed.

These are a few of the chemical problems involved in AAF research projects at Wright Field. They are examples of the essential role that chemistry is playing in aiding man to move from point A to point B in the shortest possible time. F.G.S.

(Continued on page 8)

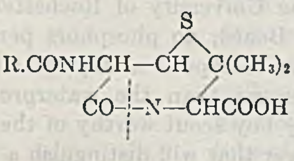
An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries

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

Biochemistry

Alphabetical Penicillin. "We have come a long way in pneumonia," says a physician in the advertisement of a pharmaceutical manufacturer. We wonder if "we have come a long way in penicillin" would not be a better way of saying the same thing. Over the past year or two real progress has been made in piecing together the molecular jigsaw puzzle of penicillin.

The chemistry of penicillin is interesting and is becoming better understood. According to the Office of Scientific Research and Development and the Medical Research Council, London, the empirical molecular-weight formula for penicillin is now confirmed to be $C_9H_{11}O_4SN_2.R$. Universal agreement has not been reached as to the structural formula, but many workers believe that the following structure, which was proposed by R. B. Woodward of Harvard University, is probably correct:



where the dotted line indicates the water-sensitive bond.

The R group is the one that has received the attention of researchers in penicillin. It is the variable in a complex compound of strong monobasic acids which have been subjected to electrometric titration, slow and rapid titration, ultraviolet and infrared absorption, studies of crystal structure by x-ray and by polarimetric and polarographic means.

Out of this work has emerged the knowledge that there are four different types of the antibiotic and, as might be expected, one type has been found to have an edge on or lead over the rest in efficiency. That type is G, and today approximately 90% of all penicillin produced is of that designation. Other types are F, dihydro F, K, and X. Type X is the penicillin of the early war days and the surface mold culture technique, which has been largely succeeded by the deep tank method. They are chemically identical except for the R group which, in the instance of type G, is benzyl and which has been determined in X penicillin as *p*-hydroxybenzyl. In type K the R is represented by *n*-heptyl; in type F it is Δ^2-pentenyl $(—CH_2CH{=}CHCH_2CH_3)$. The variable in dihydro F penicillin is *n*-amyl.

Only those engaged in the work truly appreciate the effectiveness of penicillin as represented by type G. The old type X was not retained in the patient's blood stream long enough to make its effectiveness fully felt against infection. The present type G, on the other hand, is retained as much as 75 to 100% in the body, as shown by its recovery in the urine. From a clinical standpoint it is the most desirable of the four types.

Type K is not retained satisfactorily by the body, but work has been carried on in an effort to make these other penicillins of value in the treatment of various infections. Body fluids have been found to destroy as much as 70 to 80% of the K factor. No clinical work has been conducted with the F type penicillins, but they appear to have possibilities. H.W.S.

(*Continued on page 10*)

Better Natural Rubber. The plantation interests in rubber may be watching synthetic developments with open-eyed concern, but they are at the same time doing something about it. They are engaged in long term research programs designed to improve the qualities of natural rubber, to work out more efficient systems of tapping, and to mitigate the scourge of leaf diseases. In Ceylon, third largest producer after Malaya and the Netherlands East Indies, the work continued during the war while we were scurrying around for heat exchangers and alcohol.

Both Malaya and Ceylon prepared a new form of softened natural rubber, and Ceylon engaged in a program of selective tree breeding with a view toward getting more plastic rubbers. Research was also pushed on the prevention of tackiness in crepe rubber, and it is reported that this effect can be completely arrested with the addition of small amounts of sulfur and phenyl-β-naphthylamine. Thus, the natural rubber interests show that their concern over the synthetic threat is real. Recent press dispatches tell us that the foremost question of the Ceylonese now is, "Will synthetic rubber production wipe out demands for natural rubber?" Some are so dubious they feel the question is more properly, "When will it happen?" H.W.S.

Fungicides. When science took up the battle against destructive fungi, it faced an enemy possessing some of the worst attributes of two other material-destroying plagues—corrosion and insects. The quiet malignant attack of fungi upon seeds, plants, fabrics, and foods is not unlike, in effect, the corrosion of a metal and its subsequent mechanical weakening. On the other hand, fungi spread through the air on dust particles and spray, or are transmitted by animal or man; consequently they present some of the same problems found in defending a material against the ravages of insects or microbes.

The destructive effect of fungi on the host material is believed to be due to their sapping nutrition from it; this action results in a breakdown of the chemical and mechanical structure of the material. The role of the fungicide is not quite clear, but because of its molecular shape, it is probably able to block off the addition of any "food" material to the fungus and, thereby, keep the latter in a dormant state or kill it entirely.

The vast majority of fungicides can be classified as metallic-inorganic (usually heavy metal), metallic-organic, and organic. Copper, perhaps more than any other single chemical element, has been the backbone of modern fungicides, mostly in the form of Bordeaux mixture. Unfortunately, however, this preparation has a deleterious action upon some plants; it results in leaf injury and russeting of such fruits as pears and apples. Because of this undesirable effect much effort has been spent in a search for a copper-base spray that will provide adequate protection without harm to vegetation. Copper carbonate was introduced as a dust treatment for the control of wheat bunt; copper oxides have enjoyed considerable use as soil and seed disinfectants.

(*Continued on page 14*)

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

Organic Technology

Oil-soluble copper compounds, such as the naphthenate and oleate, were successfully used by the Army's Quartermaster Corps in the battle against cellulose-destroying fungi that attacked tentage and other fabrics during the tropical campaigns of the recent war.

The U. S. Army Engineer Board tested many fungicides in a tropical testing chamber at Fort Belvoir, Va., and adopted a highly effective leather preservative based on *p*-nitrophenol. They also developed a novel method for the protection of optical instruments through the use of radium-containing foil encircling each lens element. Foil similar to that utilized in the infrared metascope viewer (described in the report "Phosphor Facts" page 16) is employed, with about $^{1}/_{16}$ inch of foil width per inch of lens diameter; this provides complete antifouling protection for optical surfaces up to 3 inches in diameter. Foil containing 15 micrograms of radium per square inch is used. (This development resulted from the observation that the cork supports in the metascope did not become fungus-infected when put into tropical use.) *m*-Cresyl acetate, a volatile fungicide prepared in capsule form with ethylcellulose, also was used for military optical instruments, but had the disadvantage of accelerating metal corrosion.

In general, mercury derivatives of an organic nature were found to be less harmful to seeds and plants than the straight inorganic mercuric compounds. Ethyl mercury phosphate and chloride, for instance, have rendered excellent service as agricultural fungicides; their high efficiency and low solubility make them adaptable to dusting grain seeds and protecting lumber against the sap-stain fungus.

Modern air conditioning brought with it the problem of preventing the growth of fungi around door and window sashes in the moisture that tends to accumulate there. This obstacle was overcome in many cases by the use of phenyl mercury oleate as fungicide.

Zinc and ferric dimethyldithiocarbamates are proving superior to copper and sulfur compounds in the control of a number of plant diseases. The ferric compound is used in the treatment of cedar rust in apples, pear scab, brown rot of sweet cherries, and blue mold of tobacco. It has also been successfully used with lead arsenate in oil sprays to control the codling moth and apple scab, both plagues to the apple farmer.

The zinc salt shows promise as a weapon in the battle against the early and late blights of potatoes, and for the control of tomato anthracnose. Applied with a waterproofing agent, this compound has also served well as a fungicide for textiles; it protects without any toxic danger to the user.

Although several attempts have been made to use direct chemical therapy and immunizing agents upon the plant to cure and prevent its diseases, nothing of note has been accomplished along these lines.

Perhaps the day is not too far off when we shall be able to "vaccinate" our plants, and not have to nurse them through their growing pains. R.L.D.

(*Continued on page 16*)

Phosphor Facts. A list of the chemicals that are important in present day infrared research vividly emphasizes the practical potentialities of academic research results. Even one well versed in the chemical field could not be blamed for considering ytterbium, samarium, columbium, germanium, europium, thallium, and lanthanum as little more than the playthings of the scientific longhairs. Yet these and more common elements, such as cerium, selenium, and beryllium, have proved to be critical constituents of infrared-sensitive phosphors.

Phosphors are important components of the metascope and sniperscope, outstanding examples of two types of infrared equipment that proved highly effective in the latter stages of the war. Especially in the metascope, developed by the University of Rochester for the U. S. Army Engineer Board, do phosphors perform a critical function. The metascope is a tiny, plastic-cased instrument scarcely larger than the waterproof match case coveted by every boy scout worthy of the name. Essentially it is a viewer that will distinguish a point source of infrared radiation, such as an infrared flashlight, by reflecting the light on a phosphor screen that translates it into visible light.

A large share of the credit for the development of the metascope goes to Franz Urbach, who came from Nazi Germany in 1939 with an immense knowledge of the subject to become a refugee professor at the University of Rochester. The head of the school's Institute of Optics, Brian O'Brien, had already suggested to the National Defense Research Council that infrared research be undertaken; consequently when O'Brien discovered on his own campus a man who possessed much of the know-how for such an investigation, things began to happen.

The infrared developments with which Urbach had been associated in Germany were handicapped because the sensitivity of the phosphors then known dropped greatly as temperatures rose to values common in the tropics. Substantial advances were made here in overcoming this limitation, and the American instrument was fully effective, even in the torrid Pacific theater of operations.

The mechanism of phosphorescence depends on the fact that some molecules possess electrons which can be made to jump out of their normal structural positions into "electron traps". When material so energized is "tripped" with an appropriate stimulator—in this case, infrared radiation—these electrons return to their normal positions and, in doing so, emit visible light. The trick in the research problem was to get a phosphor that would respond immediately to the stimulus of infrared rays and be sensitive, yet immediately cease glowing when the long-wavelength light no longer fell upon it. The phosphor adopted for the metascope consists of strontium selenide to which are added trace proportions of cerium and samarium. These last two materials are almost completely responsible for the special optical characteristics of the resulting phosphor.

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

Infrared Research

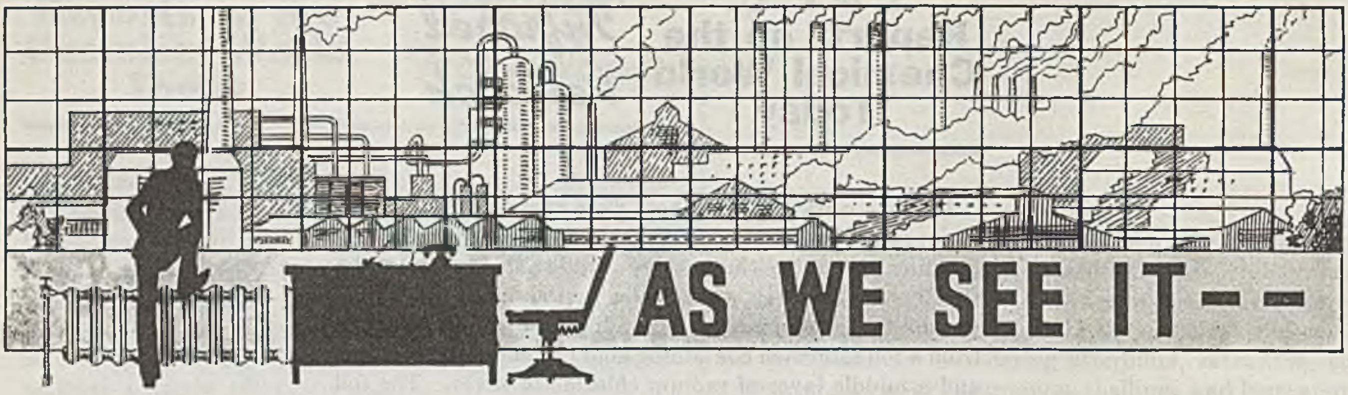
In early work the phosphors were energized with ultraviolet radiation. Later it was accidentally discovered that certain phosphors had three times their ultraviolet threshold sensitivity when alpha particles were used. In the military instrument alpha radiation is neatly supplied from a foil sandwich containing gold top and bottom layers and a middle layer of radium chloride in silver. The foil is coated on both sides with a silver chloride deposit to prevent radon from seeping out, Radon, the radioactive gaseous disintegration product of radium, produces undesirable flashes or sparks when it contacts the phosphor surface.

The sniperscope operates on a principle differing from that of the metascope. It consists of an infrared searchlight, which illuminates the field of view, and a viewer. Rays reflected from the searchlight-illuminated area strike a cesium oxide photo surface, which emits electrons at a rate proportional to the intensity of infrared light striking it. These electrons are electronically focused on a willemite screen essentially similar to the vacuum image tube of present day television sets. This system, on which the basic scientific research was done by Radio Corporation of America and Farnsworth Television & Radio Corporation, possesses the sensitivity and definition necessary for such uses as gun-aiming devices.

An eye-opening variety of military infrared devices utilizing these research discoveries has been developed by the Engineer Board, Fort Belvoir, Va. Examples are the sniperscope and combinations (type Z binoculars) for night driving of vehicles.

The research on phosphors has been tremendous: over 14,000 compositions have been investigated by Urbach alone, and many additional thousands have been studied at Brooklyn Polytechnic, the RCA, the New Jersey Zinc laboratories, and elsewhere. Urbach believes that the potentialities of the systems studied have been fairly well exploited by now. Present research on the principles embodied in the sniperscope and metascope is slanted toward attainment of a better fundamental understanding of the phenomena, and some progress is being made. Practical postwar uses for the development will depend on how well American industry answers the challenge of finding worthy jobs for these particular children of war.

D.O.M.



AS WE SEE IT- -

Particle Size. We are indebted to the Twelfth Chemical Engineering Symposium of the A.C.S. Division of Industrial and Engineering Chemistry, held at Brooklyn Polytechnic Institute last December, for six articles on particle size that are now appearing in print after some postpresentation rewriting and the usual reviews. Through an editorial operation more analogous to segregation than to size reduction, the six papers have been divided between the July Industrial and the June Analytical Editions. The three presented in this issue are by C. E. Berry, of Du Pont, on modern fine-grinding equipment, by Henry Green, of Interchemical Corporation, on avoiding some pitfalls in particle size evaluation by microscope examination, and by Doty and Mark of Brooklyn Poly on determining size and shape of polymer molecules in solution. The three articles that appear in the most recent Analytical Edition are concerned with measurement of particle size. The first, by Jacobsen and Sullivan of National Lead, is about a centrifugal sedimentation method; the second, by Bailey of Du Pont, treats of particle size measurement by spectral transmission; the third, by Pechukas and Gage of Pittsburgh Plate Glass, concerns measurement of specific surface by gas permeability.

L. T. Work, who arranged the program, contributed a brief general discussion during which he commented as follows on the particularly important operation of fine grinding: "The energy requirements, particularly for fine grinding, are an important consideration. Long before the beginning of this century, the laws of Kick and of Rittinger were propounded to define this energy. The former indicated that it was a function of the work of deformation to produce fracture, and this seemed to fit in coarse crushing. The latter indicated that it was proportional to the new surface produced, and that appeared to be the case in fine grinding. However, accurate measurement below sieve size was scant, and it was not until the past fifteen years that information became more definite. Calculations of surface energy for new surface produced show that this is but a small part of the energy used in a ball mill. This is confirmed by calorimetric study whereby it is shown that most of the energy is dissipated as heat. Yet some work done by Martin in England seems to indicate reasonably good adherence to Rittinger's law in ball mill grinding.

"The great divergence of materials in their reduction characteristics has been studied in the design of mills and their capacity ratings. There are standard tests of grindability which give an improved basis for this estimation. No longer is it necessary to make production runs on a coal to establish that an 8-ton-per-hour capacity with bituminous coal becomes 3 tons per hour to reduce an anthracite coal to combustible fineness. This does not, however, yield all the answers. Ball mill packing as a function of moisture or of the character and fineness of the material may still vitiate all the calculations."

The three articles presented in this issue attempt to cover only a small fraction of the large fields of operations relating to particle size. However, we believe you will find them informative discussions of the subjects they consider.

Penicillin Pilot Plant. The public has become well acquainted in the past year or so with the far reaching medical potentialities of penicillin. Familiar, too, is the saga of bold risks taken in telescoping what would normally be years of process development into months or even weeks under the terrible stress of war. Our lead-off article this month, "Pilot Plant Equipment for Submerged Penicillin Production", by Stefaniak, Gailey, Brown, and Johnson of the University of Wisconsin, presents satisfyingly substantial fare to those interested in the technical aspects of the outstanding penicillin process. The paper reports on production in a pilot plant with a tank capacity of 100 gallons. The authors tell us that test yields have, for over a year, been consistently better than those generally obtained industrially; one of our reviewers commented that the data should be of great potential value to producers of penicillin.

Chemical production by means of processes utilizing living organisms has received serious scientific attention only in relatively recent years. The potentialities of the method are fast receiving recognition, however, and it will not surprise us to find many more contributions in this field in the future.

Brown points out in his monthly column how very small proportions of alloying elements have marked effects on the properties of steels. The use of steel scrap in making new steel has brought about an increase in the amount of these minor constituents in many present day metals, and Brown thinks the design engineer should take advantage of the improved physical properties that have resulted.

Munch devotes most of his column to a description and drawing of a bellows-type absolute pressure gage. He reports that instruments of this design are available for pressure ranges as low as 0 to 20 mm. of mercury, with a claimed sensitivity of one five-hundredth of the range and an accuracy of one three-hundredth. He also makes brief mention of a small slide-rule calculator for selecting control valves of the proper size for a given use, and calls attention to a catalog offering sight flow devices for conventional and unusual applications.

Murdock continues the subject of the special problems encountered when industrial waste is discharged through municipal sewage systems, which he started last month. If you tuned in late on this item, we suggest you read both articles. This month's discussion is a logical sequel to June's more generalized presentation; here he goes on to a consideration of critical concentrations and volumes in specific waste problems.

Von Pechmann takes up the timely question of foreign trade. He points out that special knowledge of regulations, preferences, and customs in the market regions and the details of ocean shipment procedures are essential if the exporter expects to hold his own. Sources of such information are given.

The Editors

INDUSTRIAL AND ENGINEERING CHEMISTRY
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Editorials
WALTER J. MURPHY, EDITOR

Our Stake in Fundamental Research

THE dramatic story of the atom bomb brings home to informed Americans the startling and thoroughly disturbing fact that a large proportion of the advances in pure or fundamental research, not only in physics, but in biology, chemistry, medicine, and in practically every field of science, has been made by citizens of other countries. Comparison with any one other country will indicate that the United States has played a very significant role in the forward march of science, but when the rest of the world is lumped together, we find that the contributions in pure science coming out of our research institutions compare unfavorably in number with the total reported in the scientific journals devoted to the fundamental sciences.

When we consider advances in applied and industrial research, the opposite is true—America is in a most enviable position.

There must be reasons why the United States lags, so to speak, in fundamental research and excels in the practical application of basic scientific principles. Some explain this phenomenon by saying that it is wholly a matter of temperament, that Americans are more practical minded, seek immediate and tangible results, are more gadget conscious, and more interested in the profit motive. Such an indictment, if it be an indictment, may well be true, but it is not the complete explanation.

The period when the pure scientist labored incessantly and unceasingly solely for the love of science, unmindful and uninterested in the material things of life, is past, if indeed it ever existed other than in fiction. True, in the past there have been men and women who have made notable discoveries and have cared little or nothing about remuneration other than that obtained from the satisfaction of knowing that they have contributed to the advancement of the sum total of the world's scientific progress. In the future, too, there will be men and women motivated solely by these lofty ideals, who will feel that recognition by their contemporaries as outstanding geniuses is entirely satisfactory compensation, but, as it has been in the past so will it be in the future—the number of such individuals will constitute but a very small minority. The wife of the scientist is as desirous of a nice home, a fur coat, an expensive automobile as is the wife of the banker, manufacturer, lawyer, or doctor. The scientist is as keen to see his children receive the benefits of a good education as is his neighbor.

The main reason we do not develop more top-flight scientists in fundamental research is not that our young men and women do not possess the necessary qualifications nor that they do not desire to follow such paths, but that the practical reward—the monetary return—is uncertain. Many do, of course, receive satisfactory remuneration and recognition, but the number is relatively small.

America must awaken to the danger inherent in such a situation. Unless quick progress is registered in the establishment of a United Nations Organization, or some such organization at the international level which guarantees the future peace of the world, research inevitably will be forced to go behind closed doors. In this day and age science and warfare are so intimately wedded that, unless the possibility of war is eliminated entirely, the free exchange of scientific information will be stopped abruptly by the military. If, unhappily, the trend of future events is in the direction of war, America will no longer have full access to the fundamental research of the scientists of other nations, but will have to depend solely upon its own efforts for the basic contributions that always precede the development of practical applications.

Whether the future history of the world is one of permanent peace or frequent and violent struggles of one group of nations against another group, America must understand the importance of fostering fundamental research on a much greater scale than heretofore. Bush, Conant, and many others have called attention to this problem again and again. Encouraging signs indicate that we are aware of the necessity of doing something practical. Several plans for the establishment of a National Science Foundation by the Federal Government are before Congress. One phase of this work would call for federal support of capable and deserving students. Other organizations, including the AMERICAN CHEMICAL SOCIETY, are making money available for a limited number of students in predoctoral and postdoctoral courses; many industrial concerns are likewise devoting considerable sums for scholarships of one kind or another. Our armed forces are now fully cognizant of the necessity of supporting in a major way both applied and fundamental research programs. In the aggregate, however, we do not have enough money available to assist a sufficient number of students, nor have we as yet created in this country enough organizations devoted solely to the pursuit of fundamental scientific knowledge.

When we do all these things we still will not have guaranteed the future success of a broad plan of research in fundamental science.

Correspondent Eddy Gilmore, recently returned from Russia, reports that heavy emphasis—heavier than on any other single field—is being placed on science in Russia. "Always respected," he goes on to tell us, "scientists now have been raised several stations beyond any position they've ever enjoyed." They are, in his words, "on a level with the top brackets." The Russian Government is building new laboratories, is finding new equipment, is giving them the green light they need. "In fact," says he, "whatever scientists want they can have for the asking."

American scientists, both those engaged in fundamental and in applied research, do not ask to be pampered, to be set apart, to be recognized as a special class, but they do seek a reasonable amount of remuneration and recognition, commensurate with the contributions they make to the general welfare of the country. It is just good common sense. Indeed, it is imperative that they receive their just rewards. Otherwise the future of the country is dark and uncertain.

Pilot Plant Equipment for
SUBMERGED PRODUCTION OF

J. J. STEFANIAK, F. B. GAILEY,
C. S. BROWN, AND M. J. JOHNSON
University of Wisconsin, Madison, Wis.

THE development of corn steep liquor-lactose media by the Northern Regional Research Laboratory (*5*) and the isolation of improved penicillin-producing cultures at that laboratory (*6*) and elsewhere made possible large scale penicillin production by the submerged culture procedure. When tank fermentations were first tried, penicillin yields were often very low. It was necessary to determine the proper medium, aeration level, and operating procedure. Aeration and agitation were often found to be critical. In this laboratory experimental fermentations were carried out in 100-gallon tanks. Some data on the chemical changes during fermentation in these tanks were given by Koffler *et al.* (*4*). The effect of variations in steep liquor concentration was reported by Bowden and Peterson (*1*). The present paper deals with the design of equipment, the operating procedure, and the effect of variations in aeration and agitation. Some experiments on metal toxicity are also reported. Another paper (*2*) describes the results obtained by the use of various penicillin-producing cultures. The cultures for the experiments here reported are the following: *Penicillium notatum* NRRL 832, *P. chrysogenum* NRRL 1951-B25, *P. chrysogenum* X-1612 (Carnegie), and *P. chrysogenum* Q176 (Wisconsin). Data on these cultures and on the methods used for their maintenance and propagation are given elsewhere (*2*).

FERMENTATION EQUIPMENT

The equipment includes a tank for producing inoculum (Figure 1), two fermenters (Figure 2), and accessory equipment. Figure 3 is a flow diagram of the apparatus.

The inoculum tank (Figure 1), which has a total volume of 115 liters, is 16 inches in inside diameter and 36 inches long, with a full length jacket. The working capacity of the tank is 68 liters of medium. It is stirred at 360 revolutions per minute by means of a two-blade stirrer 12 inches in diameter, mounted on a central shaft 2 to 3 inches above the sparger which is located 2 inches above the bottom of the tank. A baffle plate minimizes coning. The aerator is a 9-inch square sparger and has sixteen holes, $^1/_{32}$ inch in diameter. These holes are countersunk in order to shorten the bore of the hole.

One of the accessory pieces of equipment (3, Figure 3) is a small tank for measuring the inoculum. This cylindrical tank has three outlets located at levels such that 5, 10, or 20 liters can be measured.

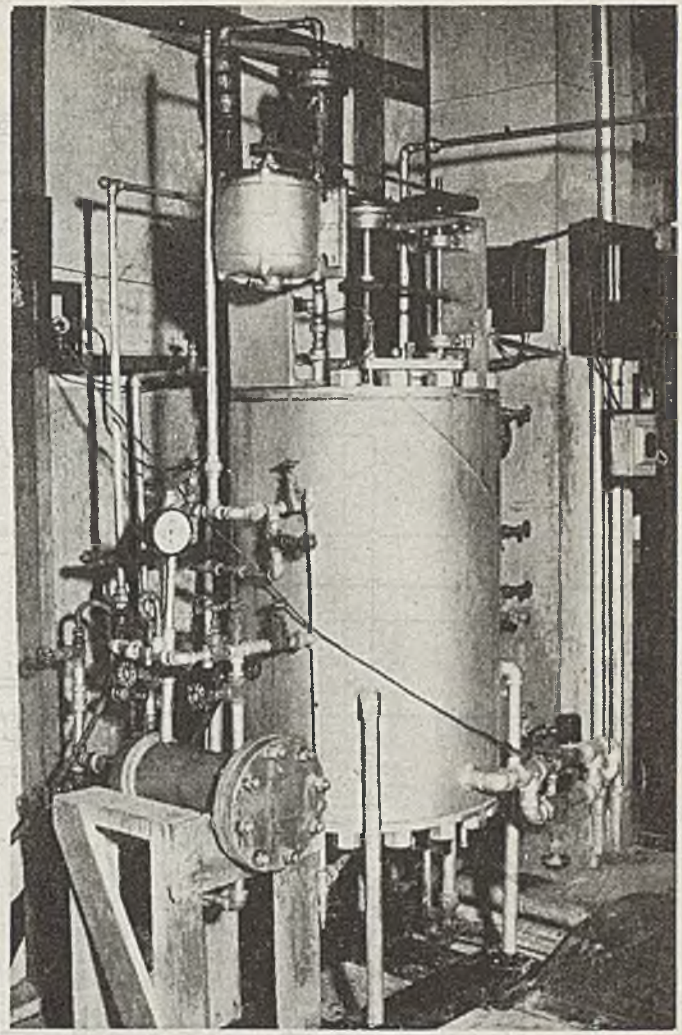
The two 100-gallon fermenters (Figures 2 and 3) were not designed for penicillin fermentations, but accessory equipment, such as antifoam vessels and air filter, was designed and constructed to meet the conditions of this fermentation. The two fermenters are identical in construction; Figure 4 shows one of them in detail. Inside the fermenter are a sparger, an agitator, a baffle, and an electrode. The sparger, a 12-inch square, is made of $^3/_8$-inch stainless steel pipe and standard pipe fittings. It contains 54 holes $^1/_{32}$ inch in diameter on its upper side. These holes are also countersunk. The agitator, which is 18 inches in diameter, runs at 270 r.p.m. and consists of two flat blades, 2.5 × 5 inches in size, set at a pitch 30° from the horizontal. The pitch is such that rotation of these blades impels the medium upward. The agitator is located 6 inches above the bottom of the tank, and the sparger is 2 inches below the agitator. The baffle plate, 6 inches wide and 22 inches long, is welded to the thermostat well. This baffle aids aeration and minimizes coning. A jacket for temperature control covers the lower half of the tank.

The air for aerating the medium is supplied by a service line at 85 pounds per square inch gage. To eliminate line fluctuations, the service line pressure is reduced to 50 pounds per square inch gage before the air is sterilized by passage through a cotton filter. Air sterilizing filter 10 (Figure 3) consists of an 11-inch length of 3-inch pipe (packed length, 9 inches) and is packed with 9 ounces of nonabsorbent cotton. During sterilization steam is circulated through the jacket of filter 10, through the cotton filter, and finally through the pipe lines connected to the sparger. Condensate formed in the jacket is drained before the steam is passed through the cotton. A steam pressure differential between jacket and filter prevents wetting of the cotton.

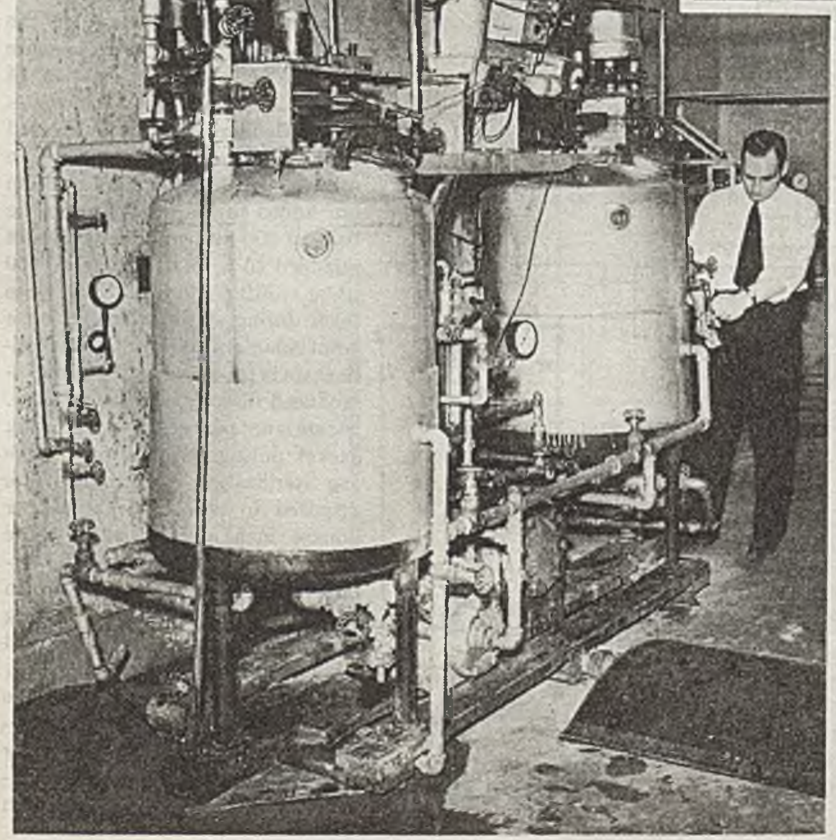
Antifoam agent is added automatically by the arrangement shown in Figure 3. Jacketed vessel 12, containing antifoam agent, is mounted directly above the fermenter. This vessel is filled through standpipe 13 and two valves 15 and 16. The internal construction of the vessel is shown in Figure 5. The antifoam agent is sterilized by passing steam through the jacket at a pressure of 25 pounds per square inch gage. The condensate is drained through steam cock 17. The automatic mechanism and the fermenters are sterilized simultaneously. Throughout sterilization, steam from the fermenter, at 15 pounds per square inch, is passed through lower magnetic valve 14*b*, through chamber 19, through upper magnetic valve 14*a*, and finally out of valve 18 at the lower end of the standpipe. During fermentation, the vessel and the chamber are connected to the sterile air line at a point between the check valve and the rotameter. The pressure in the jacketed vessel and the chamber, therefore, always exceeds the pressure in the fermenter by an amount equal to the pressure drop through the sparger. The antifoam agent is added as needed through the chamber and magnetic valves which are controlled by a relay connected to a foam-detecting electrode. When the foam level is below the electrode level, upper magnetic valve 14*a* is open, and the antifoam agent fills chamber 19. Lower magnetic valve 14*b* is closed. When the foam level reaches the electrode, lower magnetic valve 14*b* is opened and upper valve 14*a* is closed by a relay. The air under pressure in the line leading to the chamber blows the antifoam agent into the fermenter. The foam-detecting electrode consists of a Pyrex tube extending about 6 inches down into the tank. The lower end of the tube bears an electrode made from a standard $^1/_4$-inch pipe cap sealed to the flared ends of the tube by means of babbitt metal. A copper wire passes through the tube and is embedded in the babbitt metal.

PENICILLIN

Equipment for production of penicillin in 100-gallon tanks is described. Accessory equipment includes an inoculum tank, air filters, and agitators. With this equipment penicillin yields could be reproducibly obtained of more than 200 units per ml. with culture 1951-B25 (NRRL) and more than 400 units per ml. with culture X-1612 (Carnegie). An aeration rate of one volume of air per minute per volume of medium was found optimal. Agitation was essential. Metal toxicity experiments with *Penicillium notatum* 832 showed that aluminum and Allegheny metal were nontoxic whereas iron exhibited slight toxicity. A total iron content of 500 micrograms per ml. or more in the fermentation medium lowered penicillin yields in shake flasks.



↑ Figure 1. Inoculum Tank and Accessory Equipment

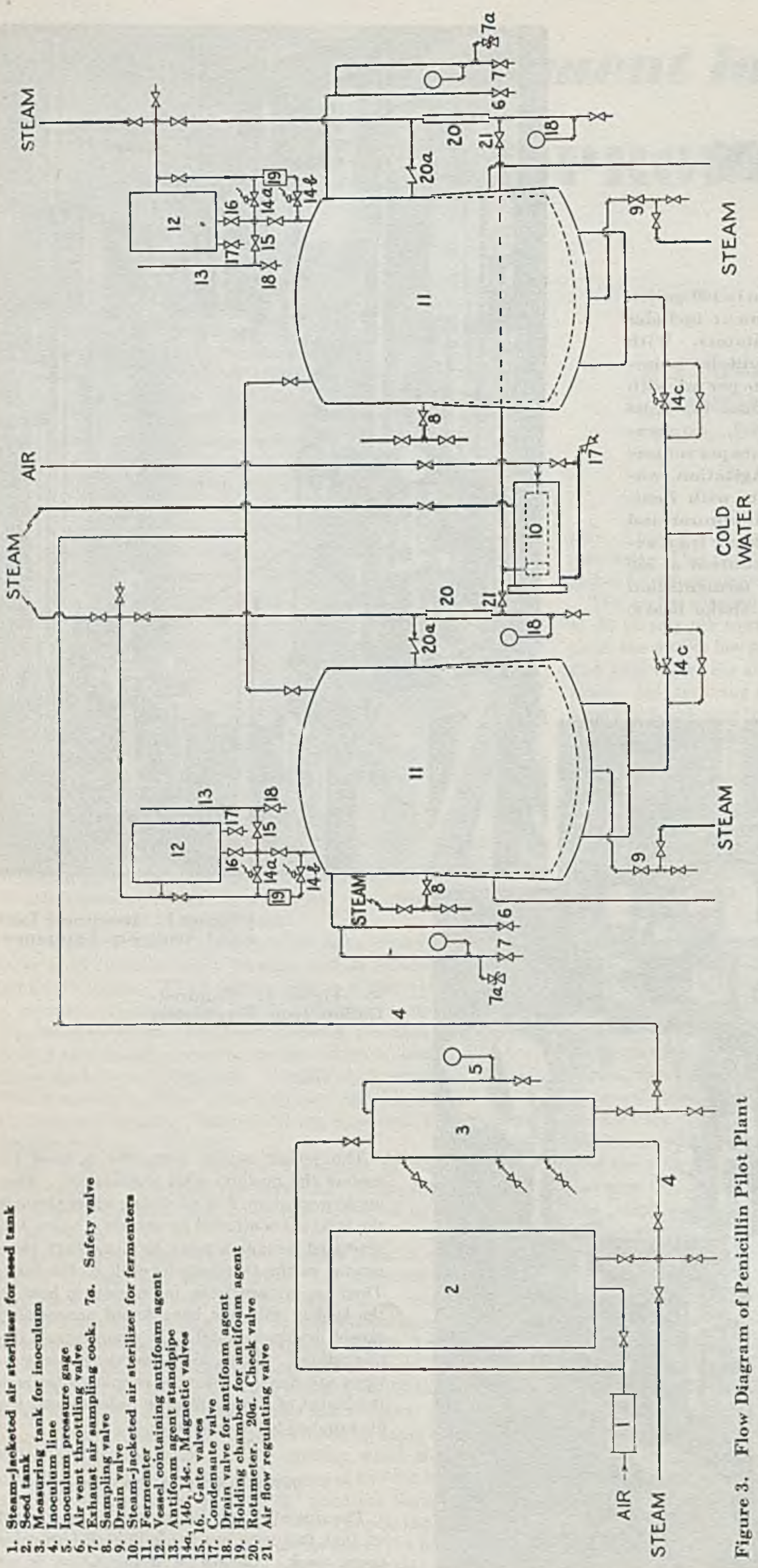


←Figure 2. Hundred-Gallon Iron Fermenters

The jacket of the fermenter is used for cooling the medium after sterilization. During fermentation, flow of cooling water through the jacket is controlled by magnetic valve 14c, activated through a relay by a mercury thermostat in the thermometer well of the tank. There is no provision for supplying heat to the tanks; this has been found unnecessary except in experimental high temperature fermentations. When high operating temperatures are desired, steam is circulated through the jacket of the air filter in order to heat the air supplied to the fermenter.

OPERATING PROCEDURES

The operation of the fermenters is planned so that two runs are made in each fermenter every week. Length of fermentation is set



1. Steam-jacketed air sterilizer for seed tank
2. Seed tank
3. Measuring tank for inoculum
4. Inoculum line
5. Inoculum pressure gage
6. Air vent throttling valve
7. Exhaust air sampling cock. 7a. Safety valve
8. Sampling valve
9. Drain valve
10. Steam-jacketed air sterilizer for fermenters
11. Fermenter
12. Vessel containing antifoam agent
13. Antifoam agent standpipe
14a, 14b, 14c. Magnetic valves
15, 16. Gate valves
17. Condensate valve
18. Drain valve for antifoam agent
19. Holding chamber for antifoam agent
20. Rotameter. 20a. Check valve
21. Air flow regulating valve

Figure 3. Flow Diagram of Penicillin Pilot Plant

at 72 hours; this allows a period of 12 hours for cleaning and setting up the fermentors. During fermentation the inoculum is prepared for the succeeding run.

Inoculum. For production of inoculum, bottle spore plates are inoculated from soil stocks and incubated 4 days at 23° C. After 4 days' growth the spore plates are placed in a refrigerator and used as needed within the following two weeks. An aqueous spore suspension from one plate is used to inoculate two shake flasks, each containing 100 ml. of medium 1 (Table I). Meanwhile, medium 2 is sterilized in the inoculum tank. The sterilization and operation procedures for this tank are similar to those used for the fermenters, except that the heating and cooling periods are shorter. After the shake flasks have been incubated at 23° C. for 24 hours, their contents are transferred to the inoculum tank. The inoculum is grown in this tank at 23° C. for 36 hours with an aeration rate of 100 liters per minute. At 36 hours the growth is heavy and has the consistency of paper pulp. Generally, 50% of the glucose in the inoculum medium has been fermented. Twenty liters of this growth are blown to the measuring tank and then through pipe line 4 (Figure 3) to a fermenter.

Fermenter. While the fermenters are being cleaned, the antifoam agent is sterilized because a long period of sterilization (4 hours) is necessary for this material. Medium 3 is normally used in the fermenters (Table I). The solid constituents of the medium are added to the fermenter on the basis of 200-liter volume, and water is added to a total volume of 150 liters. Fifty liters of condensate form during sterilization, giving a total volume of 200 liters. This condensate is produced by the steam introduced directly into the medium. Steam is not passed through the tank jacket during sterilization. During sterilization 42 minutes are required to obtain 15 pounds per square inch gage steam pressure within the fermenters. This pressure is held for 25 minutes, at which time the steam is shut off; cooling water is run through the jacket, and an air pressure of 10 pounds per square inch is maintained within the fermenter. A total of approximately 112 minutes is required for sterilization and cooling. The agitators are in continuous operation

TABLE I. MEDIA USED IN FERMENTATIONS, IN GRAMS PER LITER

Constituents	Medium 1 (Shake Flasks)	Medium 2 (Inoc. Tank)	Medium 3 (Fermenter)	Medium 4 (Fermenter)
Dextrin	60	....	..	....
Glucose	..	40	..	....
Lactose	..	....	30	20
Corn steep solids	20	20	40	20
Sodium nitrate	..	3	..	3
Potassium phosphate, monobasic	..	0.5	..	0.5
Magnesium sulfate	..	0.125	..	0.125
Calcium carbonate	..	5	10	1.8

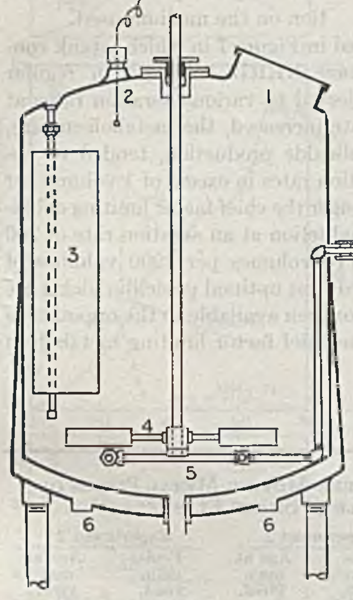


Figure 4. Fermenter Assembly

1. Handhole
2. Foam-detecting electrode
3. Baffle plate
4. Agitator
5. Sparger
6. Cold water inlets

during sterilization, cooling, and fermentation. Fermenters, pipe lines for air and antifoam agent, air filter, and rotameters are all sterilized simultaneously.

As soon as operating temperature is reached, 20 liters of inoculum are blown into each fermenter from the measuring tank. Aeration is started immediately Foaming limits the rate of aeration to 60 liters per minute per tank during the initial 6-hour period of fermentation. At 6 hours the rate of aeration is increased to 200 liters per minute per tank. The air flow measurements are made by rotameter 20 connected to the sterile air line (Figure 3). Throughout fermentation the air pressure within the tanks is maintained at 20 pounds per square inch, although a pressure of a few pounds is sufficient to prevent contamination.

Sterilization of the antifoam agent is discontinued a few minutes before the fermenters are inoculated. When the tanks are inoculated, approximately 300 ml. of antifoam agent are added from the antifoam vessel by manual control. The automatic antifoam system is not put into operation until after the initial 6-hour period of growth. During this period foaming cannot be controlled by the antifoam agent if the rate of aeration is above 60 liters per minute per tank. As an antifoam agent, a 3% solution of octadecanol in lard oil (Swift's Mellocrust or Swift's prime burning oil) is used.

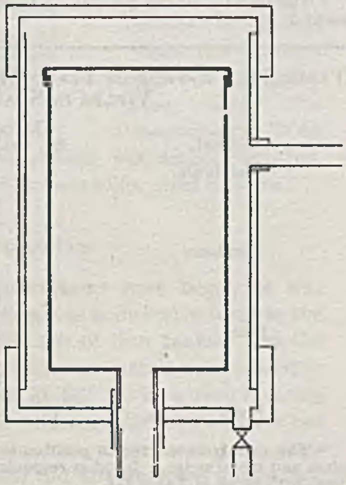


Figure 5. Construction of Vessel for Antifoam Agent

SAMPLING. When possible, samples for analyses are taken at 12-hour intervals for 48 hours and at 6-hour intervals thereafter. These samples are analyzed for penicillin, pH, total sugar, and ammonia nitrogen. The exhaust air is analyzed at intervals for carbon dioxide content.

Samples for contamination tests are taken from the tank inoculum before it is used, and from the fermenters at 36 hours. Contamination tests are made by inoculating 15 ml. of glucose-beef extract-peptone medium with 0.15 ml. of the growing culture. The inoculated tube is incubated at 30° C. and observed for 48 hours. Positive tests are usually visible within 12 hours. Contamination has not been detected in the past 110 or more runs.

ANALYSES. The methods for determining chemical changes in the medium are described elsewhere (*2*). Determination of carbon dioxide is described in another paper (*7*). The total iron content of shake flask and tank samples is determined by the method described by Kitzes, Elvehjem, and Schuette (*3*). Five

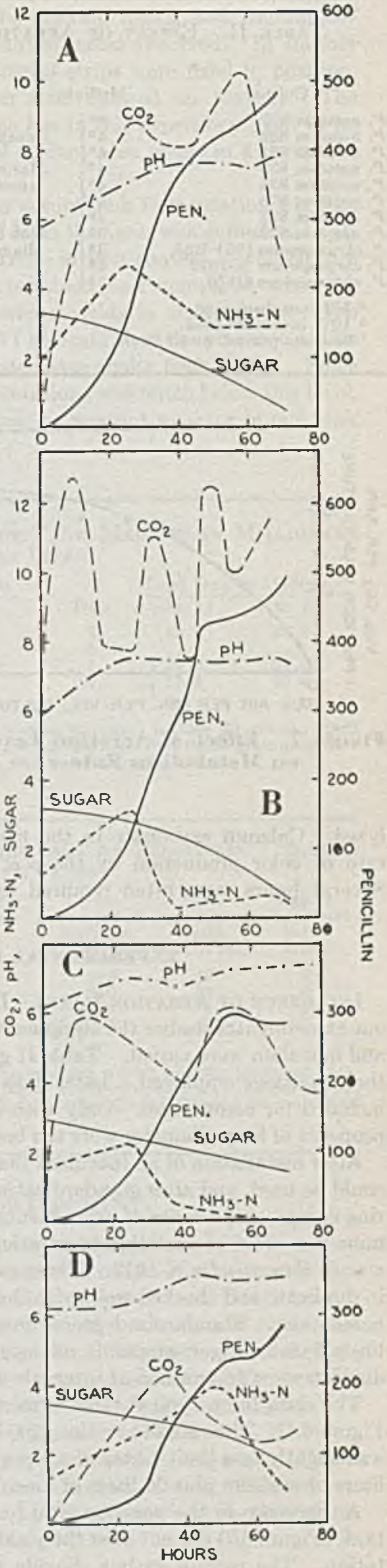


Figure 6. Typical Fermentation Aerated at Different Rates

Carbon dioxide, volumes per minute per 1000 volumes of culture; sugar, grams per 100 ml.; ammonia nitrogen, mg. per 10 ml.; penicillin, units per ml.

A. 200 liters per minute
B. 300 liters per minute
C. 80 liters per minute
D. 30 liters per minute

Table II. Effect of Aeration and Agitation on Production of Penicillin

Culture	Medium	Type of Stirrer	Stirring Rate, R.P.M.	Rate of Aeration, L./Min.	Maximum Yield, Units/Ml.	Time to Maximum
P. notatum 832	4[a]	Sweep arm	30	50	29	11 days
P. notatum 832	4[a]		105	60	35	10 days
P. notatum 832	4[a]		105	65	40	8 days
P. notatum 832	4[a]	Marine propeller, 10-in. diameter (downward thrust)	350	60	35	7 days
P. notatum 832	4[a]		350	120	46	6 days
P. notatum 832	4[a]		250	170	49	3 days
P. notatum 832	4[b]	Flat blade propeller, 16-in. diameter (upward thrust)	270	275	62	58 hours
P. notatum 832	3[b]		270	200	99[c]	71 hours
P. chrysogenum 1951-B25	3[b]		270	200	245	64 hours
P. chrysogenum X-1612	3[b]		270	200	470	72 hours
P. chrysogenum Q176	3[b]		270	200	737	66 hours

[a] 5% inoculum used.
[b] 10% inoculum used.
[c] 93 units per ml. at 50 hours.

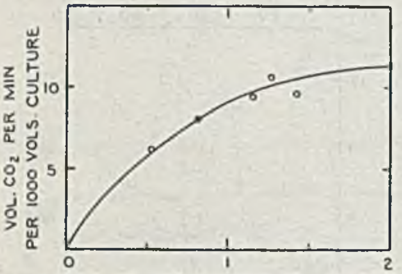


Figure 7. Effect of Aeration Level on Metabolism Rate

milliliters of sample were digested for 15 minutes with 5 ml. of concentrated nitric acid and 1 ml. of concentrated sulfuric acid. After digestion the sample was adjusted to a pH between 2.0 and 5.0 by the addition of ammonium hydroxide. Aliquots of the diluted material were analyzed. Calcium carbonate in the medium interfered with the rate of color production by the α,α'-dipyridyl—iron complex. Several hours were often required for full color development.

EXPERIMENTAL DATA

Influence of Aeration Rates. During the early period of our experimental studies the equipment, stirring, rate of aeration, and inoculum were varied. Table II gives yield data for some of the conditions employed. Later data on improved cultures are included for comparison. Only with high aeration rates and a propeller of large diameter were the best yields obtained.

After installation of an inoculum tank so that a 10% inoculum could be used, and after standardization of the aerating and stirring equipment, a series of experiments were carried out to determine the effect of variation in aeration rate. The culture used was *P. chrysogenum* X-1612. These experiments were performed in duplicate and checked well, with the exception of one contaminated tank. Standardized procedures were followed. Penicillin, pH, total sugar, ammonia nitrogen, and carbon dioxide production were determined at intervals during the fermentation.

The data for a typical tank fermentation are summarized in Figure 6*A*. The rate of aeration, 200 liters per minute per tank, was slightly less than 1 liter of air per liter of medium since 200 liters of medium plus 20 liters of inoculum were used.

An increase in the aeration rate to 300 liters per minute per tank (Figure 6*B*) did not alter the yield or the time of the fermentation. The rate of carbon dioxide production was increased, and the pH plateau was reached in a shorter time. There was considerable fluctuation in the observed values for rate of carbon dioxide production. Because of bicarbonate formation, the solubility of carbon dioxide at pH 7.5 is fifteen times its solubility at low pH values; therefore, slight fluctuations in the tank pressure during sampling resulted in large fluctuations in the carbon dioxide content of exhaust air. As a result of this and of small variations in the rate of aeration during sampling, it was difficult to obtain accurate carbon dioxide measurements.

When the aeration rate was lowered (Figure 6, *C* and *D*), the penicillin yields decreased, pH values were not so high, and rate of carbon dioxide production was much less than that for a typical run. Sugar utilization for both runs was only 50% of that for the normal run. It is apparent that, under our conditions, an aeration rate sufficient to give peak carbon dioxide production rate of 8 to 10 volumes carbon dioxide per 1000 volumes culture per minute was essential to good penicillin production on the medium used.

An experiment is summarized in Figure 7 in which a tank containing culture *P. chrysogenum* NRRL 1951-B25 in regular medium (medium 3) was subjected to various aeration rates at 20 hours. As the aeration rate increased, the metabolism rate, measured as rate of carbon dioxide production, tended to approach a maximum. At aeration rates in excess of 1 volume per minute, available air was no longer the chief factor limiting oxidation rate. Carbon dioxide production at an aeration rate of 200 liters per minute was about 10 volumes per 1000 volumes of medium. It may be concluded that optimal penicillin yields are obtained when the amount of oxygen available to the organism is such that air supply is not the chief factor limiting metabolism rate.

Table III. Effect of Free-Moving Metal Pieces on Penicillin Yield in Shake Flasks[a]

Metal	Metal Area, Sq. Cm./100 Ml.	Experiment 1 Penicillin yield, units/ml.	Experiment 1 Age at max. yield, days	Experiment 2[b] Penicillin yield, units/ml.	Experiment 2[b] Age at max. yield, days
None	..	65	5	60	6
Steel	2	52	5	45	6
	6	6	5	0	.
	10	3	5	0	.
Allegheny	2	63	5	45	6
	5	61	5	54	5
	10	27	5	30	6
Aluminum	2	61	5	50	6
	5	51	5	54	6
	10	75	5	50	5

[a] *P. notatum* 832 was grown on medium of following composition: lactose 20 g., steep liquor solids 20 g., $MgSO_4.7H_2O$ 0.15 g., KH_2PO_4 0.25 g., $NaNO_3$ 1.5 g., and water to 1 liter. Each figure given represents the average of three replicate 500 ml. Erlenmeyer flasks, each containing 100 ml. medium.
[b] The metal pieces in experiment 1 were used without cleaning in experiment 2.

Table IV. Effect of Fixed Metal Pieces[a] on Penicillin Yields in Shake Flasks

Metal	Metal Area, Sq. Cm./100 Ml.	Penicillin Yield[b], Units/Ml.
Aluminum	2	53
	6	45
	10	45
	20	42
Allegheny	2	39
	6	46
	10	58
	20	51
Steel	2	39
	6	34
	10	37
	20	37
None	..	29

[a] The metals were fixed in position so that no friction occurred between glass and metal strips. In other respects experimental conditions were identical with those of Table III.
[b] Maximum yields were obtained at 5.5 days in all cases.

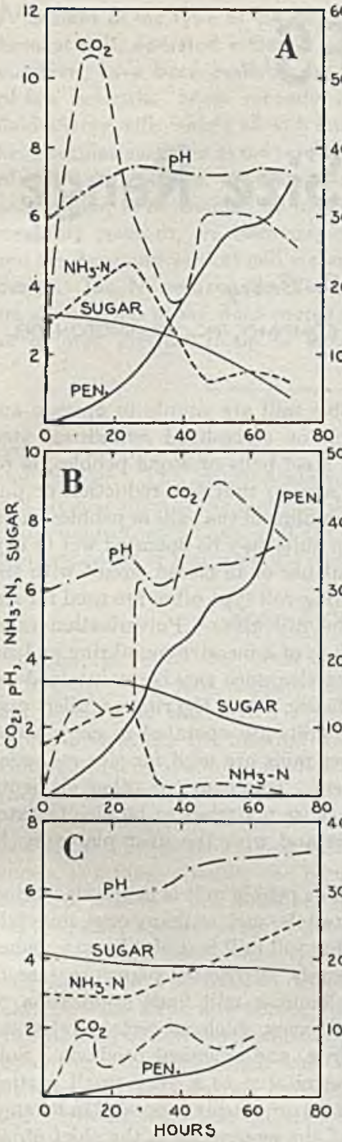


Figure 8. Results of Aeration Studies

Carbon dioxide, volumes per minute per 1000 volumes of culture; sugar, grams per 100 ml.; ammonia nitrogen, mg. per 10 ml.; penicillin, units per ml

A. **Effect of change in aeration rate: 0 to 6 hours, 60 liters per minute; 6 to 24 hours, 200 liters; 24 to 72 hours, 50 liters**

B. **Effect of low aeration rate for first 42 hours: 2 to 24 hours, 50 liters per minute; 24 to 72 hours, 200 liters**

C. **Effect of aeration without agitation**

INFLUENCE OF AERATION RATE CHANGES. Two experiments were performed in which the aeration rate was changed after periods of low or high aeration. For the first of these experiments (Figure 8*A*) the penicillin yield and rate of carbon dioxide production were lower than those for a typical fermentation (Figure 6*A*). However, the ammonia nitrogen, sugar utilization, and pH curves were similar. In a second experiment (Figure 8*B*) the fermentation was very slow during the initial 24-hour period of low aeration. When the aeration rate was increased, fermentation recovered and a good penicillin yield was obtained. Low ammonia nitrogen content during fermentation may be correlated with low pH values.

EFFECT OF STIRRING. Because of mechanical breakdown of the stirring equipment, a fermentation was run without agitation. Figure 8*C* shows the results obtained where the agitator was not in operation after the second hour. With an aeration rate of 200 liters per minute, but without stirring, growth was exceedingly slow and the penicillin yield was low.

METAL TOXICITY

When experimental tank fermentations were begun, it was necessary to determine whether iron was sufficiently toxic to the organism to make impractical the use of iron tanks. For the shake flask experiments, pieces of different metals were placed in the flask. It was then incubated at 23° C. in a reciprocating shaker which had a 4-inch stroke and operated at 92 cycles per minute. The results obtained in two experiments are summarized in Table III. Aluminum did not decrease yields, but Allegheny metal was toxic at the higher levels, and steel was very toxic. In these experiments, however, the pieces of metal were allowed to move freely in the shaking flasks, and friction undoubtedly increased the amount of metal dissolved. In another experiment (Table IV), the metal strips were fixed in position. Under these conditions even steel showed no toxicity. The yield on the control flasks was low in this experiment, but in no case did an increase in metal surface area result in a decreased yield.

In order to determine in an actual tank fermentation whether the amount of iron dissolved from the tank was sufficient to affect penicillin yields, the increase in iron content of the culture during fermentation was determined and compared with the level of iron required to decrease yields in shake flasks. The data given in Tables V and VI indicate that the presence of 200 micrograms of iron did not decrease shake flask yields. Since the iron content of tank fermentations was much below this level, it was concluded that iron toxicity was not a factor in our tank fermentations.

TABLE V. IRON CONTENT OF TANK MEDIUM[a] IN MILLIGRAMS PER LITER

Day	Total Iron in Medium		Day	Total Iron in Medium	
	Run 11	Run 12		Run 11	Run 12
0[b]	7.8	6.6	5	43.7	47.2
0[c]	48.4	24.8	6	..	..
2	57.1	48.3	7	79.0	63.8
3	53.7	41.7	8	75.2	60.5
4	41.6	35.2			

[a] Composition of the medium was as follows: lactose 20 grams, steep liquor solids 20 grams, $NaNO_3$ 3.0 grams, $MgSO_4.7H_2O$ 0.125 gram, $ZnSO_4.7H_2O$ 0.4 gram, KH_2PO_4 0.5 gram, and water to make 1 liter.

[b] Before sterilization.

[c] After sterilization, pH 4.6.

TABLE VI. EFFECT OF ADDED IRON ON PENICILLIN YIELDS IN SHAKE FLASKS

Iron Content of Medium[a], Mg./L.	Penicillin Yield, Units/Ml.	Age at Maximum Yield, Days	Iron Content of Medium, Mg./L.	Penicillin Yield, Units/Ml.	Age at Maximum Yield, Days
10	37	6	210	43	6
20	35	6	510	22	6
35	39	7	1010	4	5
60	42	6	5010	0	..
110	37	7			

[a] Iron was added as $FeCl_3$ to the medium, which had the following composition: lactose 20 grams, steep liquor solids 20 grams, $NaNO_3$ 1.5 grams, $MgSO_4.7H_2O$ 0.125 gram, KH_2PO_4 0.25 gram, $ZnSO_4.7H_2O$ 0.02 gram, and water to 1 liter.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Bowden, J. P., and Peterson, W. H., *Arch. Biochem.*, 9, 387 (1946).
(2) Gailey, F. B., Stefaniak, J. J., Olson, B. H., and Johnson, M. J., *J. Bact.*, 52 (in press).
(3) Kitzes, G., Elvehjem, C. A., and Schuette, H. A., *J. Biol. Chem.*, 155, No. 2, 653 (1944).
(4) Koffler, H., Emerson, R. L., Perlman, D., and Burris, R. H., *J. Bact.*, 50, 517 (1945).
(5) Moyer, A. J., and Coghill, R. D., *Ibid.*, 51, 79 (1946).
(6) Raper, K. B., *Ann. N. Y. Acad. Sci.* (in press).
(7) Stefaniak, J. J., Gailey, F. B., Jarvis, F. G., and Johnson, M. J., *J. Bact.*, 52 (in press).

MODERN MACHINES for Dry Size Reduction in Fine Size Range

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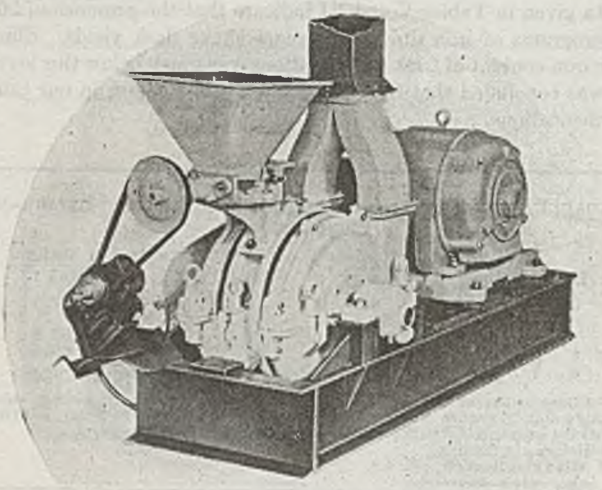

Figure 1*A*. Mikro-Atomizer with 12-Inch-Diameter Rotor

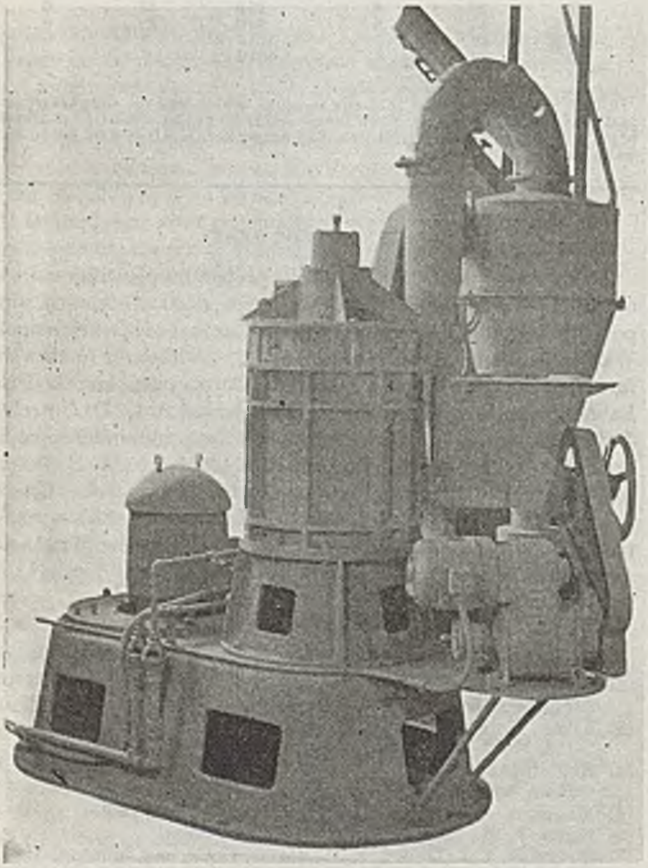

Figure 1*B*. Raymond Vertical Mill with 18-Inch-Diameter Rotor

THE ball mill and the pebble mill are simple to operate and versatile in use. A steel- or stone-lined cylindrical steel shell, containing a charge of steel balls or stone pebbles, is rotated horizontally about its axis so that size reduction or pulverization is effected by the tumbling of the balls or pebbles on the material between them. The mills may be operated wet or dry, either in batch or open-circuit use or in closed circuit with size classifiers. Machines of the ring-roll type often are used for size reduction of materials in the dry state. Pulverization takes place between the inside surface of a massive metal ring and the surfaces of the rollers. Close clearance can be maintained between the ring and roller surfaces; either the ring or rollers may be driven. Generally, these mills are operated in conjunction with size classifiers. Hammer mills are used for size reduction with or without size classifiers. Hammers, or other elements, attached to a rotating shaft cause materials to be disintegrated by impact with the hammers and with the liner plates in the housing of the machine.

The salient field of the ball or pebble mill is in the size reduction of hard and abrasive materials, such as many ores, minerals, or sintered products. The ring-roll mill is useful for size reduction of the less abrasive minerals, aggregated pigments, insecticides, and chemicals. The hammer mill finds application on materials of minimum abrasiveness, such as certain talcs and clays, as well as on food, drug, and chemical products. Substances which have been precipitated to a very small particle size and subsequently aggregated are readily processed in hammer mills. Here disintegration of the aggregates is the chief objective.

The machines cited are capable of yielding fine size products, but the increased value found, in many instances, for still finer materials has caused new units to be designed for a superior degree of size reduction. Indeed, the testing sieves have become inadequate for characterizing the particle size of materials. Air or liquid sedimentation methods in numerous modifications (*1*, *9*, *10*), are used to determine particle size distribution. Particle size counting methods which use a microscope equipped with an eyepiece containing a calibrated length scale sometimes are employed (*2*), but more often maximum or average particle size is observed by examination of one or more fields of the sample. The air permeability method is gaining acceptance for determining the average particle size of dry powders (*4*, *7*). It is simple to use but furnishes no information about particle size distribution. The range of such instruments is 0.2 to 50 microns. (There are 25,400 microns to a linear inch, and the nominal edge length of the openings in a 325-mesh testing sieve is 44 microns.)

When consideration is given to the functioning of machines for size reduction in the fine size range, it is revealed that size classification plays an essential role. Particles must be kept in the size reduction zone until they are as small as required in the finished product. This is the function of the size classifier.

Modern machines generally make use of intense centrifugal fields to effect classification in the fine size range. High speed hammer mills and fluid-energy mills, nearly all with integrally fabricated size classifiers, have become available for the produc-

Machines of the type of the ball mill, the ring-roll mill, and the hammer mill, operated either in open or closed circuit with size classifiers, have been available for many years for the production of fine materials. More recently high speed hammer mills and fluid-energy mills, nearly all with integrally fabricated size classifiers, have become available as the result of a demand for the production of still finer materials. Average size specifications of 20 microns and smaller, as determined by microscope examination and air permeability methods, are becoming common. The Mikro-Atomizer and the Raymond vertical mill are machines of the high speed rotor design. The Micronizer, the Reductionizer, and the Eagle mill are all machines of the fluid-energy type which utilize compressed air or high pressure steam to effect the desired size reduction.

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MIKRO-ATOMIZER

Figure 1*A* shows the motor and machine assembled on the same base. The feed hopper, feedscrew drive, product outlet, and annular air inlet are visible. The schematic drawing in Figure 2 identifies the internal components. The rotating elements carried on the horizontal shaft are the hammers, separator wheels, and fans. The main castings are of Ni-Resist, an iron alloy containing 18% nickel and 3% copper. Stainless steel is used for the liners (not shown in Figure 2), hammers, separator wheels, and fans. Stellite can be employed for the vanes in the separator wheels. The machines being sold have 12-inch-diameter rotors and are driven by 20-horsepower motors. The fabrication of larger and smaller sizes is planned.

Operation. The fans, *C*, at the extreme ends of the rotor shaft, *G*, cause air to flow through the annular inlets, *D*, the separator wheels, *B*, and the product outlets, *E* (Figure 2). Material enters the machine through feed screw *F* and comes in contact with the moving T-shaped hammers, *A*, designed to divide the feed material into two streams in opposite directions. The material moves in spiral paths away from the middle and toward the ends of the rotor while disintegration takes place. Air entering the annular inlets creates a dispersion of the particles leaving the ends of the rotor. The dispersion of particles travels to the separator wheels, which contain closely spaced radial vanes at their peripheries.

Centrifugal force and aerodynamic drag are opposing forces on the particles between the vanes of the separator wheels. When the centrifugal force on a particle is the larger, it is returned to the size-reduction region, *A*. When the force due to aerodynamic drag on a particle is the larger, the particle passes between the vanes of the separator wheel, around the rotor shaft, into the fans, and out one of the product outlets, which generally converge into a single conduit. The fine particles are separated from the air stream by a cyclone collector, cloth bag filter, or a combination of the two.

Performance. A Mikro-Atomizer with a 12-inch-diameter rotor usually is operated at speeds of 5000, 6000, or 7000 revolutions per minute with 14-, 12.5-, or 11.25-inch-diameter fan wheels, respectively. The air rate for the machine varies between 1000 and 850 cubic feet per minute, depending on the rotor speed and fan-wheel combination used. High rotor or separator-wheel speed and low air rate are the conditions for producing materials of smallest particle size. The particle size of the product also can be controlled by variation in the width of the vanes in the separator wheels. With other factors remaining fixed, a finer product is obtained with wide vanes than with

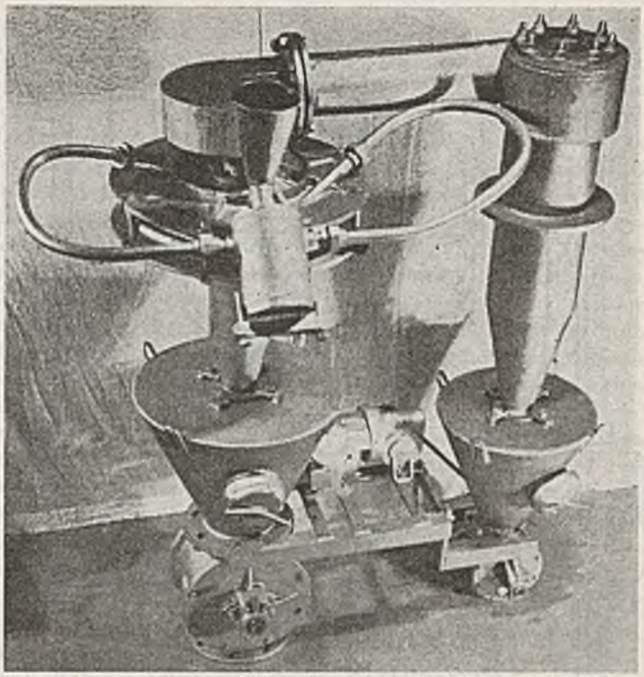


Figure 1C. Twenty-Inch-Diameter Micronizer (*left*) and Dust Collection System (*right*)

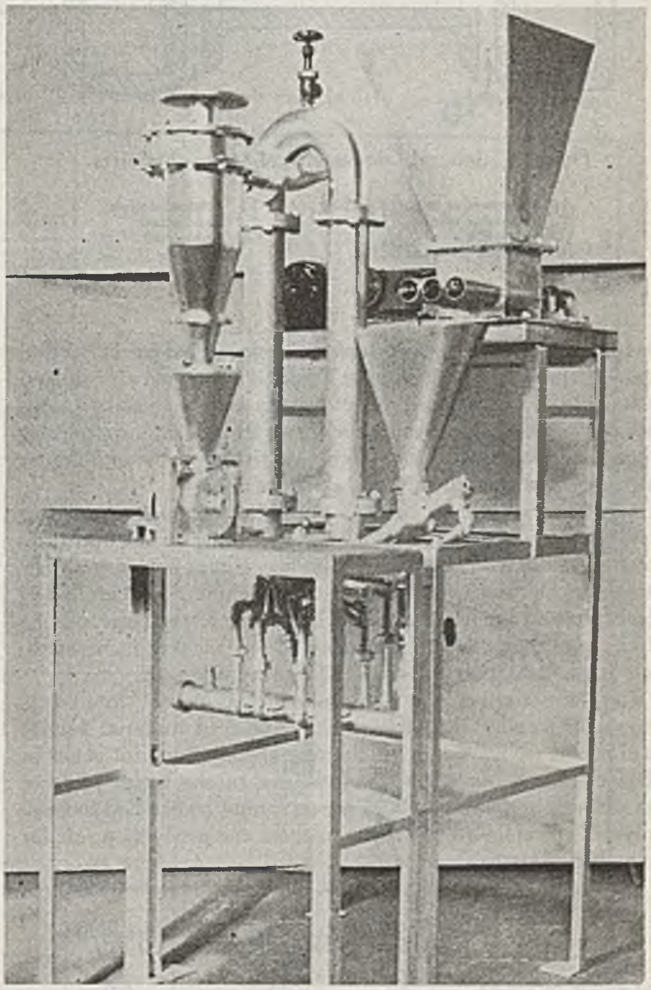


Figure 1*D*. Small Reductionizer Unit, Showing Feeding and Collection System

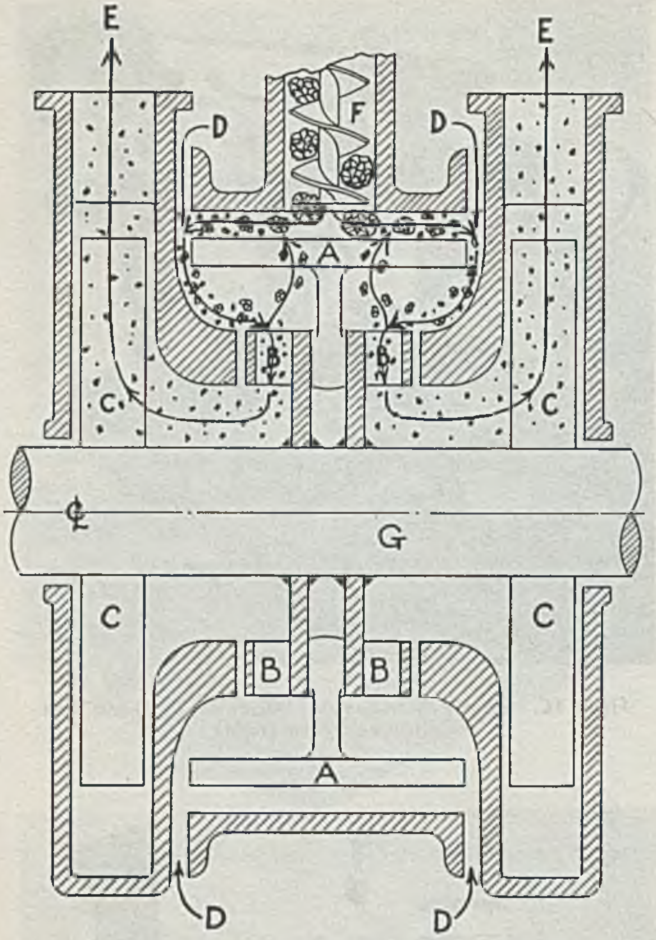


Figure 2. Internal Components of Mikro-Atomizer

A. Hammers or impact members
B. Separator wheels
C. Fan wheels
D. Annular air inlets
E. Product outlets
F. Feed screw
G. Rotor shaft

narrow vanes. Calculated separating particle size is plotted against separator-wheel speed in Figure 3 for a fixed air rate and vane width. If the two product outlets are connected to separate particle collection systems and two sizes of fan or separator wheels are used, it is possible to obtain two products of different fineness at the same time from the one machine.

Air and solids passing through the Mikro-Atomizer experience a temperature rise of 25° to 55° F., depending on the operating conditions, but a 35° F. rise is common. Hot or cold air or other gases can be circulated through the machine if a manifold is placed around the annular inlets. Because of the large volume of air employed, the size reduction of low melting-point materials is practical, particularly if the air is refrigerated.

The feed size to the 12-inch-diameter Mikro-Atomizer is limited to smaller than 0.75 inch. The feed material cannot be abrasive. Native talc has limiting abrasiveness if it is low in silica content. Materials which adhere to the metal parts of the machine and build up thick layers cannot be handled successfully. Typical figures follow for fineness and production rate for a number of materials:

Material	Particle Size, Microns		Production Rate, Lb./Hr.
	Average	Maximum	
Sugar	19	40	400
Calcium carbonate	5	25	600
Nickel carbonate	5	20	650
Nickel carbonate	2.5	10	300
Lead oxide	2	5	1250

RAYMOND VERTICAL MILL

The Raymond vertical mill and motor are shown in Figure 1*B*, assembled on a single base. The feeder and product collector are apparent. Figure 4 shows the internal parts. The rotating components carried on the vertical shaft are the size-reduction element, double whizzer classifier, and fan. The housing, base, and top casting are of gray iron. Replaceable liners of Hi-Mang annealed steel are provided on the inside wall of the size-reduction chamber. The hammers of the grinding element can be provided with Stellite or Carboloy inserts on their leading faces. The whizzer classifier blades can be coated with Stellite. Machines are available with rotor diameters of 18 and 35 inches, driven by 20- and 100-horsepower motors, respectively. The larger mill is directly connected to a vertical motor.

Operation. Fan *D* at the top of rotor shaft *G* causes air to flow through inlet *F* and the annular opening around the shaft. It passes around hammer element *B*, through the blades of whizzer classifier *C* and fan *D*, and is discharged at product outlet *E* (Figure 4). The size-reduction element at the bottom of the vertical shaft is provided with sufficient spaces for a large or small number of short bar-shaped pieces, called "hammers", which are free to swing from one end. The clearance between the ends of the extended hammers and the wall of the chamber is not critical; clearances from 0.25 to 0.5 inch have long been common.

Material is introduced into the machine by screw feeder *A*, which extends above the size reduction element and toward the rotor shaft. Disintegration of the coarse material takes place when it falls on the rotating size reduction element and is accelerated to high speed in an upward spiral path as a result of the air entering at the bottom of the shaft. As the disintegrated material rises to the double whizzer classifier, its rotational velocity is increased, and coarse particles are concentrated along the wall of the chamber because of the centrifugal force acting on them. The coarse particles are continually returned to the size reduction element while the fine particles pass between the radial blades of the whizzer classifier and are carried in the air stream through the fan and discharge port. The fine particles are separated from the air stream by a cyclone collector into a suitable container. The air discharged by the cyclone can be returned to the machine in any desired proportion or be vented to a cloth bag collector.

Performance. The nominal rotor speed for the 18-inch Raymond vertical mill is 6500 r.p.m., and is 3600 r.p.m. for the 35-inch machine. In general, the relative production rates for the two machines are directly proportional to the power applied. Product fineness is controlled by the number of blades used in each bank of the whizzer classifier and by the size of the fan wheel. Materials of the smallest particle size generally are produced when the maximum number of whizzer blades and the smallest fan are used—that is, for greatest centrifugal force and longest spiral path. The whizzer classifier minimizes the grossly oversize particles which tend to be present in some fine materials. The air rate for the 18-inch machine can be controlled between 300 and 1000 cubic feet per minute; for the 35-inch machine the range is 800 to 2000 cubic feet per minute.

A temperature rise is encountered in the Raymond vertical mill, particularly at the low air rates required for a very fine product. The temperature of finished material ranges from 125° to 275° F., depending on operating conditions. Product temperature is lower when no air is recirculated from the cyclone collector to the machine. The machine can be jacketed to provide for cooling water, and refrigerated air can be conducted into the unit when required. Inert gas can also be employed in the unit instead of air.

The feed size to the Raymond vertical mill is preferably smaller than 0.25 inch, and for the harder materials a feed size not to exceed 10-30 mesh is recommended. The size reduction of abrasive materials, or those with hardness index greater than 4, would be uneconomical in most instances because of excessive wear of the machine. Materials which coat the metal surfaces in thick layers due to violent contact cannot be handled. The machine is suitable for the size reduction of such materials as barytes, limestone, talc, marble, graphite, and kaolin, as well as many manufactured chemicals and colors.

The field of application of the Raymond vertical mill is for producing materials which range in size from those having 99% passing a U. S. 325-mesh sieve to those having 99% smaller than 5 to 10 microns, depending on the state of aggregation of the feed. A production rate of 500 pounds per hour is achieved with a chemical in an 18-inch machine consuming 18 horsepower when the product is substantially smaller than 15 microns. In a talc operation on a 35-inch machine requiring 100 horsepower, a production rate of 400 pounds per hour is obtained when the product is 95% smaller than 10 microns. At a production rate of 3000 pounds per hour, a sample of the product leaves only a trace of talc on a 325-mesh testing sieve.

MICRONIZER

A Micronizer with a 20-inch-diameter size reduction chamber is shown in Figure 1*C*. It is used for the size reduction of talc with superheated steam. A steam injector (not visible) causes lumps of the material to pass from the feed hopper to the impact chamber, where they are shattered and suspended for transport through the two feed conduits to the annular feed manifold (not visible) and then to the size-reduction chamber. The primary dust collector is shown, directly under the size-reduction chamber, emptying into a dust bin which discharges through a rotary gate. The secondary dust collector is shown at the right of the picture, discharging into its dust bin. The internal construction of the Micronizer is better described by reference to Figure 5, which shows a machine having a 36-inch-diameter grinding chamber, to a patent granted the inventor (*3*), or to a previous article (*8*).

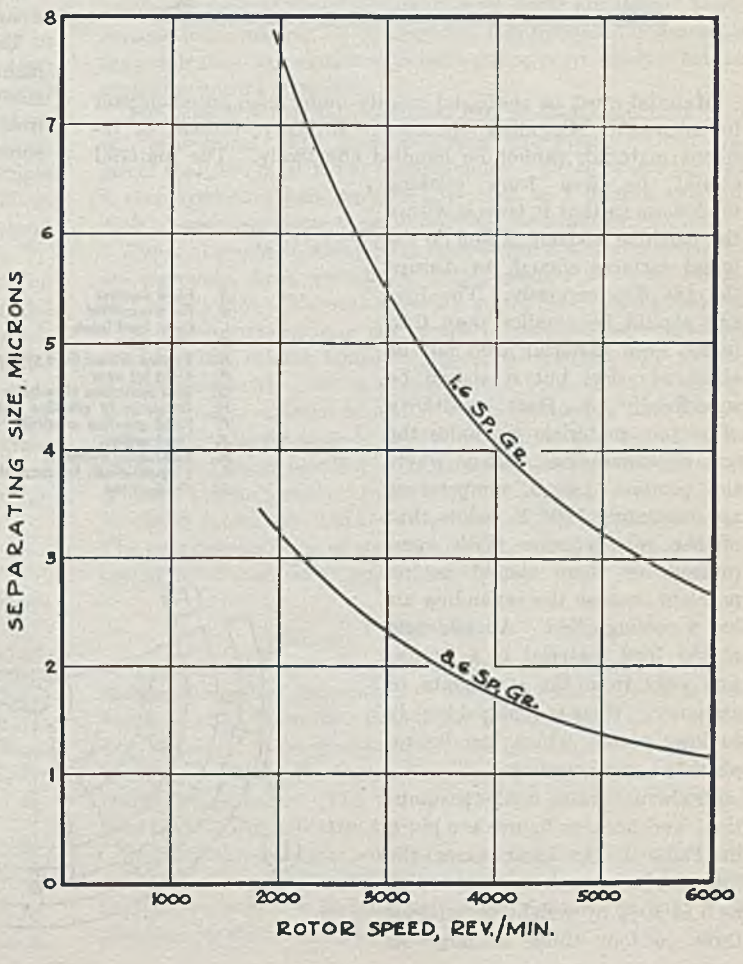
The Micronizer materials of construction generally are welded mild steel, but some operations use white cast iron or stainless steel. Micronizers are available with grinding chamber diameters from 8 to 48 inches. Energy consumption in terms of compressed air or superheated steam is in the range 50 to 3000 cubic feet per minute and 700 to 7000 pounds per hour, respectively. Production machines generally consume a minimum of 350 cubic feet per minute of air or 1000 pounds per hour of steam. Minimum fluid pressure is 100 pounds per square inch gage. Steam is superheated to 375-450° F. to prevent condensation.

Operation. As Figure 5 shows, a controlled flow of material passes from a feed funnel through feed injector *A* and feed manifold *B* into size reduction chamber *G*. A high pressure fluid, such as air or superheated steam, passes through inlet *D* to manifold *I* and orifices *E*. Size reduction and classification take place simultaneously in the same chamber, *G*, which is essentially a cylinder of low axial height. High velocity fluid jets issuing from orifices *E* in the wall of the cylinder are directed so as to set up a rapid rotation of the gas-solids suspension in the chamber. Centrifugal force resulting from this rotation tends to hold the coarse solids in a path following the cylindrical wall. The size reduction is accomplished by the impact of particle upon particle and shearing effects as the high speed fluid jets intersect the path of the rotating suspension. The classifying action is obtained by balancing the centrifugal force on a particle, due to its circular path, against the entraining force of the expanded gases which leave the size reduction chamber near its axis. A barrier is created in which particles larger than a certain size are rejected to the periphery of the chamber for further size reduction, while particles smaller than this size are swept from the size reduction chamber.

The classified product is collected by directing the spirally rotating gaseous suspension from size reduction chamber *G* into a cyclone collector of relatively small diameter, *K*, located immediately below and concentric with the chamber. The cyclone discharges dry finished product into a closed bin, *M*. Recovery of product in this cyclone is generally 90% complete. Further recovery can be made by employing a second cyclone or a cloth bag filter, in case air is used, on the exhaust gas from the primary cyclone as it leaves the machine through fluid outlet *J*, concentrically located on the top of the size reduction chamber. In the operation of superheated steam Micronizers, complete recovery of exhaust dust cannot always be made with cyclone collectors. Cloth fabric filters have short life, and woven glass fabric is not satisfactory because of water condensation and plugging of the meshes with wet dust. Complete condensation of the steam with water will overcome any dust nuisance and allow recovery of a valuable product.

Performance. The Micronizer product size is basically dependent on the rotational speed, fluid flow rate, internal size, and proportions of the size reduction chamber. Control of the first and second factors is usually accomplished by controlling the rate of solid feed and the fluid pressure at the orifices. The size and shape of the chamber are determined for best performance during initial experimental work with a particular material. Fluid pressure is controllable within a close range so that product uniformity is largely a matter of close control of the feed rate.

Figure 3. Calculated Separating Particle Size for Mikro-Atomizer



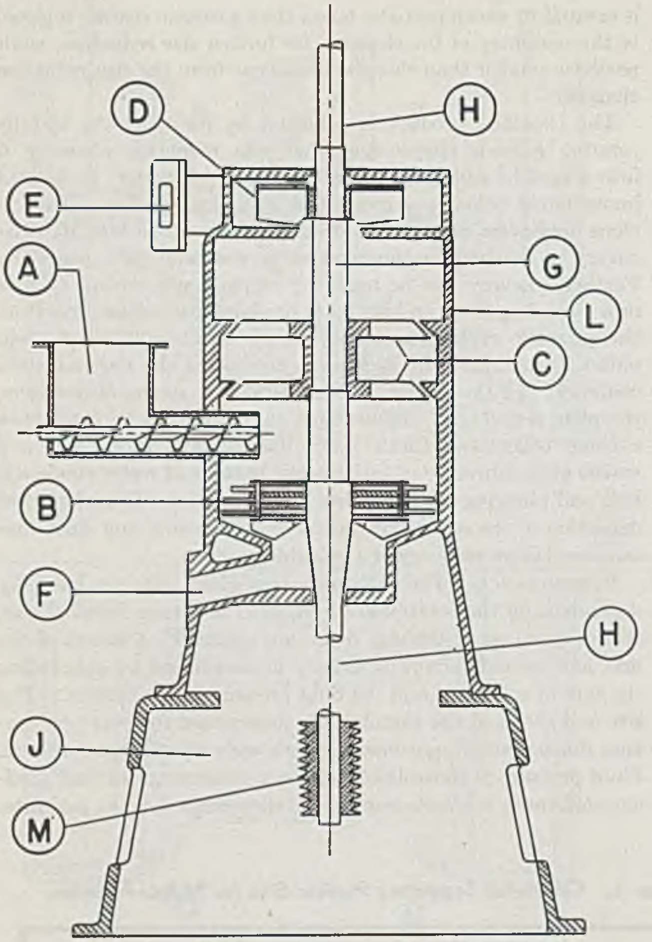


Figure 4. Internal Parts of Raymond Vertical Mill

A. Feeder
B. Size reduction or grinding element
C. Double whizzer classifier
D. Fan
E. Product-in-air outlet
F. Air inlet
G. Rotor assembly shaft
H. Shaft bearing position
J. Mill base
L. Mill-side removable section
M. Mill V-belt drive

Material must be shattered readily under high speed impact for successful Micronizer operation. Rubbery, fibrous, or resilient materials cannot be handled effectively. The material should be free from sticking tendencies so that it travels within the machine without caking on the metal surfaces enough to disrupt the gas flow seriously. The feed size should be smaller than 0.25 inch. Feed material need not be absolutely dry, but it should be superficially so. Heat sensitivity of certain materials precludes the use of superheated steam where the product has a temperature approximately 100° F. below that of the inlet steam. With compressed air there should be no problem because the expanding air has a cooling effect. Abrasiveness of the feed material is a limitation only from the standpoint of economy. Wear is confined largely to liner plates, which can be replaced at small expense.

Production rate, fluid consumption, and fineness figures are given in Table I. In most cases the fine product contains as much as 5 to 10% by weight of particles three to four times as large as the average size. The largest particles present in the product may exceed considerably the U. S. 325-mesh size, although in amount they constitute between 0.0001 and 0.01% of the total weight. Increase in the average size above the range of 10 to 15 microns generally breaks down the sharpness of classification, and 325-mesh residues of 0.5 to 1% may been countered for material of 20-micron average size.

REDUCTIONIZER

The Reductionizer reduces solid materials to small particle size by the impact and attrition between particles in a tube having at least one curved portion into which fluid energy is introduced in the form of superheated steam or compressed air (*6*). The photograph reproduced in Figure 1*D* shows a small unit complete with feeding and collection system. The machine can be described by reference to Figure 6. Coarse material is transported from feed funnel *E* by Venturi injector *G* into size reduction tube *GBA*. Fluid under pressure enters the tube through nozzles *F* from manifold *J*. Fluid and finished material pass from outlet *D* into cyclone collector *K*. The top tube turn, *A*, constitutes the size classifier.

Ceramics, glass, plastics, and metals are used in the construction of Reductionizer units. Most materials of construction last well because the low linear velocity around the tube causes little wear.

Reductionizers having tube diameters of 1, 3, 4, 5, 6, and 8 inches are in industrial use. Compressed air is employed in amounts from 30 to 500 cubic feet per minute, and steam at rates from 100 to 5000 pounds per hour. Fluids are used in the machine at various temperatures, depending on the properties of

A. Feed injector
B. Feed manifold
C. Eight feed inlets
D. Fluid inlet
E. Twelve drilled fluid orifices
F. Fluid jet axes
G. Size reduction chamber
H. Diameter of grinding chamber
I. Fluid pressure manifold
J. Fluid outlet
K. Concentric collector
L. Hypothetical, jet tangent circle
M. Product bin

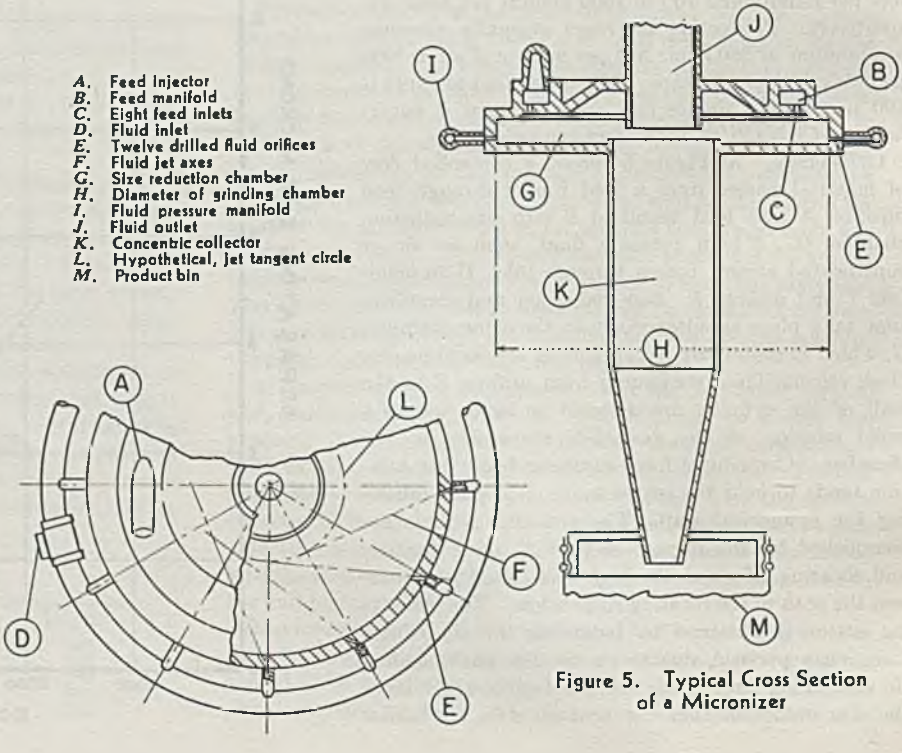


Figure 5. Typical Cross Section of a Micronizer

the material to be processed. Compressed air is generally at room temperature but may be cooled or heated. Although saturated steam is employed in some operations, it is usually superheated to 500° or even 650° F. for some materials. Pressure of air and steam at the nozzles is generally 100 pounds per square inch gage, although higher and lower pressures are sometimes employed. The pressure inside the machine is only a few pounds per square inch above atmospheric.

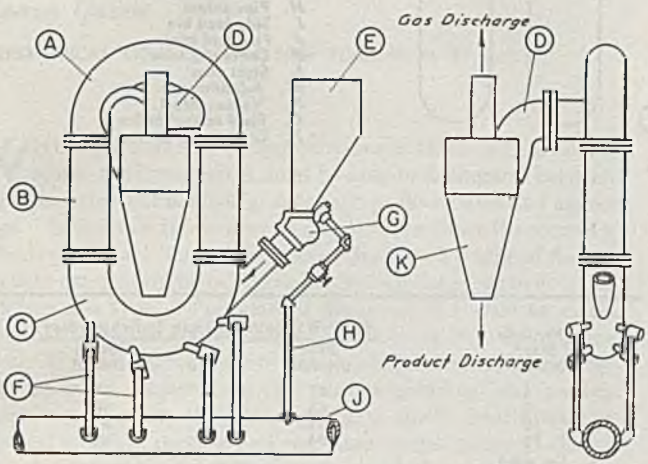


Figure 6. Elevation Drawings of a Reductionizer Having 6-Inch Tube Diameter

A.	Top tube turn	*F.*	Fluid nozzles
B.	Straight section of size reduction tube	*G.*	Venturi-type feed injector
C.	Bottom tube turn	*H.*	Fluid line to feed injector
D.	Product outlet	*J.*	Fluid pressure manifold
E.	Solids feed funnel	*K.*	Cyclone collector

OPERATION. Size reduction and classification take place in the same apparatus although the latter occurs only in the 180° tube turn, *A*. Materials introduced into the machine are entrained in and conveyed by the fluid so that intimate and rapid contact reduces them to small particle size. Classification takes place in the tube turn because of the division of the entering single stream of entrained particles into two substantially helical streams which advance on either side of a hypothetical vertical plane passing through the center line of the tube (Figure 7). The streams rotate in opposite directions at high velocity. The paths of two particles entering the tube turn on either side of the vertical plane are illustrated in Figure 7. For the purpose of explanation, the particles are shown piercing five planes along the tube. The helical paths on the sixth plane are defined by composites on that plane of the preceding pierce points. Centrifugal force causes the coarse particles to travel closer to the larger radius wall of the tube turn; the finest particles traveling closer to the smaller radius wall are removed through the outlet (*D*, Figure 6) when the entraining force of the fluid is greater than the centrifugal force exerted on them.

TABLE I. PRODUCT FINENESS AND PRODUCTION RATE FOR THE MICRONIZER

Material	Product Av. Size, Microns	Feed Size, Sieve Mesh	Production Rate, Lb./Hr.	Fluid Consumption		Unit Fluid Consumption, Lb. Fluid/ Lb. Solid	
				Air, cu. ft./ min.	Steam, lb./hr.	Air	Steam
Ceylon graphite	2	3	200	....	1700	..	8.5
Fatty talc	3.5	20	1000	....	4000	..	4.0
Fatty talc	6.5	20	1800	....	4000	..	2.2
Bituminous coal	2	10	1300	....	1500	..	1.2
Sulfur	3.5	3	800	1000	....	5.6	...
Wolframite ore	5.5	10	800	1000	....	5.6	...
Barytes	3.5	40	1800	....	4000	..	2.2
Cryolite	3	60	900	....	3600	..	4.0
Copal resin	5	2	600	1000	....	7.5	...
Silica gel	5.5	40	500	1000	....	9.0	...
Limestone	3.5	80	1000	..	4000	..	4.0

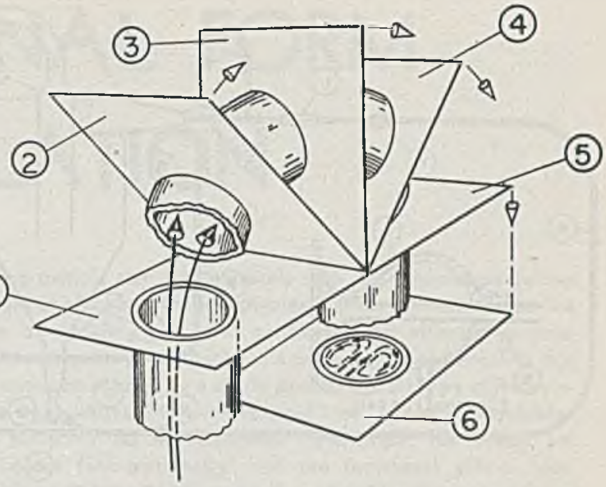


Figure 7. Sectional Drawing of Reductionizer Tube Turn to Illustrate Size Classification Function

Special types of cyclone collector are used to separate the fine product from the fluid. The collector is not an integral part of the Reductionizer and can be placed at a distance from it. Exhaust dust can be completely recovered from superheated steam Reductionizers by condensing the exhaust steam.

PERFORMANCE. The particle size of the Reductionizer product is controlled through variation of the fluid flow rate and the solids flow rate. The finest products are obtained with high fluid and low solids flow rates.

When materials sensitive to heat are handled, fluids such as compressed air at room temperature or lower are used. Many organic materials can be processed in this manner. Flammable materials may be handled with inert gases, particularly when an explosion hazard is present.

Although 0.5-inch feed material can be used, generally it is not economical. For most industrial operations a feed size larger than 100 mesh is not recommended. Often even finer feed is employed to obtain particle sizes such as 1 micron average, with no particles larger than 10 microns, for example.

Types of products which have been disintegrated commercially are pigments, dyes, chemicals, drugs, ceramic powders, waxes, and insecticides. Natural materials which have been processed in Reductionizers include talc, graphite, phosphates, magnesite, mica, calcium sulfate, bentonite, silica, earth colors, clay, and diatomaceous earth. These materials can be reduced in size so that nothing is retained on a U. S. 325-mesh testing sieve and no particles are larger than 5, 10, 20, or 30 microns, depending on the material being handled. The feed fineness is about 100 mesh or less. Production rates range from 35 to 4600 pounds per hour for steam consumption in the range 600 to 5000 pounds per hour. The unit consumption of steam is as low as 1 to 2 pounds steam per pound of material in many instances.

EAGLE MILL

The Eagle mill makes use of a length of tube, *K*, and an ejector nozzle, *E*, to effect size reduction when the solid material is conveyed through them by a fluid, such as compressed air or steam (*5*) (Figure 8). Size classification takes place in the expansion or settling chamber, *B*, operated in closed circuit with the size reduction elements. The fine product is separated from the fluid in cloth bag collector *A*.

Stainless steel or other suitable metals can be used for the construction of the Eagle mill. Sheet metal and standard pipe and fittings are used. A replaceable Stellite Venturi bushing, *N*, is provided for the most abraded part of the mill.

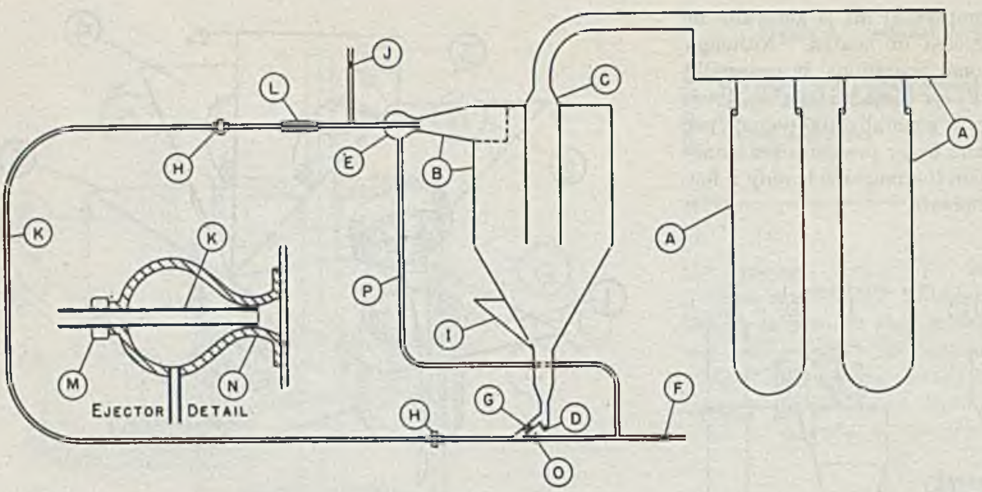


Figure 8. Schematic Drawing of Eagle Mill with 1¼-Inch-Diameter Ejector Tube

A. Cloth-bag product collector
B. Expansion chamber or size classifier
C. Product outlet
D. Cleanout plug
E. Ejector nozzle
F. Fluid control valve
G. Solids gate valve
H. Pipe unions
I. Side feed bin
J. Fine feed inlet
K. Conveying tube
L. Sight glass
M. Adjusting nut
N. Venturi throat
O. Fluid control orifice
P. Compressed air line

Eagle mills are available in two sizes. The smaller unit makes use of a 0.5-inch-diameter ejector tube and requires 40 cubic feet per minute of air to be compressed to 80 pounds per square inch gage pressure. The larger unit has a 1.25-inch diameter ejector tube. The air consumption is 290 cubic feet per minute at 90 pounds per square inch gage pressure. The total length of the tube, *K*, is 200 feet. Steam at 100 pounds per square inch pressure can be used and is superheated to a temperature of 750° F.

OPERATION. The Eagle mill is put into operating condition by closing valve *G* and opening valve *F* to admit compressed air through line *P* and ejector nozzle *E*. The position of tube *K* in the ejector nozzle is adjusted until a maximum negative pressure is obtained with no air flowing in tube *K*. This negative pressure is of the order of 18 inches of mercury. The air is then shut off and free-flowing granular material for size reduction is loaded into side bin *I*. This material flows through the hole in the bin and into the bottom of expansion chamber *B*. Flow of material from the bin stops when the discharge hole becomes sealed with it. The air is turned on, and valve *G* is opened to allow material to flow into tube *K*. Air passes through orifice *O* at the rate of about 60 cubic feet per minute to convey the material. The resulting attrition and impact between particles causes them to be reduced in size. The suspension can be observed in sight glass *L* just before it passes through the ejector nozzle. Further size reduction takes place as the suspension emerges from the nozzle into expansion chamber *B*. Coarse particles fall to the bottom of the chamber and are recirculated while fine particles are carried through product outlet *C* to collector *A*. Feed materials which are not free flowing are admitted to the unit at fine feed inlet *J*, which is under suction.

PERFORMANCE. The Eagle mill product is controlled with respect to particle size by the air rate used or the cross-sectional area of the size classifier—i.e., by the upward air velocity in the classifier. The finest products are obtained with large diameter classifiers or expansion chambers. Feed size for the 0.5-inch-diameter tube unit should not exceed 10 mesh, nor should it be greater than 0.25 inch for the 1.25-inch-diameter tube unit.

The Eagle mill has been used for the size reduction of talc, graphite, mica, grains such as wheat and corn, pigments, clays, and insecticides. In the size reduction of natural graphite for use in pencils, two products are obtained from the Eagle mill by inserting a larger-diameter settling chamber between the expansion chamber and cloth bag product collector shown in Figure 8. The finer product is recovered at a rate of 25 and the coarser one at 50 pounds per hour. The air consumption is 290 cubic feet per minute, compressed to 90 pounds per square inch gage pressure. The particle size distribution of the products follows:

Particle Size[a], Microns	% by Wt. Smaller Than Indicated Size	
	Fine product	Coarse product
4	47	13
9	83	69
18	91	81
31	94	89
Av. size[b], microns	0.9	1.6

[a] Sedimentation method (*1*).
[b] Air permeability method (*7*).

CONCLUSION

From the viewpoint of the user of size reduction machines, there should be considerable application for equipment developed to accomplish fine size reduction of plastic or polymeric materials which are so resilient and tough that they are not fractured readily by impact and attrition. Closely sized fine powders should have many advantages which could result from improvement in the sharpness of classification of size reduction machines. Novel methods for fine size reduction which will be economical in the use of energy and capital investment, while providing materials of still smaller particle size, will meet with approval.

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LITERATURE CITED

(1) Am. Soc. for Testing Materials, Standards, D422-39, Part II, pp. 616-25 (1944).
(2) *Ibid.*, E20-33T, Part II, pp. 1575-9 (1944).
(3) Andrews, N. H., U. S. Patent 2,032,827 (March 3, 1936).
(4) Blaine, R. L., *ASTM Bull.*, 108, 17-20 (1941).
(5) Chesler, I., U. S. Patent 2,315,083 (March 30, 1943).
(6) Kidwell, C. H., *Ibid.*, 2,219,011 (Oct. 22, 1940).
(7) Lea, F. M., and Nurse, R. W., *J. Soc. Chem. Ind.*, 58, 277-83 (1939).
(8) Lissman, M. A., *Chem. & Met. Eng.*, 45, 238-9 (1938).
(9) Loomis, G. A., *J. Am. Ceram. Soc.*, 21, 394-9 (1938).
(10) Roller, P. S., IND. ENG. CHEM., ANAL. ED., 3, 212-16 (1931).

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TWO-DIMENSIONAL FORM OF FLOCCULATION

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In making particle size measurements with the microscope (either white light or electron), the investigator is often confronted with the problem of deciding just what constitutes the ultimate particle. This article presents photographs of a certain type of flocculate that can be mistaken readily for a single particle. This type of flocculation has been called "two-dimensional" or "sheet" flocculation. During mounting for microscopical observation, the sheets are broken down (unintentionally) and the individual pieces look like single particles. Nothing can be gained by measuring them, for their size is artificially created by the microscopist. Several tests have been described here for detecting sheet flocculation.

WHEN particle size measurements are taken with a microscope, the investigator must be able to distinguish between single particles and particle groups such as flocculates and aggregates. Sometimes this is easy to do; at other times it becomes a difficult problem. The present paper deals with a type of flocculate that can readily be mistaken for a single large particle.

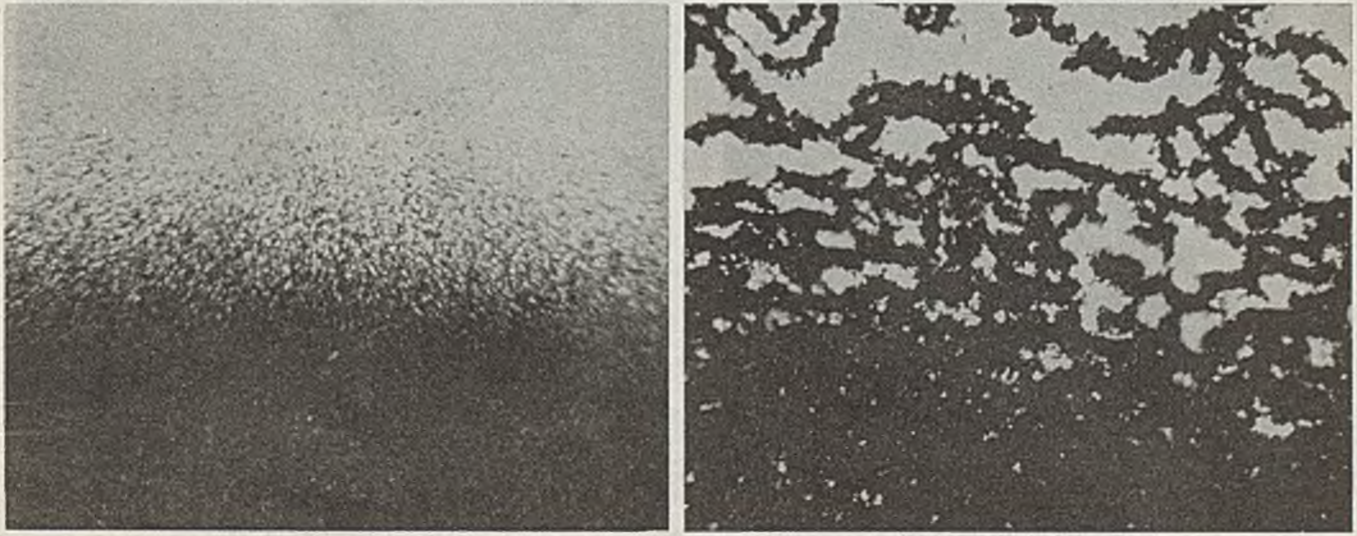
Before this type of flocculate is discussed, it should be made clear that there are many cases where particles form firm aggregates. If these aggregates are not crushed but retain their original size when subjected to the various grinding and milling operations required, then the aggregate itself constitutes the practical ultimate particle and can be measured as such. However, if interest is centered in the size of the actual ultimate particle, then the investigator must isolate the particle or else resort to some means of measurement other than that employed by the microscope.

The term "flocculate" is used here to designate a group of particles loosely held together. The group is not held firmly because at some time prior to its formation each particle is separate and in complete contact with the vehicle in which it is suspended. Under such conditions hard aggregates do not form, unless some chemical reaction takes place that produces a cementing agent.

If there is a decrease in the free energy of the system when two separate particles collide, they will adhere and form a group. This group is easily dispersed upon stirring but is also easily reformed when the currents thus produced subside. The group is not likely to be held together strongly because the particle surfaces are too uneven to form large surface contacts. That is, the actual particle surface lost when two particles touch is probably of molecular magnitude only. The drop in free energy, then, would be relatively small in comparison with what it would be if the entire pigment surface was involved. Only a slight force would be necessary to deflocculate such a group mechanically. As a rule, deflocculation can be carried out temporarily by pressing on the cover glass under which the material is in suspension.

The technique for studying the structure of a pigment vehicle suspension is simple. A very small drop (1 or 2 mg.) of the material is placed on a microscope slide. This drop is covered with some of the vehicle from which the suspension is made. A cover glass is placed on top and pressed down rather firmly. The original drop of the suspension will flow out into a flat disk. Microscopical examination of the edge of this disk will show the state of flocculation in which the pigment exists. Figure 1 illustrates this point.

There are cases where pressing on the cover glass causes no visible deflocculation but instead simply squeezes the material out into a thin sheet. This sheet might tear, break, or wrinkle without showing any signs of deflocculation. It is obvious that such a particle group is not a hard aggregate, for under the cir-



X 600

X 150

Figure 1. Edge of Drop of Gas Black Suspension Showing Deflocculation

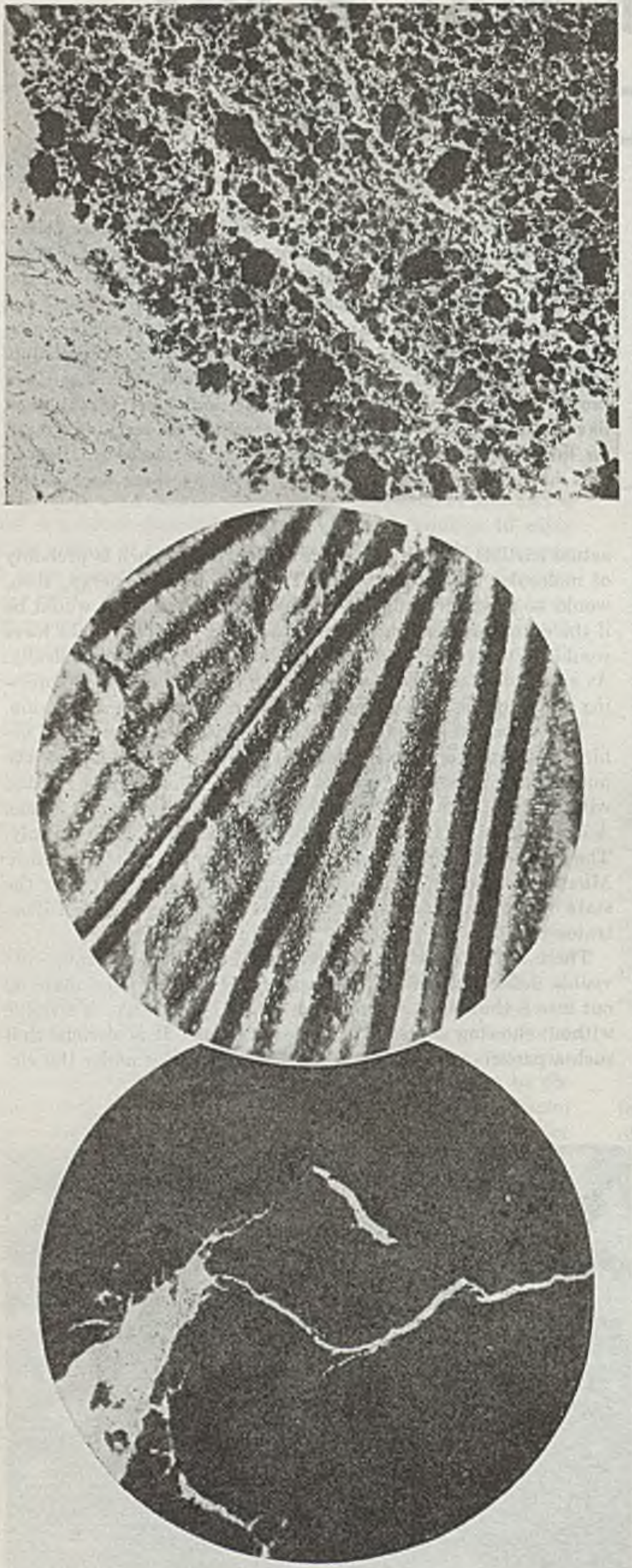


Figure 2. Photomicrographs of Copper Powder

(*Top*) Two-dimensional flocculate (X 300)
(*Center*) Wrinkle test (X 10)
(*Bottom*) Tear test (X 10)

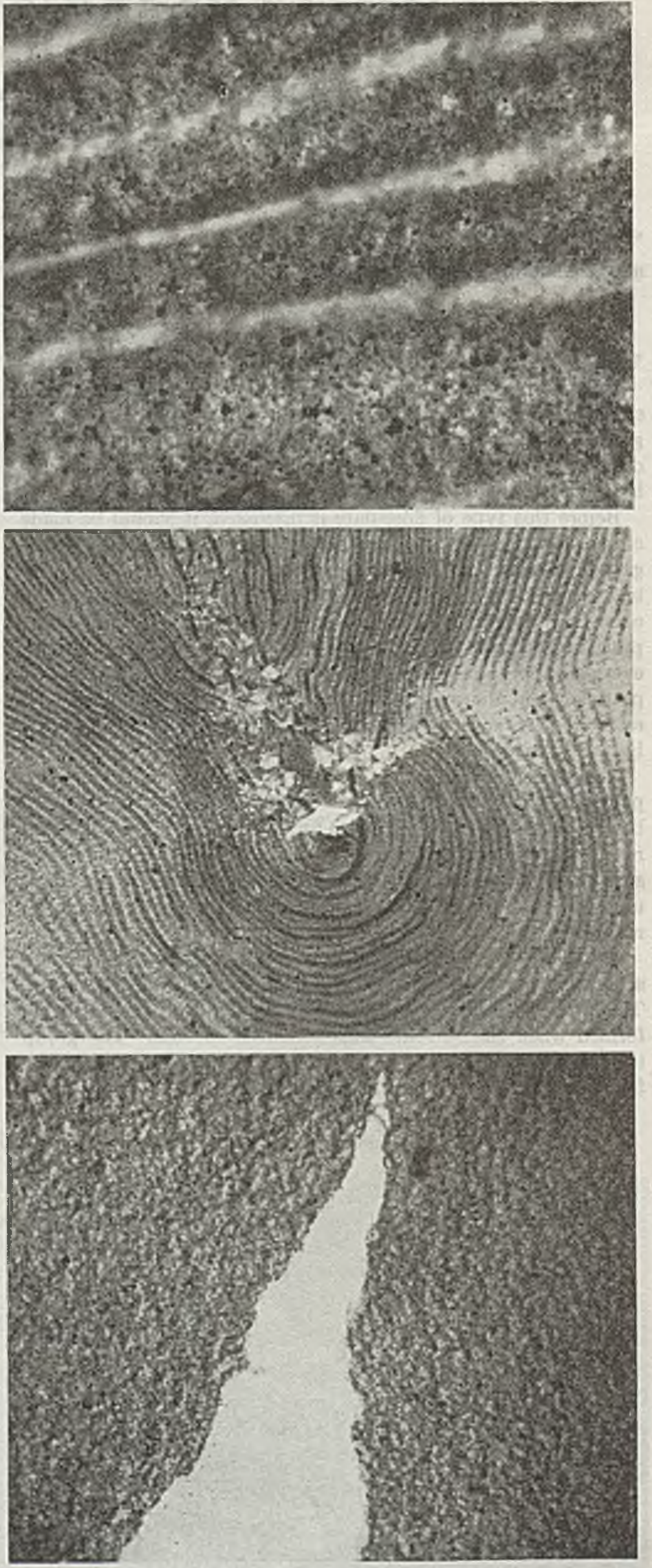


Figure 3. Photomicrographs of a Blue Pigment

(*Top*) Wrinkle test showing individual particles (X 800)
(*Center*) Wrinkle test (X 150)
(*Bottom*) Tear test (X 150)

cumstances it would be crushed into many individual pieces. The fact that it flows and, in the main, retains its identity as a group indicates that it is a form of flocculate. It will be called "two-dimensional" or "sheet" flocculation.

Sheet flocculation can be produced in ways other than squeezing. Whenever a precipitate is formed in a liquid interface such flocculation might occur there. When two liquid solutions that precipitate each other come into contact, a two-dimensional flocculate is formed in the interface. If these liquids are continuously stirred, the flocculate breaks up into fine pieces which settle out while new flocculation is taking place in the new liquid interface that is constantly being formed. In this way a pigment is produced which is composed only of finely broken pieces of sheet flocculate. The inexperienced microscopist could easily be misled into believing that these broken pieces are the ultimate individual particles. In appearance they often resemble very thin rectangular crystals.

However, to the more experienced microscopist these particles do not look quite like real crystals. First, the opposite angles of the rectangular pieces (which are obviously not hemimorphic) are never exactly equal. Second, the edges of the particle are not quite so straight as they would be in a real crystal. These facts are brought out clearly in electron micrographs. Third, the particle has an unnatural thinness.

There is still another but rather unusual way to form a two-dimensional flocculate. Copper powder which has been given a water-repellent coating will float on the surface of water and form a tenacious sheet of particles. The individual particles are large enough in this case to be seen under low magnification (Figure 2, upper photomicrograph). There are two tests for sheet flocculation. A sheet can be made to wrinkle or it can be torn.

Figure 4. Electron Micrographs of Naphthol Blue

(*Top*) Two-dimensional flocculation, individual particles just visible (X 3600). (*Center*) Wrinkle test (X 5000). (*Bottom*) Tear test (X 7000)

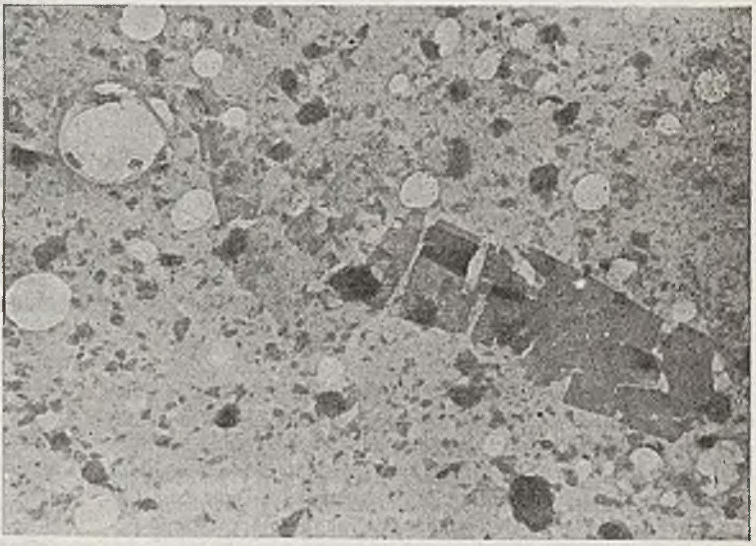


Figure 5. Electron Micrograph of Barium Lithol Toner (X 13,000), Showing Large Sheets

The white oval spaces are holes in the nitrocellulose supporting film

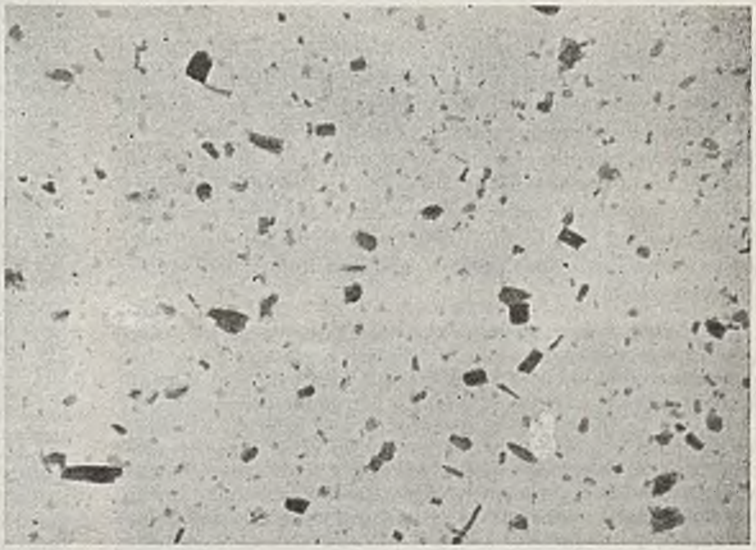


Figure 6. Electron Micrograph of Sodium Lithol Toner (X 13,000)

Sheets broken up into particlelike pieces during dispersion and mounting on supporting film

Figure 2 also shows the sheet of copper particles which wrinkled after it had been pushed against a barrier, as well as the same sheet that had been torn. Normal three-dimensional flocculation shows little or no evidence of such reactions.

As long as the individual particles are large enough to be visible, there is no question of confusing the flocculate with the ultimate particle. Only when the ultimate particle is microscopically invisible is trouble encountered. Figure 3 shows a blue pigment, the particles of which are so small that they have about reached the limit of resolution of the white light microscope. However, the particles can still be seen, and no difficulty arises in interpreting the group as a flocculate. Figure 3 also includes the wrinkle and tear tests on this material.

In the upper micrograph of Figure 4 the particles of Naphthol Blue are almost invisible even with the electron microscope, and appear as a mass of fine dots. Figure 4 also shows the wrinkle and tear tests. When the particles are so small (Figure 5) that they cannot be detected by any microscopical means, the sheet flocculate can readily be mistaken for a large rectangular particle. Since this flocculate is very thin, it will break up into small pieces when it is being mounted for microscopical examination. This means that the size of the group observed depends on how the microscopist has treated it and not upon the manufacturing process. The conclusion is obvious that particle measurements made on sheet flocculates can be of no service in evaluating the quality of the pigment as produced by the manufacturer. Figure 6 is a Sodium Lithol Toner which has been broken down, during mounting, to such an extent that the small pieces of sheets could readily be mistaken for the ultimate particle. Furthermore, this is a case where the argument cannot be advanced that, whether the pieces are ultimate particles or not, they happen to be the ultimate working units actually used. These particular units are those made by the microscopist.

ACKNOWLEDGMENT

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SIZE AND SHAPE OF MACROMOLECULES IN SOLUTION

Polymer molecules are chain- or threadlike structures of very small cross-sectional area. Consequently, although the coiled molecule may extend over distances of several thousand Ångström units, the determination of its size, shape, and weight is not susceptible to most of the direct methods used for particle size determinations of more compact particles. Indirect methods of determining the size of polymer molecules are reviewed here with the hope that they may be applicable to the determination of particle size of other substances where the ordinary direct methods fail or need corroboration. Methods based on the ultracentrifuge, on osmotic pressure, on light scattering, and on streaming birefringence are discussed.

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MOST natural and synthetic high polymers are soluble, and extensive investigation of their dilute solutions has contributed considerably to our knowledge of the size and shape of the dissolved macromolecules. Conditions, however, are in general more complicated than those prevailing during the investigations of suspensions or dispersions. Before enumerating the various methods and reviewing some of the most significant results obtained with them, it may be useful to point out those factors which distinguish polymer solutions from other, simpler dispersed systems.

1. Many polymer molecules have the character of a long, thin, more or less flexible chain. A cellulose acetate chain with a molecular weight of about 300,000 has, if fully extended, a length of about 5000 Å. (500 mμ or 0.5 μ), whereas its diameter is only 6 or 7 Å. In the course of its internal and external Brownian motion, such a molecule exhibits a considerable space requirement and has, therefore, ample opportunity to collide with other molecules and become momentarily attached to them. During these transient contacts, the two polymer molecules do not act as completely independent kinetic units and would not be registered as such by the methods to be described here. Aggregation and other factors do, in such cases, falsify the result of the analysis in the sense that the molecular weight or, better, particle weight as observed experimentally, is different from the "true" molecular weight—namely, the weight of that particle in which all monomers are held together by strong chemical bonds (*35*).

In order to ensure obtaining the correct molecular weight, it is advisable to perform osmotic pressure measurements in at least two different solvents and to carry out the measurements at as low concentrations as possible. In extreme cases it may be necessary to carry out the measurements at a higher temperature in order to eliminate agglomeration.

2. All polymer samples, as available synthetically or from natural products by certain purification procedures, are mixtures of macromolecules of different size and, in many cases, even of different internal structure. There is good experimental evidence that cellulose in wood pulp consists of a mixture of chains, each of which is, in principle, built up by glucoside-bound β-*d*-glucose residues. The number of monomer units, however, differs from chain to chain, and it may well be that the degree of polymerization of the shortest chains in the sample is only around 40 or 50, whereas that of the largest molecules amounts to several thousand. In addition, it is known that in some of the glucose units the primary hydroxyl group is oxidized to a carboxyl group and that in some others carbon atom 6 is missing altogether. We must therefore recognize the existence of two differences between individual chains: the degree of polymerization or chain length and the presence of groups of different chemical character. In other cases, such as polystyrene or polyvinyl chloride, there are three (or more) significant differences between individual chains: their length, the degree to which they are branched, and the presence of chemically different groups. Therefore, it must in general be recognized that a molecular weight distribution curve, as obtained by various fractionation procedures, really represents a separation of the various species of molecules in the sample in regard to their solubility characteristics rather than to their molecular weight alone. The latter does, of course, influence the solubility of the different species in the various mixtures of solvent-precipitant, but the above-mentioned structural details cannot be a priori neglected. It may be that in certain cases, such as uniformly saponified cellulose acetate or polystyrene (polymerized in solution up to a low degree of conversion), the "chemical" differences between the individual chains are of

minor importance, but there is ample evidence that in other cases, such as commercial vinyl polymers and particularly copolymers, fractionation according to solubility does not lead to a simple molecular weight distribution curve.

3. Unlike most colloidal dispersions, the inherent flexibility in polymer molecules causes the shape to be variable. Most soluble polymers consist of long-chain molecules with a certain internal flexibility, the degree of which depends greatly upon the nature of the backbone of the chain and of the substituents distributed along its length. Cellulose and its derivatives are characterized by a comparatively stiff main chain, whereas rubber and butadiene-vinyl copolymers have chains with a more flexible backbone. Under the influence of the Brownian movement of the surrounding solvent molecules, each macromolecule in solution assumes continuously different configurations. It carries out what has been termed a "micro" (*19*) or "internal" Brownian motion, which produces irregular coiling and uncoiling of the long chain. One can therefore speak only of the instantaneous shape of a polymer molecule in a given moment or of its mean shape, as hypothetically obtained by observing the molecule over a longer period and averaging over-all instantaneous configurations. Depending upon the intrinsic flexibility of the chain, upon the interaction between it and the solvent, and upon temperature, a wide variety of average shapes ranging from an almost stiff rod to a randomly shaped and highly entangled coil are possible. It is, therefore, necessary to specify the experimental conditions rather precisely whenever one speaks of the shape of macromolecules in solution.

One extreme case is represented by rather stiff chains, such as cellulose derivatives in good solvents, where the individual molecules can be compared with slightly undulated threads or wires, which change their individual convolutions continuously but never collapse into a tightly coiled ball. The solvent can stream freely along and around the various parts and segments of these molecules; they have, therefore, to be termed "free draining" chains (*20, 32*). The existence of this extreme can be experimentally ascertained by observing the velocities of sedimentation and diffusion or by investigating flow birefringence and intrinsic viscosity.

The sedimentation constant, s, of free-draining chains is expected to be independent of the molecular weight, M. The effective action of the centrifugal force increases directly as the weight of the molecule, and, because of its rigid character, the resistance offered by the solvent is directly proportional (or very nearly proportional) to it. The sedimentation constant is the ratio between force and resistance, and is therefore independent of the molecular weight. This has actually been observed (*18, 20*) for cellulose nitrate and ethylcellulose.

Diffusion constant D, on the other hand, should be inversely proportional to the molecular weight. The driving force for diffusion per molecule is kT (RT per mole) and does not depend upon the molecular weight, whereas the resistance varies directly with the reciprocal of M. This has also been observed for certain cellulose derivatives (*16, 18, 36*). Free-draining chains should show a coefficient of flow birefringence which is, over a wide range, proportional to the rate of shear between the cylinders; their intrinsic viscosity-molecular weight relation should be characterized by an exponent, a, which is near unity (*1, 3, 4, 12, 29, 33, 38*).

The other extreme case is represented by very flexible chains such as rubbery polymers or some proteins in poor solvents, where the chains are irregularly folded up into a more or less tight coil. Considerable amounts of solvent can be immobilized by the entangled segments of the molecule and are consequently carried around with it during its kinetic migration through the liquid ("macro" or "external" Brownian motion, *19*). Such polymer molecules have been termed "matted particles" (*32*); their existence can again be made evident by their behavior in sedimentation, diffusion, flow birefringence, and viscosity. The driving force during the sedimentation of a matted particle in a centrifugal field is proportional to its molecular weight, M, as it was before for a free-draining chain. However, the resistance is now proportional to the square root of M because of the statistical coiling of the chain (*20*). Hence, the sedimentation constant is proportional to $\sqrt{M}$, whereas it was independent of M for a free-draining chain. A similar consideration shows that diffusion constant D for a matted particle is proportional to $1/\sqrt{M}$.

The flow birefringence of matted particles is proportional to the rate of shear in the range of small shearing forces but shows a more than proportional increase as the shearing stress becomes large enough to stretch the individual coils and to increase their axis ratio. Polystyrene has shown some indications for such a behavior.

Exponent a in the intrinsic viscosity-molecular weight relation should not greatly exceed 0.5 for matted particles. In fact, polyisobutylene (*12*) and other rubbery polymers show values for a which are within this range. Apparently, therefore, the two extreme cases—namely, free-draining chains and matted particles—are at least approximately represented by certain systems but, as is to be expected, many intermediate cases are encountered.

These introductory remarks may serve to show that size and shape of polymer molecules in solution are ill-defined quantities; even to define them requires considerable caution. Those experimental methods which are capable of producing numerical data in this field will now be briefly outlined.

OSMOTIC METHOD

The osmotic pressure of a dilute ideal solution is given by the van't Hoff law:

$$\pi = (RT/M)c \tag{1}$$

where π = osmotic pressure
R = gas constant
T = absolute temperature
M = molecular weight of solute
c = concentration

This law holds for normal (low molecular weight) substances up to concentrations of several per cent and can be used to compute M from a measurement of π at known T and c.

A large number of experiments have shown that polymer solutions (with the exception of a few proteins) present distinct deviations from the van't Hoff law at all finite concentrations. Experiment and theory (*2, 13, 17, 23*) have shown that Equation 1 should be replaced by

$$\pi = (RT/M)c + Bc^2 \tag{2}$$

where B is a new constant depending upon the polymer-solvent system, and expressing both the interaction between the molecules of the solvent and the segments of the dissolved macromolecules and the abnormal entropy of dilution encountered in polymer solutions. Even at very high dilutions (0.1% and less) the two parameters, M and B, are required to characterize the osmotic behavior of a polymer solution.

The conventional way to determine these two constants experimentally is to measure π at a given temperature for four or five concentrations (below 0.8 or 1.0%) and then to plot π/c against c. In accordance with Equation 2 a straight line is obtained, the intercept of which on the ordinate represents RT/M, whereas its slope is B. Figure 1 shows such a graph for three polystyrene fractions (M = 340,000, 240,000, and 167,000) and confirms that the experimental points fall fairly well on a straight line. The three fractions exhibit different intercepts but identical slopes. This indicates that their molecular weights are different, as is to be expected from their preparation by fractional precipitation, whereas their specific interaction with the solvent is the same (*4, 10, 12, 22*).

Experience has shown that the intercepts of the π/c *vs.* c plot usually do not depend upon the nature of the solvent and are proportional to the absolute temperature. The osmotic pressures of most polymer solutions lead to satisfactory straight lines, if interpreted according to Equation 2. In a few cases (*1*, *12*) where very high molecular weights were involved, it was observed that the π/c *vs.* c plots gave slightly curved instead of strictly straight lines. In general, then, the molecular weight of a polymer fraction or the number-average molecular weight of an unfractionated material can be determined from a number (four or five) of osmotic measurements at different concentrations.

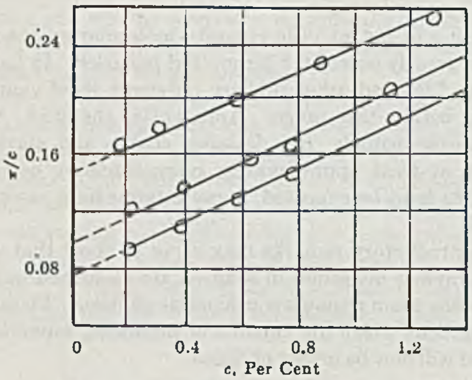

Figure 1. Plot of π/c *vs.* c for Three Polystyrene Fractions

The best experimental procedure is the direct measurement of π in an osmometer. In principle, two techniques are available, the static and the dynamic methods. Each has certain advantages and shortcomings, and it seems that the two methods complement each other satisfactorily. The dynamic method is recommended whenever the individual measurement should not be too time consuming (unstable solutions, danger of diffusion of the solute through the membrane, etc.). The static method is probably more precise, and allows small quantities and elevated temperatures to be used quite easily. A considerable number of individual osmometers and their practical operation have been described during the last few years (*7*, *12*, *15*, *18*, *24*, *39*); a comprehensive description of most of these was recently given by Wagner (*39*). The results of the osmotic method become doubtful if the molecular weight of the polymer is less than 20,000 or if the material contains fractions with molecular weights below this limit. Use of denitrated nitrocellulose membranes shows that molecules of such low weight diffuse through the membrane to a considerable extent. Special precautions (cellophane membranes and short measurements with the dynamic method) may reduce the errors caused by diffusion. In the high molecular weight range the osmotic method becomes difficult because of the low osmotic pressure of the solution. Molecular weight of one or even more millions can still be determined as far as their order of magnitude is concerned, but little claim of precision can be made for such figures.

The most favorable range for the osmotic method is between molecular weights of 50,000 and 500,000. In this laboratory molecular weights of 3,000,000 have been measured with a reproducibility of ±10%. It should be pointed out that the determination of chain end groups by chemical (*28*) or physical (*26*, *27*) methods also leads to the number-average molecular weight of a polymer in solution. The limits of the experimental accuracy, however, restrict this method to comparatively low molecular weights.

The slope of the straight lines in Figure 1 allows the determination of the second parameter, B. The parallelism of the three lines indicates that B does not depend upon the molecular weight, but does depend upon temperature and the nature of the solvent. It is probable that in a set of fractions extending over a wide range of molecular weights (50,000 to 1,000,000) the slopes of the lines in the π/c *vs.* c graphs are not exactly identical but decrease slightly with increasing molecular weight. This may be taken as an indication that in a certain polymer-solvent system the fractions of lower molecular weight approach the behavior of free-draining chains, whereas the higher ones act to a certain extent like matted particles. The different accessibility of some parts or segments of a straight chain as compared with a strongly coiled-up molecule would require a slight change in the entropy term of B as one goes from shorter chains ($M \approx 50{,}000$) to very long ones ($M \approx 1{,}000{,}000$). This effect, however, is only small, and in first approximation the slope of the straight lines in the π/c *vs.* c plot does not depend upon M. Recent theoretical considerations on the dependence of the osmotic pressure in polymer solutions upon concentration lead to expressions for B which are either independent or almost independent of the molecular weight (*14*, *40*).

SEDIMENTATION AND DIFFUSION

Svedberg's ultracentrifuge (*37*) is the classical instrument for measuring sedimentation velocities and equilibria in polymer solutions. For a number of years it was almost exclusively used in the studies of proteins, which proved to be particularly suitable objects for its successful application. More recently a number of typical chain polymers have been investigated with considerable success (*16*, *18*, *25*, *30*, *36*).

As in the case of osmotic measurements, it is necessary to carry out sedimentation velocity runs at very high dilutions (0.1% and less) and to extrapolate from a number of measurements at low concentrations to zero concentration. This extrapolation sometimes meets with considerable difficulties, but in general the sedimentation constant at zero concentration, s_0, can be obtained by measuring sedimentation constant s at various concentrations, c, and extrapolating with the aid of the equation

$$1/s = 1/s_0 + (k/s_0)\,c \tag{3}$$

Plotting $1/s$ against c often yields a straight line, the ordinate intercept of which is $1/s_0$; its slope leads to a new characteristic constant, k, which is connected with constant B of Equation 2, and permits certain conclusions as to the average effective shape of the sedimenting particles and their interaction with the solvent (*5*).

It is usually found that diffusion constant D of polymer solutions also depends noticeably upon concentration and can be expressed as

$$D = D_0\,(1 + k_1c) \tag{4}$$

In order to evaluate Equation 4, it is necessary to determine diffusion constant D of a dissolved polymer at several low concentrations (0.5% and below) and to plot it against c. Then a straight line is obtained, the ordinate intercept of which is the diffusion constant for zero concentration, D_0, whereas its slope leads to a new constant, k_1, which again is related to B in Equation 2. The determination of S_0 and k requires four or five independent sedimentation velocity runs; the determination of D_0 and k_1 requires an equal number of diffusion experiments.

A certain average molecular weight of the dissolved macromolecules can be obtained by introducing s_0 and D_0 into the original Svedberg equation

$$M = s_0RT/D_0\,(1 - V\rho) \tag{5}$$

where R = gas constant
T = absolute temperature
V = partial molar volume of polymer
ρ = density of the solvent

Which of the various existing average molecular weights (number average, weight average, etc.) results from Equation 5 depends upon what kind of averages of s_0 and D_0 are measured in the sedimentation and diffusion runs. This, in turn, is determined by the free-draining or matted character of the dissolved macromolecules (*20, 32*).

In the case of relatively uniform samples, Equations 2 and 5 should give identical values for M because the difference in the averages should eventually become insignificant. A few cellulose acetate fractions have recently been investigated in this laboratory by osmotic, sedimentation, and diffusion measurements, with the result that the molecular weights agreed within the limits of error of the experimental methods. This shows that macromolecules of reasonable homogeneity comply in dilute solution with the assumptions which lead to Equations 2 and 5. Hence their molecular weights can be determined by independent methods. If the results of these methods agree, it may be taken as an indication that they are not too far from the true value.

Instead of using independent sedimentation and diffusion velocity measurements, it is also possible to carry out a sedimentation equilibrium run, in the course of which sedimentation and diffusion act against each other and establish a certain stationary concentration gradient of the polymer. By measuring these stationary concentrations, $c_1, c_2, \ldots\ldots$, at different heights $x_1, x_2, \ldots\ldots$, in the cell and by introducing them into the second Svedberg equation,

$$\overline{M} = \frac{2RT\,[\log c_2/c_1 + (k + k_1)\,(c_2 - c_1) + (kk_1/2)\,(c_2^2 - c_1^2)]}{(1 - V\rho)\,\omega^2(x_2^2 - x_1^2)} \qquad (6)$$

where x_1, x_2 = two different heights in rotating cell
c_1, c_2 = concentration of polymer at x_1 and x_2
k, k_1 = constants of Equations 3 and 4
ω = angular velocity of the rotation
R, T, V, ρ = density of solvent
$\overline{M}$ = a certain average molecular weight, depending on average effective shape of dissolved macromolecules

Molecular weights obtained from Equations 5 and 6 have been compared with one another for a number of (mostly unfractionated) polymers, such as cellulose in cuprammonium and nitrocellulose. They have the same order of magnitude but do not agree closely in actual numerical value. This may be due to the fact that the samples have not been sufficiently homogeneous. As yet no case exists in which Equations 2, 5, and 6 have been applied to relatively homogeneous polymer fractions.

Ultracentrifugal data can be interpreted to give information regarding the average effective shape of the dissolved polymer molecules. Sedimentation constant, s_0, allows the computation of the actual frictional resistance, f_s, for sedimentation:

$$f_s = M(1 - V\rho)/s_0 \qquad (7)$$

This value can be compared with the theoretical frictional resistance which a molecule of weight M would exhibit according to the Stokes law if it were spherical. The ratio f_s/f_0 has been called the "asymmetry coefficient"; it can be interpreted in terms of an axis ratio of idealized ellipsoidal particles. The farther f_s/f_0 deviates from unity, the larger is this axis ratio. This procedure has found many successful applications in the field of protein (*37*) and virus (*21*) studies; it has not yet been systematically applied on solutions of fractionated chain polymers of known osmotic molecular weight.

LIGHT SCATTERING

Debye (*6*) recently showed that the turbidity of polymer solutions is closely connected to the molecular weight of the dissolved macromolecules. This turbidity can be determined by observing the loss of intensity of a light beam passing through a cell with the solution according to

$$I = I_0\, e^{-\tau l} \qquad (8)$$

where I_0, I = intensity of light entering and leaving cell
l = length of cell
τ = turbidity of solution

τ can also be obtained from measuring the intensity, which is scattered by the solutions in directions off the primary beam and is usually (and most conveniently) measured at right angles to the incident light. If τ is determined for different low concentrations, c, of the polymer in solution and if Hc/τ is plotted against c, the theory requires:

$$Hc/\tau = 1/M + (2B/RT)c \qquad (9)$$

where M = weight-average molecular weight
B = same constant as in Equation 2

Quantity H contains the wave length of the scattered light and the refractive index of the pure solvent and of the solution, and has to be determined by an independent refractive index measurement for each polymer-solvent system; it does not contain any empirical term or factor (*6, 9, 41*). Plotting Hc/τ against c should give a straight line, the intercept of which represents $1/M$ similar to Equation 2, whereas the slope should be related to that obtained from osmotic pressure data.

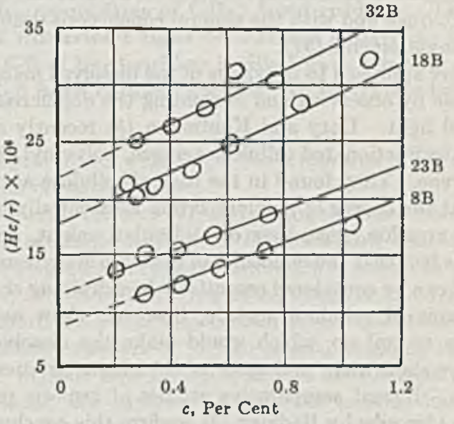

Figure 2. Results of Light Scattering Measurements for Four Cellulose Acetate Fractions

Figure 2 shows the results of light scattering measurements for four cellulose acetate fractions (*34*) in the same solvent. The measured points are reasonably arranged along straight lines, and these lines have different intercepts but about the same slope. From the intercepts on the ordinate, the following molecular weights were obtained after certain corrections were introduced: fraction 8B, 173,000; 23B, 135,000; 18B, 77,000; 32B, 60,000. The corresponding osmotic molecular weights obtained from graphs such as Figure 1 are 163,000, 133,000, 75,000, and 65,000, respectively. This shows that, at least in the case of solutions of cellulose acetate fractions in acetone, the osmotic molecular weights agree reasonably well with those computed from turbidity measurements. As mentioned previously, ultracentrifuge measurements also agree with the osmotic data. Therefore, it can be concluded that for cellulose acetate fractions in acetone the three absolute methods (osmotic pressure, turbidity, and the combination of sedimentation velocity and diffusion data) lead to fairly consistent results as far as molecular weight is concerned.

The slopes of the straight lines in Figure 2 result in an average value of B which also agrees fairly well with the corresponding value derived from osmotic measurements (*4, 34*). This shows that light scattering and osmometry lead not only to a conformation of molecular weights for the various fractions, but also to an agreement as far as interaction between solvent and solute is concerned.

With the light scattering method it is also possible to investigate the shape of the dissolved macromolecules if their largest dimension exceeds one tenth the wave length of the light. When the solute molecules have their largest dimensions (considerably smaller than λ), the scattered intensity does not depend upon the angle under which it is observed. However, as soon as the largest dimension of the scattering particles becomes about one twentieth of λ or still larger, then the scattering in the backward direction is preferentially decreased as a result of intramolecular interference, and a dissymmetry in the angular intensity distribution becomes apparent. This dissymmetry can be interpreted to give information regarding the shape of the dissolved polymer molecules. In the case of the mentioned cellulose acetate fractions, Stein and Doty (*34*) found that a low molecular weight fraction (M = 52,000), which would have a length of about 1000 Å. in the fully extended state, actually exhibits approximately the same maximum length in acetone solution. This indicates that smaller molecules of cellulose acetate in acetone (up to a molecular weight of about 80,000) behave like free-draining chains. On the other hand, the higher molecular weight fractions (up to M = 170,000) show a maximum length in solution of about 1500 Å., whereas the length of the fully extended chain would amount to about 3000 Å. This is in fair agreement with axis ratio measurements of cellulose acetate carried out in the ultracentrifuge and with the general conclusions drawn from viscosity measurements (*31*).

Another approach to the shape of the dissolved macromolecules is possible by observing and evaluating the depolarization of the scattered light. Doty and Kaufmann (*8*) recently applied this method to fractionated cellulose acetate, polyvinyl chloride, and polystyrene. They found in the case of cellulose acetate in acetone that the degree of polymerization is essentially independent of concentration, regardless of molecular weight, and conclude from this fact that the molecules of cellulose acetate are relatively stiff and can be considered essentially free-draining chains. Very long chains of cellulose acetate, however, show an increasing tendency to coil up, which would make the dissolved polymer molecules show more and more of the characteristics of matted particles. Recent comparative studies of osmotic pressure and intrinsic viscosity by Badgley (*3*) confirm this conclusion.

This brief survey of light scattering data available at present shows that in a few cases the Debye method of evaluating the turbidity of polymer solutions has made valuable contributions to our knowledge of the size and shape of polymer solutions.

STREAMING BIREFRINGENCE

If an isotropic solution of polymer molecules is subjected to a shear, it becomes, under certain conditions, anisotropic and exhibits birefringence between crossed polaroids. Two quantities are available for measurement: (*a*) the degree of double refraction as a function of concentration and of rate of shear, and (*b*) the angle of maximum extinction as a function of concentration and rate of shear. Edsall (*11*) recently discussed the theory, experimental setup, and general results of this method. It has been mainly applied on protein solutions. Linear macromolecules have been investigated (*30*) and discussed (*20*) by this procedure only superficially.

In principle, the method permits the determination of the average effective axis ratio of the dissolved macromolecules, and it changes as one goes to higher concentrations and higher rates of shear. If the particles are elongated and rigid, proportionality between the degree of streaming double refraction and the rate of shear should be expected. If, however, the dissolved macromolecules represent loosely entangled coils which are elongated at higher rates of shear, a more than proportional increase of birefringence should be expected as the rate of shear is increased. Indications of such behavior have been found with polystyrene and nitrocellulose solutions (*30*), which seem to offer an interesting way to study the elasticity of single, coiled-up macromolecules in various solvents and at various temperatures.

The results of streaming birefringence measurements would be of particular interest if the dissolved polymer molecules were uniform and if independent data about their size and shape were available from the application of the other quantitative methods. With the exception of the work of Signer and Gross (*30*), no concerted results are available on linear macromolecules, whereas there are many interesting studies on proteins. It seems, therefore, that the application of this method to polymer fractions which have been thoroughly characterized by osmotic, turbidity, sedimentation, and diffusion measurements promises to give additional conclusions concerning the shape of these macromolecules under given conditions and to its changes with solvent, temperature, and rate of shear.

LITERATURE CITED

(1) Alfrey, T., Bartovics, A., and Mark, H., *J. Am. Chem. Soc.*, 65, 2319 (1943).

(2) Alfrey, T., and Doty, P. M., *J. Chem. Phys.*, 13, 77 (1945).

(3) Badgley, W. J., *Polymer Bull.*, 1, 17 (1945).

(4) Bartovics, A., and Mark, H., *J. Am. Chem. Soc.*, 65, 1901 (1943).

(5) Beckmann, C. O., and Rosenberg, J., *Ann. N. Y. Acad. Sci.*, 46, 329 (1945).

(6) Debye, P., *J. Applied Phys.*, 15, 338 (1944).

(7) Dobry, A., and Ouang, C.-H., *J. chim. phys.*, 36, 296 (1939).

(8) Doty, P. M., and Kaufmann, H., *J. Phys. Chem.*, 49, 583 (1945).

(9) Doty, P. M., Zimm, B. H., and Mark, H., *J. Chem. Phys.*, 12, 144 (1944); 13, 159 (1945).

(10) Duclaux, J., *J. chim. phys.*, 41, 209 (1944); 42, 1 (1945).

(11) Edsall, J. T., "Advances in Colloid Science", Vol. I, p. 269, New York, Interscience Publishers, 1943.

(12) Flory, P. J., *J. Am. Chem. Soc.*, 65, 372 (1943).

(13) Flory, P. J., *J. Chem. Phys.*, 10, 51 (1942).

(14) *Ibid.*, 13, 453 (1945).

(15) Fuoss, R. M., and Mead, D. J., *J. Phys. Chem.*, 47, 59 (1943).

(16) Gralen, N., dissertation, Uppsala, 1944.

(17) Huggins, M. L., *Ann. N. Y. Acad. Sci.*, 43, 1 (1942); 44, 431 (1943).

(18) Jullander, I., dissertation, Uppsala, 1945.

(19) Kuhn, W., *Kolloid. Z.*, 68, 2 (1934).

(20) Kuhn, W., and Kuhn, H., *Helv. Chim. Acta*, 26, 1394 (1943).

(21) Lauffer, M. A., *J. Am. Chem. Soc.*, 66, 1188, 1195 (1944).

(22) Meyer, K. H., and Wertheim, M., *Helv. Chim. Acta*, 24, 217 (1941).

(23) Miller, A. R., *Proc. Cambridge Phil. Soc.*, 39, 54 (1943).

(24) Montonna, R. E., and Jilk, J. R., *J. Phys. Chem.*, 45, 1376 (1936).

(25) Mosimann, H., *Helv. Chim. Acta*, 26, 61, 369 (1943).

(26) Pfann, H. F., Salley, J. D., and Mark, H., *J. Am. Chem. Soc.*, 66, 983 (1944).

(27) Pfann, H. F., Williams, Van Zandt, and Mark, H., *J. Polymer Sci.*, 1, 14 (1946).

(28) Price, C. C., *et al.*, *J. Am. Chem. Soc.*, 64, 1103, 2508 (1942); 65, 757, 2380 (1943).

(29) Signer, R., *Trans. Faraday Soc.*, 32, 269 (1936).

(30) Signer, R., and Gross, H., *Helv. Chim. Acta*, 17, 59 (1934).

(31) Simha, R., *J. Chem. Phys.*, 13, 188 (1945).

(32) Singer, Seymour, *Polymer Bull.*, 1, 79 (1945).

(33) Sookne, A. M., and Harris, Milton, Ind. Eng. Chem., 37, 475 (1945).

(34) Stein, R. S., and Doty, P. M., *J. Am. Chem. Soc.*, 68, 159 (1946).

(35) Steurer, E., *Z. physik., Chem.*, A190, 1, 16 (1941).

(36) Stern, K. G., Singer, S., and Davis, Sanford, *Polymer Bull.*, 1, 31 (1945).

(37) Svedberg, The, and Pedersen, K., "The Ultracentrifuge", Oxford University Press, 1940.

(38) Tamblyn, J. W., Morey, D. R., and Wagner, R. H., Ind. Eng. Chem., 37, 573 (1945).

(39) Wagner, R. H., Ind. Eng. Chem., Anal. Ed., 16, 520 (1944); Wagner, R. H., in Weissberger's "Analytical Methods in Organic Chemistry", Vol. I, p. 253, New York, Interscience Publishers, 1945.

(40) Zimm, B. H., *J. Chem. Phys.*, March, 1946.

(41) Zimm, B. H., Stein, R. S., and Doty, P. M., *Polymer Bull.*, 1, 90 (1945).

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Comparison of Natural and Synthetic Hard Rubbers

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GR-S, nitrile, and natural hard rubbers are compared as regards compounding, processing, vulcanization, and physical and dielectric properties. Natural rubber and GR-S compounds intermediate in sulfur content between hard and soft rubber also are compared. GR-S and nitrile rubber compositions suitable for commercial ebonite fabrication are described. Extensive breakdown of the basic copolymers has little effect on the physical properties of synthetic ebonites. The time required for the beginning of exothermic reaction in vulcanization is longer for GR-S than for natural rubber ebonites. Rockwell hardness is greater for GR-S. Some GR-S ebonites are penetrated to the same depth as natural ebonites, with a greater tendency toward instantaneous recovery. The two are similar in impact strength, but the ability to withstand a sharp bend is characteristic of natural ebonites alone. The latter are superior to GR-S ebonites in heat deformation below 60° C., but above this temperature the reverse is true and nitrile ebonites are superior to both. GR-S ebonites are more stable and nitrile ebonites less stable chemically than natural ebonites. GR-S ebonite dust as a filler increases brittleness. A diatomaceous earth improves the processing properties of GR-S hard rubbers. The adverse effect of ultraviolet light on surface resistivity is reduced when a GR-S hard rubber is filled with whiting. Natural and GR-S hard rubbers are alike in dielectric behavior.

THE wartime replacement of natural rubber with synthetics required an unusual expenditure of effort by the hard rubber industry in a short time. At first, curtailment of normal production, coupled with War Production Board restrictions of formulations, mitigated the urgency for synthetic hard rubber research. It soon became evident, however, that a complete line of synthetic hard rubbers would be desirable. These materials could be fabricated with standard rubber processing equipment, and would offer physical and electrical equivalents for the various grades of natural hard rubber developed during nearly a century.

A program was started in these laboratories with the realization that rapid progress might be difficult; research on the compounding of natural hard rubber over the years had failed to produce improvements in over-all properties compared with the original "ebonites". The latter, according to the accepted nomenclature (*14*), are simple mixtures of rubber with large amounts of sulfur vulcanized by heating until chemical saturation of the rubber is almost complete. The first approach to the problem was through a study of vulcanizing characteristics, and through examination of the hard products resulting from the reaction of sulfur with butadiene-styrene copolymers[2]. As the program progressed, the work was extended to cover the processing of GR-S for ebonite fabrication and the compounding of GR-S hard rubbers for specific applications. Studies also were conducted relating to the compounding and processing of nitrile hard rubbers, and new tests were developed to supplement standard procedures used in the physical evaluation of hard rubbers.

Earlier work in these laboratories had indicated that approximate dielectric equivalents of standard hard rubbers could be obtained; the method suggested was direct replacement of first quality smoked sheet rubber with polybutadiene and GR-S synthetic rubbers from both foreign and domestic sources. Earlier work had indicated also that the dielectric properties of these materials could be improved by washing the rubber prior to compounding in order to remove water-soluble impurities. The processing characteristics of these materials had revealed that their behavior in production would necessitate a revision of some standard procedures which were being followed in the commercial fabrication of hard rubber.

Stöcklin (*22*), Gartner (*7*), and Roelig (*18*) discussed the use of the Buna synthetic rubbers in German hard rubber manufacture, and English and Russian interest was shown in the work of Scott (*20, 21*), Kashin (*11*), and Alexandrov and Lazurkin (*1*). These reports disclosed that certain properties of hard products from synthetic rubbers of foreign origin, including resistance to moisture, organic liquids, acids, and to deformation at elevated temperatures, are superior to those of natural hard rubbers. Consistently mentioned shortcomings were difficulties in fabrication and a pronounced brittleness in fully cured synthetic hard rubbers.

Limited information on GR-S hard rubbers was published by Cheney (*5*), who studied various vulcanizates including compounds containing 25 and 35% sulfur. The vulcanization temperature was 157° C., and mention was made of the vigorous evolution of hydrogen sulfide during the cures; this behavior indicated that the reaction involved considerable substitution. Morris (*17*) and co-workers described a series of experimental GR-S hard rubbers in which types and amounts of sulfur were varied, and the effects of different fillers and softeners on physical properties were investigated. The compounding and properties of nitrile hard rubbers were described by Garvey and Sarbach (*8*).

COMPOUNDING AND VULCANIZATION OF GR-S EBONITES

The GR-S used had 10.76% acetone-extractable matter and 2.50% ash. The iodine number after acetone extraction was 354.3 and the styrene content (ash corrected), as determined from the iodine number, was 21.9%. The unsaturation, as estimated from analytical data by the method of Kemp and Peters (*15*), showed that for complete vulcanization at a temperature at which substitution would be minimized, the required sulfur would be approximately 40 parts per hundred of whole polymer. No chemical examination was made of the Hycar OS-10, which was a sample of standard material obtained from the Hycar Chemical Company and assumed to have a butadiene-styrene ratio of 50-50. Stauffer tire-brand sulfur was used in all of the experimental mixtures.

Individual batches consisting of 300 grams of GR-S and the required amounts of sulfur were mixed on a water-cooled standard laboratory mill (*2*), allowing 10 minutes for mastication and 5 minutes for the addition of sulfur. After overnight storage the batches were given an additional 10-minute remix before vulcani-

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[2] Unless otherwise stated, the GR-S was obtained from the Goodyear (Akron, Ohio) plant.

zation. None of these compounds mixed on an open mill was sufficiently tacky or free from nerve to be suitable for calendering, plying, and tin plating according to the method employed in processing natural rubber. Compression-type molds faced with tin foil were used to make uniform test sheets. The foil facilitated removal from the molds and assured uncontaminated surfaces for electrical tests.

Sheets $^1/_2$, $^1/_8$, and $^1/_{16}$ inch thick and 6 inches square were vulcanized in steam platen presses with the temperature carefully controlled. The sheets were cured individually and positive pressure was maintained during vulcanization, to compensate for shrinkage and to eliminate the necessity of surface grinding in the preparation of test specimens. Two-hour intervals were used to study the time effect on the vulcanization reaction and on the resulting products. The lowest vulcanizing time, producing a Rockwell hardness above HR-80 in a half-inch sheet, was utilized to establish the range of cures for each compound.

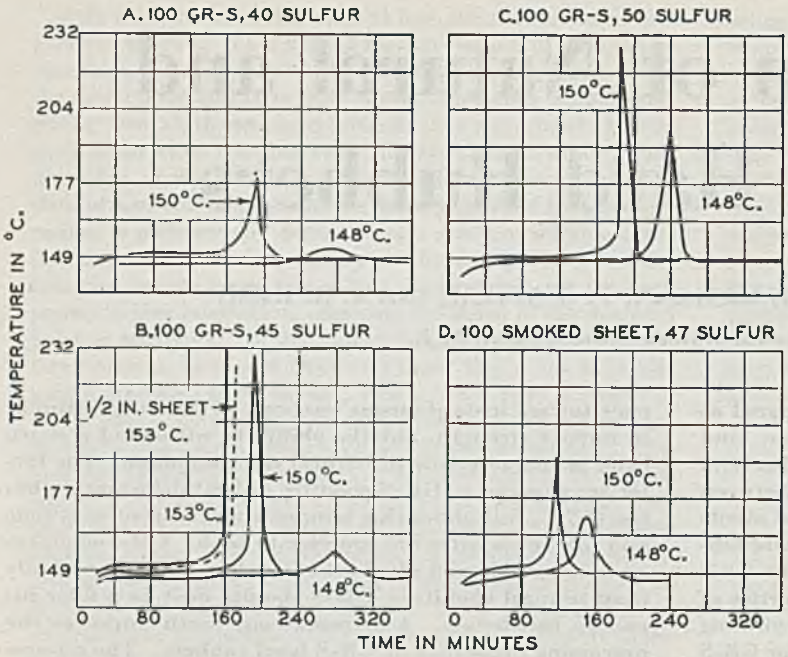


Figure 1. Heat of Exothermic Reaction of GR-S and Natural Rubber Ebonites during Vulcanization

HEAT OF EXOTHERMIC REACTION

The effects of sulfur content and temperature of vulcanization on the exothermic reaction in GR-S ebonites are shown in Figure 1. Cylinders ($1^1/_8 \times 1^3/_8$ inches) of GR-S ebonite mixtures, containing 40, 45, and 50 parts by weight of sulfur, were cured in a steel mold placed in the center of steam platens and shielded from external air currents. Iron-constantan thermocouples were inserted into the center of each specimen through a transite plug in the side of the mold. Similar data were obtained for a natural rubber ebonite of 68:32 composition, because, although this reaction in natural hard rubber has been the subject of a number of investigations, the most recent of which was reported by Church and Daynes (*6*), it was considered advisable to obtain a direct comparison under identical conditions. Platen temperatures of 148° and 150° C. were used for curing all samples; a cure also was run on the 100:45 GR-S ebonite at 153° C.

With natural rubber and sulfur, compounded in ebonite proportions (68:32) and subjected to a vulcanizing temperature of 148° C., the internal heat formation became evident after 80 minutes and reached a maximum of 170° C. after 138 minutes. Increasing the temperature of vulcanization to 151° C. advanced the start of exothermic reaction to 50 minutes; a peak temperature of 191° C. was observed at 116 minutes. Sections were cut from the centers of the cured hard rubber cylinders and fractured for examination. The specimens vulcanized at 148° C. were dense and free from porosity, whereas the 150° C. vulcanizing temperature yielded a porous product, permeated with hydrogen sulfide.

The curves in Figure 1 show that the time required for the beginning of the exothermic reaction is considerably longer for the GR-S than for the natural rubber. The reaction, when it does occur, produces a much higher rise in temperature in the case of the GR-S containing 45 and 50 parts sulfur and vulcanized at 150° C.

PHYSICAL PROPERTIES

The A.S.T.M. procedures (*3*) for testing hard rubber products were followed in determining tensile strength, elongation, flexural strength, impact strength (Izod), cold flow, and Rockwell hardness. Measurements of deformation under the conditions of the cold flow test were made at 71° C., and elastic moduli were calculated from load-deflection data taken in conjunction with flexural strength tests. The data for GR-S and Hycar OS-10 ebonites are listed in Tables I and II, respectively. These results show the variations obtainable through changes in sulfur content and time of cure. Changes produced by continued heating are particularly evident in the GR-S ebonites compounded with less sulfur than is required for theoretical saturation. There is a striking similarity between the over-all properties of the GR-S ebonites compounded with 40 or more parts of sulfur per hundred of whole polymer, and the corresponding data for a fully cured natural ebonite. The fully cured Hycar OS-10 ebonite compounded with 40 parts of sulfur appears to be superior.

Table I. Physical Properties of GR-S Ebonites

Compd.	Sulfur as Compounded, %	Cure Hr.	Cure ° C.	% Cold Flow 49° C.	% Cold Flow 71° C.	Impact Strength (Izod), Ft.-Lb. per In.	Flexural Properties, Lb. per Sq. In. Strength	Flexural Properties, Lb. per Sq. In. $E^a \times 10^3$	Tensile Strength, Lb. per Sq. In.	Elongation, %	Rockwell Hardness, HR
100:25	20.0	16	153	39.3	73.3	1.119	9,130	242	5,980	5.8	83
		20		35.4	48.0	0.963	10,100	263	6,525	4.0	89
		24		26.2	39.4	0.759	10,230	295	7,380	3.9	94
100:30	23.07	8	153	35.8	43.7	0.871	9,300	255	6,670	7.2	83
		10		34.6	45.7	0.932	9,830	265	7,560	6.0	88
		24		2.8	21.6	0.684	12,770	301	8,280	5.4	104
100:35	25.92	6	153	18.0	33.2	0.732	10,570	319	8,380	5.3	92
		8		17.4	35.5	0.661	11,800	296	8,280	5.8	95
		10		5.0	27.1	0.583	11,800	305	7,920	3.9	101
100:40	28.57	6	153	3.0	20.5	0.552	13,070	323	8,740	7.0	103
		8		1.4	9.9	0.523	12,470	317	7,870	5.2	107
		10		1.4	9.5	0.515	14,000	325	9,100	8.5	107
100:45	31.03	8	148	4.7	26.6	0.517	13,300	318	7,570	7.2	103
		10		2.2	17.2	0.501	13,700	323	8,420	4.8	108
		12		2.2	17.8	0.496	13,870	325	8,160	3.2	109
100:50	33.33	8	148	12.0	27.5	0.547	13,030	332	8,325	5.7	101
		10		1.5	11.2	0.562	14,270	337	8,130	3.1	109
		12		1.8	8.4	0.563	14,700	333	7,410	2.4	111
Natural rubber ebonite, 100:47		10	148	2.5	18.0	0.53	15,000	330	10,600	4.0	99

[a] E = Modulus.

Table II. Physical Properties of Hycar OS-10 Ebonites

	Cure		% Cold Flow		Impact Strength (Izod), Ft.-Lb. per In.	Flexural Properties Lb. per Sq. In.		Tensile Strength, Lb. per Sq. In.	Elongation, %	Rockwell Hardness, HR
Compd.	Hr.	° C.	49° C.	71° C.		Strength	$E \times 10^3$			
100:30	4	153	21.3	44.8	0.485	14,200	368	9,310	7.7	100
	6		1.4	21.9	0.491	15,800	364	8,670	5.0	109
	8		1.7	26.7	0.483	15,300	360	10,700	6.7	107
100:35	4	148	37.3	54.8	0.502	11,500	341	9,350	4.0	92
	6		3.6	28.8	0.500	14,500	363	9,400	4.1	104
	8		0.8	2.7	0.441	12,200	392	10,850	6.3	113
100:40	4	148	2.2	25.6	0.500	14,400	376	9,980	4.3	105
	6		1.1	13.9	0.499	12,900	376	10,800	5.8	110
	8		0.4	1.4	0.507	17,100	359	10,610	4.3	116
100:45	4	148	1.4	12.4	0.448	16,400	399	9,540	5.0	110
	6		0.5	1.7	0.332	17,800	339	10,740	5.4	116
	8		0.3	0.7	0.352	12,400	387	11,340	6.0	118

Table III. Brittleness and Penetration Recovery of GR-S and Natural Rubber Ebonites

Compn.	Brittleness Breaking Angle for $^1/_{16}$-In. Strips Deflected 6°/Sec., Degrees	Tests with $^1/_2$-In. Specimens and $^1/_4$-In. Ball	
		Penetration[b]	Residual deformation
GR-S: sulfur			
100:35	39	121.5	26
100:40	30	115.0	21
100:45	27	115.0	22
100:50	26	108.0	19
Natural ebonite: sulfur, 100:47	90[a]	116.0	31

[a] Specimen did not break.
[b] One scale division = 0.002 mm.

The Rockwell hardness values for the GR-S ebonites are higher than those commonly observed in natural ebonites, and a reduction in impact strength is evident in the Hycar OS-10 ebonite of 100:45 composition; but none of the other measured properties furnishes any indication of the brittleness mentioned by European investigators. Brittleness is known to exist in these materials through observations made in the course of preparing test specimens.

To add further significance to the differences in Rockwell hardness, penetration and recovery measurements after 15-second intervals were made on a series of GR-S ebonites compounded with different sulfur contents, in comparison with a natural ebonite of 100:47 composition. Using the conditions specified by the Rockwell hardness test for hard rubber, the data in Table III were obtained. They demonstrate that GR-S ebonites containing 40 and 45 parts of sulfur are penetrated to approximately the same depth as the natural ebonite. Their tendency toward instantaneous recovery when the load is removed is of a higher order than that of the natural ebonite. The GR-S ebonite of 100:35 composition is somewhat less resistant to penetration than the natural ebonite but nevertheless exhibits a greater recovery upon removal of the deforming load. Increasing the sulfur content to 50 parts per hundred of GR-S increases the resistance to penetration to a marked degree and also effects a further reduction in the deformable phase.

The similarity of impact strength values for the natural and GR-S ebonites might lead to the assumption that strips of natural and synthetic ebonites of equal thickness can be bent to the same degree before breaking. A discussion in the literature of the brittleness of ebonite (*4*) was based on the results of Charpy impact tests. If, however, brittleness is defined as the degree of bending that a given material will withstand at 25° C. before breaking, instead of as the energy a supported sample will absorb from a pendulum before breaking, a fundamental difference between the natural and synthetic products becomes evident.

Several methods were investigated for determining the degree to which natural and synthetic ebonites can be bent before fracture occurs. The apparatus shown in Figure 2 was used to apply a sharp bend over a constricted area to test specimens $^1/_2 \times {}^1/_{16}$ inch in cross section. Table III compares the bending properties of natural and GR-S ebonites as made by this method. Another type of equipment used for brittleness tests was the Olsen-Tour-Marshall stiffness tester (*23*). Although it was primarily designed for measuring modulus in flexure of a rigid material, this tester was adapted to the quantitative measurement of brittleness by the use of a $^7/_{16}$-inch span. Figure 3 shows typical results comparing the stiffness, *A*, and brittleness, *B*, of natural and GR-S ebonites.

It appears that the ability to withstand a sharp bend is characteristic of natural ebonites and is not obtainable in GR-S ebonites, even if the latter have a relatively low sulfur content. Unsuccessful attempts were made to improve this property of GR-S ebonites by the use of selenium, which is claimed to produce an elastic phase incapable of conversion to the hard state, and by the use of polymeric plasticizers such as polyisobutylene, Butyl rubber, and a sulfur vulcanizable polyester (Paraplex S-200). It is of interest to note, however, that exposure at low temperatures reverses the order of brittleness in the natural and GR-S ebonites. After a 24-hour conditioning period at −30° C. the natural ebonite fractured when it was bent 12°, while the brittleness of a GR-S ebonite was unchanged.

The heat deformation of natural and synthetic ebonites was investigated by means of a parallel plate plastometer with electrically heated platens, and by a deforming load of 900 pounds per square inch applied for one hour. Materials examined included natural and GR-S ebonites of 100:46.5 and 100:45 composition,

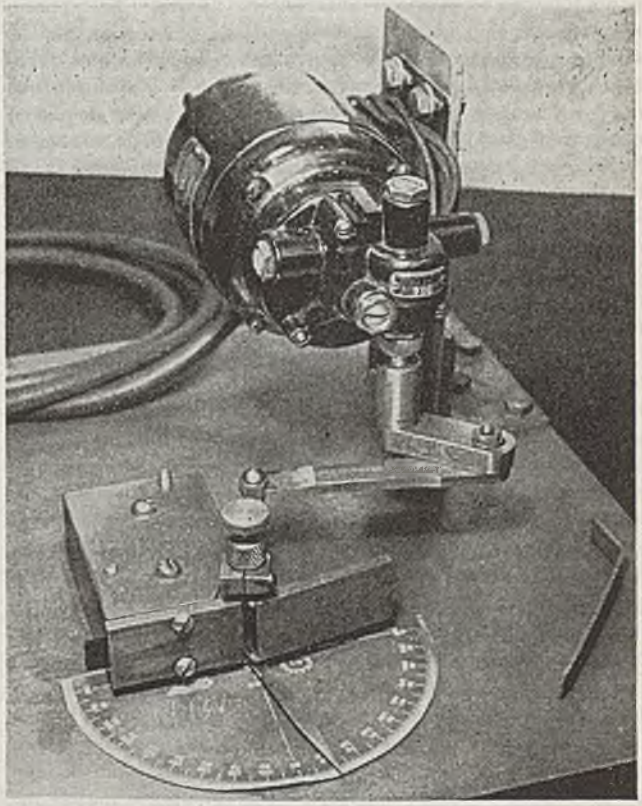
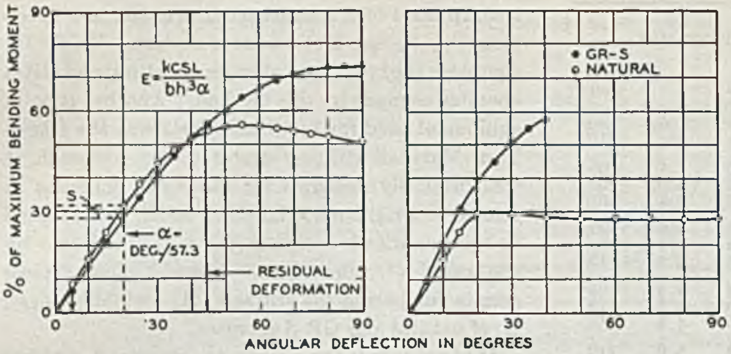


Figure 2. Apparatus for Brittleness Testing of Hard Rubbers

Strips $^1/_2$ inch wide and $^1/_{16}$ inch thick are broken by bending at 6° per second



A. **Stiffness. Span (*L*) = 2 inches. Capacity (*C*) = 6 inch-pounds**

B. **Brittleness. Span (*L*) = 7/16 inch. Capacity (*C*) = 10 inch-pounds**

Figure 3. Tour-Marshall Tests on GR-S and Natural Rubber Ebonites

respectively, and nitrile ebonites of 100:40 and 100:45 composition. The latter were compounded with a nitrile copolymer containing 26% acrylonitrile. In view of the difficulties encountered in the fabrication of nitrile ebonites, one of these materials containing 10 parts by weight of Naftolen R-100 was included in the series. The temperature-deformation curves in Figure 4 show that the natural ebonite is superior to the GR-S hard product below 60° C., but above this temperature the reverse is true. The superior heat deformation of the nitrile ebonites also is evident, but the adverse effect of using a plasticizer to improve the working properties is obvious.

CHEMICAL STABILITY

The effect of heat on the rate of hydrogen sulfide evolution from natural and GR-S ebonites was determined according to a procedure followed by previous investigators (*24*, *25*). The apparatus consisted of a glass tube with an enlarged section for the samples, and connecting inlet and outlet tubes of smaller diameter for the passage of nitrogen over the ebonite. The outlet tube was fused to the sample container, and the inlet tube connected by a ground glass joint. A glass wool filter pad at the exit end of the sample tube prevented any of the material from being swept into the precipitation bottle. The apparatus was mounted in an oven, and commercially pure nitrogen was passed through a 25-foot coil of stainless steel tubing which was also enclosed in the oven. A Fisher-Milligan bubble tower, containing a saturated solution of lead acetate acidified with acetic acid, was connected to the exit end.

The temperatures at which perceptible lead sulfide precipitates formed during a 2-hour exposure were determined with this assembly; 2.5-gram samples were removed with a wood rasp from fully vulcanized half-inch-thick ebonite sheets. The natural ebonite (100 smoked sheet, 46.5 sulfur, cured 11 hours at 148° C.) exhibited no appreciable signs of decomposition during 2-hour periods at 93° and 99° C. At 104° C., however, a lead sulfide precipitate was visible at the tip of the exit tube in the bottom of the bubble tower. At 116° and 127° C. lead sulfide appeared in appreciable quantities throughout the tower. A fresh sample placed in the heating tube for 2 hours at 138° C. resulted in the formation of 0.040 gram of lead sulfide.

A similar examination of GR-S ebonite (100 GR-S, 45 sulfur, cured 11 hours at 148° C.) produced only a slight visible formation of lead sulfide. At 143° C. some decomposition was evident in a two-hour heating period, and at 149 °C. the lead sulfide precipitate from a 9.5-hour test weighed 0.039 gram, approximately the decomposition observed for natural ebonite in 2 hours at 138° C.

A nitrile ebonite sample (100 Perbunan, 42 sulfur, cured 10 hours at 142° C.) was more unstable than the natural and GR-S ebonites. The first noticeable lead sulfide formation from this material occurred at 99° C.; after 9.5 hours at 149° C. the weight of the precipitate was 0.174 gram.

The relative chemical stabilities of natural and GR-S hard rubber dusts were tested by storing samples of similar particle size in a closed container in the presence of, but not in contact with, lead acetate-impregnated filter paper; the samples were examined at intervals during a 2-month period. Progressive darkening of the paper indicated that the rate of hydrogen sulfide evolution was decidedly more rapid from the natural hard rubber dust. After one hour a noticeable reaction was apparent on the edges and exposed side of the paper over the natural dust, but no discoloration was observed in that over the GR-S. After 2 months the reaction of hydrogen sulfide with lead acetate over the GR-S dust was barely evident, while the same exposure to the natural dust produced a lustrous gray-black formation over the entire exposed section of the indicator paper.

DUST-FILLED GR-S HARD RUBBERS

Hard rubber dust has long been used in the fabrication of thick articles, mainly because it dilutes a given mixture and reduces the exothermic heat of reaction during vulcanization. Its use results in materials which are satisfactory dielectrics and can be machined easily, although they are of reduced physical quality. Hard rubber dust also lowers the cost of articles when reduced quality is commensurate with ultimate application.

At first, commercial-type hard rubbers containing GR-S were compounded with whole-tire reclaimed rubber and natural hard rubber dust (Table IV, compound *A*). Vulcanizates of this kind, however, proved to be extremely brittle and subject to excessive deformation under the conditions of the cold flow test. As GR-S became more available and the supply of natural hard rubber dust was exhausted, formulas were investigated in which the reclaimed rubber was deleted and GR-S ebonite dust replaced the corresponding natural product (Table IV, compound *F*). The composition listed contains the minimum quantity of dust required to impart satisfactory processing characteristics to an open-roll-mill mix; the sulfur content shown produces a suitable compromise between cold flow and impact strength.

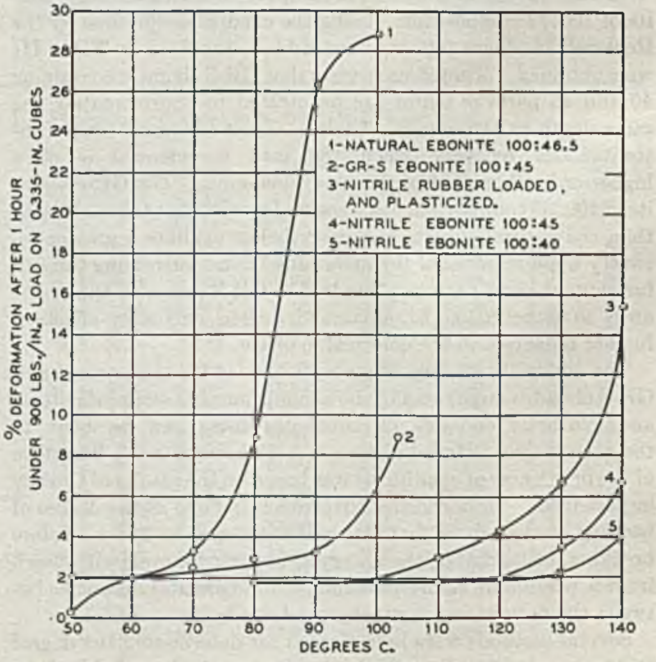


Figure 4. Flow Characteristics of Natural and Synthetic Hard Rubbers

Table IV. Technical Formulations of Synthetic Hard Rubbers

Ingredients, Parts by Wt.	GR-S Reclaim Dust-Loaded Hard Rubber, *A*	GR-S Hard Rubbers: Flexible ebonite, *B*	GR-S Hard Rubbers: Ebonite, *C*	GR-S Hard Rubbers: Whiting-filled, *D*	GR-S Hard Rubbers: Celite-filled, *E*	GR-S Hard Rubbers: Dust-filled, *F*	Nitrile Hard Rubbers: Celite-filled, *G*	Nitrile Hard Rubbers: Ebonite, *H*
GR-S, type CA	...	100.0	100.0	...	...	...	...	...
GR-S, type AC	100.0	...	...	100.0	100.0	100.0	...	...
Nitrile rubber, 26% acrylonitrile	...	...	...	...	...	...	100.0	...
Nitrile rubber, 39.5% acrylonitrile	...	...	...	...	...	...	...	100.0
Reclaimed rubber, 62% rubber hydrocarbon	121.5	...	...	...	...	...	...	...
Sulfur, tire brand	85.75	...	37.5	37.5	39.0	40.0	42.5	35.0
Sulfur, micronized SC	...	40.0	...	...	...	...	...	...
Magnesium oxide, LC	...	3.0	3.0	3.0	...	3.0	10.0	3.0
Hard rubber dust, natural	200.0	...	...	...	...	...	...	...
Hard rubber dust, GR-S	...	...	...	...	...	50.00	...	...
Atomite whiting	...	...	...	100.0	...	...	...	...
Celite 270	...	...	...	...	50.0	...	50.0	...
Naftolen R-100	32.3	...	...	15.0	12.0	12.0	10.0	...
O.E.I. (dodecyl mercaptan)	...	2.0	...	...	...	...	...	...
Synpep N	...	...	2.0	...	...	...	...	...
G-25 plasticizer	...	...	...	...	...	...	...	10.0
Total	539.55	145.0	142.5	255.5	201.0	205.0	212.5	148.0
Vulcanization								
Time, hr.	11	11	11	11	11	11	10	10
Temperature, ° C.	148	148	148	148	148	148	142	142
Physical properties								
Cold flow, %								
49° C.	16.6	2.2	1.8	1.4	2.53	7.6	0.46	0.50
71° C.	40.0	14.8	11.0	15.9	13.5	27.1	1.38	0.85
Flexural strength, lb./sq. in.	10,600	14,800	13,900	11,800	14,300	9,000	...	11,700
Modulus, lb./sq. in.	369,000	312,000	298,000	303,000	402,000	355,000	...	335,000
Izod impact strength, ft.-lb./in. of notch	0.265	0.465	0.415	0.463	0.410	0.313	...	0.398
Brittleness, degrees to break								
0.062 × 0.50 in.	12	42	30	25	20	20	16	22
0.031 × 0.50 in.	32	>90	55	...	...	...	...	...

Further studies on GR-S dust-filled hard rubbers, using hot processed copolymers, indicated that commercial compounds can be produced adequately with smaller amounts of dust, in applications where retention of shape and elimination of blowing during vulcanization require its use. However, GR-S dust in quantities as low as 5 parts by weight causes an appreciable increase in brittleness.

MINERAL-FILLED GR-S HARD RUBBERS

Experimental compounds, prepared primarily to investigate the possibilities of improving the working properties of GR-S hard rubbers, covered the range of mineral fillers commonly used in the rubber industry. With the cool open-roll-mill mixing technique, only one ingredient, a diatomaceous earth designated as Celite 270, had a favorable effect on processing characteristics. The minimum quantity required to produce a stock that could be calendered without excessive shrinkage was 50 parts by weight on the whole polymer. Further compounding experiments with formulations based on GR-S and Celite in these proportions resulted in the development of commercially adaptable compounds which have found extensive use. A typical formula of this type is listed in Table IV (compound *E*).

A GR-S whiting-filled hard rubber compound suitable for fabrication of sheets (compound *D*, Table IV) was examined for electrical surface stability after exposure to ultraviolet light, in comparison with a whiting-filled natural hard rubber and the corresponding natural ebonite. Exposure was by a General Electric S_4 sunlamp at a distance of 12 inches; the surface resistance was measured with a high sensitivity galvanometer by the direct deflection method at 30° C. and 90% relative humidity. The surface resistivity of a GR-S ebonite of 100:45 composition previously had been determined as 3.3×10^5 ohms after 110 hours, at which time the test had been discontinued because of the low value. After 800-hour exposure, the whiting-filled natural and whiting-filled GR-S hard rubbers exhibited surface resistivity values of 3.4×10^8 and 3.8×10^7 ohms, respectively, as compared to 4.8×10^5 ohms for the natural ebonite after 800 hours and 3.3×10^5 ohms for the GR-S ebonite after 110 hours. On the basis of these tests, although the surface resistivities of both the whiting-filled GR-S hard rubber and the GR-S ebonite are lower than that of the natural products, the improvement brought about by whiting is significant.

DIELECTRIC PROPERTIES

Equipment and methods described in an earlier publication (*13*) were used in most of the dielectric tests. The power factor and dielectric constant of GR-S and Hycar OS-10 ebonites were measured at 1, 10, and 100 kilocycles, with the test temperature at 25° C. and the relative humidity equal to or less than 40%. The variation of dielectric constant and power factor with frequency and sulfur content of the GR-S and Hycar OS-10 ebonites is shown in Table V. Data on nitrile hard rubbers as well as data of Scott, McPherson, and Curtis (*19*) on natural rubber ebonite are included for comparison. The sulfur content of GR-S, Hycar OS-10, and natural rubber ebonites appears to have only a small effect on dielectric properties under the given conditions. The change in dielectric constant and power factor with time of cure of the GR-S and Hycar OS-10 ebonites also is slight, as indicated in Table VI. Dielectric constant increases between 4- and 8-hour cures probably are due to increases in combined sulfur. The power factor of the Hycar OS-10 ebonites is lower than that

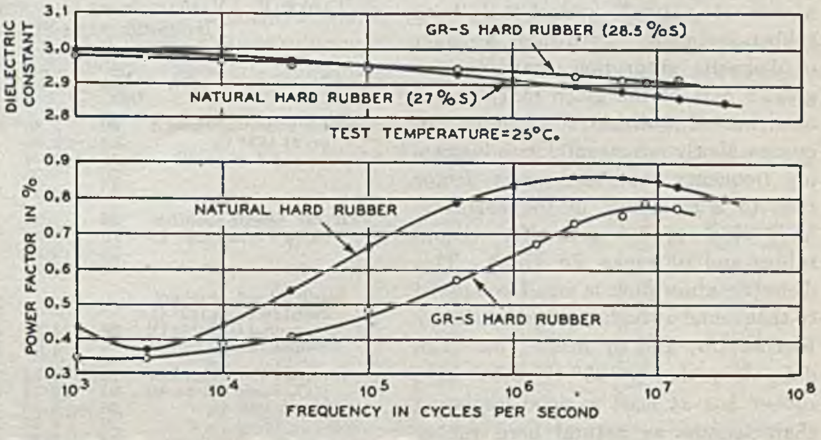


Figure 5. Frequency Variation of Dielectric Constant and Power Factor of GR-S and Natural Rubber Ebonites

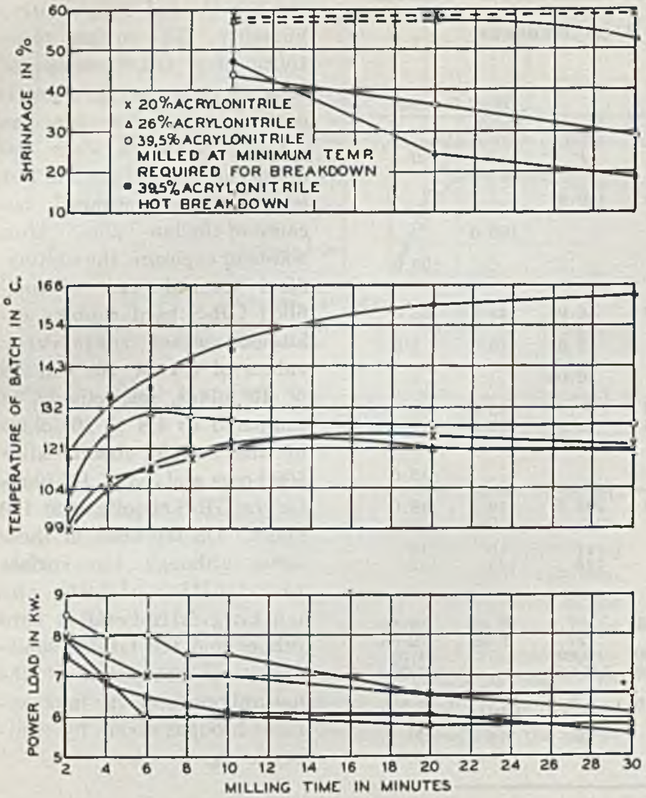


Figure 6. Milling Study of Nitrile Rubber for Ebonite Fabrication

1000-cc. batches processed in No. 0 Banbury

of the GR-S but increases to a small extent directly with curing time.

The dielectric constant and power factor of one GR-S hard rubber were measured over a frequency range of 1 kilocycle to 14 megacycles. Measurements from 100 kilocycles to 14 megacycles were made on a type 160-A Q-meter, with a substitution condenser designed by Yager (*26*) of these laboratories. The data are plotted in Figure 5 with corresponding data on a natural hard rubber. The sulfur content of the GR-S is slightly higher than that of the natural rubber. The latter had been dried over phosphoric anhydride for a month before test, whereas the GR-S sample had been kept in the laboratory at a relative humidity of 40% or less; hence the dielectric constant and power factor of the GR-S may be even lower than those shown.

It is evident that the dielectric behavior of natural and GR-S hard rubbers is similar. Both show a region of dielectric absorption spanning the greater part of the given range of frequencies. The dielectric constant decreases slowly but steadily with increasing frequency, and the power factor rises to a maximum in the neighborhood of 3 × 10^6 cycles for natural rubber and 10^7 cycles for GR-S. This dielectric absorption is small compared to that found at higher temperatures by Kitchin (*16*) and by Scott (*19*). The data show that at 25° C. GR-S hard rubber has at least as good insulating characteristics as natural hard rubber over a wide frequency range.

PROCESSING AND COMPOUNDING STUDIES

The synthetic ebonites prepared and examined as described serve to define the over-all properties obtainable; the fact that special techniques were required to produce them, however, led to an intensive study of the processing characteristics of GR-S and nitrile copolymers, to determine which of these base materials were best suited for commercial ebonite fabrication. Since Banbury breakdown is factory practice, this method was used in studies of the effect of time and temperature as well as addition of organic compounding ingredients as processing aids.

The Banbury-processed materials were worked for 5 minutes in 325-cc. portions from 1000-cc. batches on a 6 × 12 inch roll mill set for 0.040-inch clearance under constant conditions; the materials were sheeted on the front roll by gradual opening until the bank disappeared. The samples then were cut squarely across, placed on a talced surface, and measured 5 minutes after removal to determine shrinkage. A 20-minute breakdown at 149-163° C. with Naugatuck GR-S produced a base material having a shrinkage figure of 27%. One of the softest GR-S copolymers available, which forms a hole-free band in several passes through the open rolls, was found to shrink 55%. This sample was from the Firestone Lake Charles plant and was similar in open-roll-mill behavior to the GR-S used in the earlier experiments. A number of GR-S samples from other sources exhibited shrinkage values intermediate between those of the two extremes cited. The GR-S most favorable for hot Banbury processing was extremely difficult to work on open rolls, requiring 10 minutes to produce a hole-free band.

The GR-S copolymer showing the most favorable breakdown as judged by shrinkage tests was compounded with sulfur and put through the standard processing operations of calendering, ply building, tin plating, and vulcanization under water in the autoclave. The need for more surface tack was evident but other conditions were favorable. This deficiency was overcome by addition of a small quantity of magnesium oxide and small quantities of chemical plasticizers. One of these processing aids, dodecyl mercaptan, had a beneficial effect on the brittleness of the vulcanizate, for two parts by weight with a specially processed sulfur (Table IV, compound *B*) gave an ebonite of low cold flow which could be bent through an angle of 90° in thin strips. Another chemical plasticizer, Synpep N, also proved of value (Table IV, compound *C*). Two parts by weight added at the end of the mix resulted in a pronounced tack favorable to building operations. The same quantity incorporated with the GR-S at the start of the processing cycle completely inhibited the breakdown and produced a material which, although soft and tacky, had a shrinkage of 60%.

TABLE V. VARIATION OF DIELECTRIC PROPERTIES OF NATURAL AND SYNTHETIC HARD RUBBERS WITH SULFUR CONTENT AND FREQUENCY AT 25° C.

	Sulfur Content, %	Dielectric Constant					Power Factor, %				
		1 kc.	3 kc.	10 kc.	30 kc.	100 kc.	1 kc.	3 kc.	10 kc.	30 kc.	100 kc.
GR-S ebonites, cured 8 hr. at 153° C.	20	2.86	..	2.84	..	2.82	0.48	..	0.43	..	0.53
	23	2.85	..	2.84	..	2.82	0.39	..	0.37	..	0.47
	26	2.94	..	2.91	..	2.89	0.68	..	0.55	..	0.63
	29	2.98	..	2.95	..	2.93	0.66	..	0.56	..	0.61
	31	2.97	..	2.94	..	2.92	0.67	..	0.56	..	0.64
Hycar OS-10 ebonites, cured 8 hr. at 153° C.	23	2.94	..	2.92	..	2.92	0.31	..	0.34	..	0.44
	26	2.87	..	2.86	..	2.85	0.31	..	0.33	..	0.48
	29	2.86	..	2.84	..	2.83	0.31	..	0.33	..	0.40
	31	2.91	..	2.89	..	2.88	0.36	..	0.35	..	0.39
Nitrile hard rubbers, cured 10 hr. at 142° C.											
Compound *G*, Table IV	30	3.81	3.77	3.71	3.65	3.58	1.62	1.79	2.10	2.44	2.79
Compound *H*, Table IV	26	3.94	3.89	3.80	3.72	3.61	3.03	2.83	3.09	3.37	3.53
Natural rubber ebonites (*19*), cured 25 to 40 hr. at 140° C.	20	2.73	2.72	..	..	2.70	0.30	0.35	..	..	0.58
	23	2.73	2.72	..	..	2.70	0.25	0.33	..	..	0.63
	26	2.76	2.75	..	..	2.74	0.32	0.39	..	..	0.74
	29	2.79	2.78	..	..	2.75	0.42	0.48	..	..	0.75
	32	2.82	2.81	..	..	2.78	0.43	0.47	..	..	0.72

Similar studies were conducted on nitrile copolymers with variable acrylonitrile content. The base material most suitable for ebonite compounding, as judged by freedom from shrinkage, was Hycar OR-15, a copolymer containing 39.5% acrylonitrile. Data on the nitrile copolymers are plotted in Figure 6 and show temperature, power consumed, and shrinkage of the milled materials. One 39.5% compound was milled at the minimum temperature required for breakdown; the other was milled at hot breakdown.

TABLE VI. VARIATION OF DIELECTRIC PROPERTIES OF GR-S AND HYCAR OS-10 EBONITES WITH SULFUR CONTENT AND TIME OF CURE AT 1 KILOCYCLE AND 25° C.

	Sulfur Content, %	Dielectric Constant						Power Factor, %					
		4 hr.[a]	6 hr.	8 hr.	10 hr.	16 hr.	24 hr.	4 hr.[a]	6 hr.	8 hr.	10 hr.	16 hr.	24 hr.
GR-S	20	2.84	..	2.86	..	..	2.84	0.38	..	0.48	..	..	0.38
	23	..	..	2.85	..	2.91	3.01	..	..	0.39	..	0.39	0.46
	26	2.90	2.89	2.94	..	..	..	0.65	0.69	0.68	..	..	..
	29	..	2.93	2.98	2.99	..	..	..	0.61	0.66	0.63	..	..
	31	2.91	2.96	2.97	..	..	..	0.74	0.65	0.67	..	..	..
Hycar OS-10	23	2.83	2.82	2.94	..	..	..	0.22	0.26	0.31	..	..	..
	26	2.79	2.85	2.87	..	..	..	0.20	0.29	0.31	..	..	..
	29	2.82	2.90	2.86	..	..	..	0.20	0.31	0.31	..	..	..
	31	2.82	2.93	2.91	..	..	..	0.24	0.35	0.36	..	..	..

[a] Time of cure at 153° C.

When the nitrile ebonite mixture prepared with Hycar OR-15 was compounded with 35 parts by weight of sulfur and broken down for 30 minutes at the elevated temperature, it was dry and leathery but could be calendered smoothly on rolls at 66° C. Other studies directed toward adding the necessary tack to the nitrile ebonite mixture resulted in selection of a polyester plasticizer of low molecular weight, Paraplex G-25. Adding 10 parts by weight to the 100:35 nitrile ebonite base produced a stock (Table IV, compound *H*) that could be tin-plated and built up into thick sheets without ply separation. As a further guide to the selection of the most suitable nitrile hard rubber compound for general use, open-roll mixtures were made using one of the softer rapid banding copolymers (Perbunan containing 26% acrylonitrile) compounded with Celite 270 and other ingredients as shown in Table IV (compound *G*). This compound, although it could be calendered, plied, and plated did not have any advantages over the plasticized ebonite. The latter offers the most satisfactory approach to the commercial sheet fabrication of nitrile hard rubber.

Vulcanization experiments on tin-plated nitrile hard rubber sheets under water in the autoclave indicated that this process requires unusual precautions. At a vulcanizing temperature of 148° C. surface decomposition was evident after 6 hours, considerably short of the time required to produce the maximum resistance to deformation at elevated temperatures in an unaccelerated compound. Decomposition was eliminated by using a vulcanizing temperature of 142° C. This has become the standard practice of these laboratories in nitrile ebonite vulcanization. It is important that perfect contact be made between the tin and calendered sheet in the plating operation prior to vulcanization, as the conditions of autoclave vulcanization are favorable to the hydrolysis of the cyanide groups in the acrylonitrile copolymer. Ammonia generated by this reaction would be damaging.

EFFECTS OF HOT MASTICATION

Certain changes in the structure of the synthetic copolymers undoubtedly result from the prolonged hot breakdown necessary to facilitate the fabrication of ebonites. It may be assumed that the chain molecular length is shortened and the gel content increased by this treatment; furthermore the over-all reactions during vulcanization with sulfur might be different among copolymers thus treated, and the same materials prepared by mixing on a cool open-roll mill. Determinations of unsaturation showed no significant change in samples taken from a batch of GR-S originally and after 10, 20, and 30 minutes of hot Banbury mastication. Using the Kemp-Wijs method the values were 332.8, 333.5, 333.9, and 332.8, respectively, for the periods mentioned.

The physical test values determined for the GR-S ebonites prepared from hot processed copolymer (compounds *B* and *C*, Table IV) are of a high order. The fact that the commercial type of formula (compound *C*, Table IV) developed the properties listed, with a sulfur content of 37.5 parts per hundred of whole polymer, may be attributed to ingredients other than the GR-S and sulfur; or it may be taken as an indication that a lower sulfur ratio is advisable in compounding ebonites in which the GR-S has been subjected to hot breakdown. Processors of soft rubber may be surprised that this extensive breakdown of the basic copolymers has little effect on the ultimate physical properties of synthetic ebonites, since a similar technique in the fabrication of soft products results in a marked reduction in tensile strength, elongation, and other mechanical properties.

INTERMEDIATE COMPOSITIONS OF GR-S AND SULFUR

A mixture consisting of 100 parts of GR-S and 25 parts of sulfur vulcanized 16 hours at 153° C. was the first material of the series that could be evaluated by conventional test methods; nevertheless, lower cured products of this composition as well as those of a 100:20 GR-S and sulfur mixture are of interest in view of certain needs for flexible leatherlike materials. These needs are now being filled by plasticized polyvinyl chloride and other compounded flexible plastics.

Cheney (*5*) reported that the relation between sulfur content and tensile strength of GR-S vulcanizates shows a progressive increase, and that above 10% combined sulfur, the increase in tensile strength is substantial. Data of Houwink (*10*) for vulcanizates of natural rubber and sulfur indicated a maximum tensile strength at 5.5 to 6.0% combined sulfur, and a falling off to a minimum value at 12% combined sulfur with no marked increase until after 25%. The high tensile strength of natural pure gum rubbers in the low sulfur range contrasts sharply with the low tensile strength of the corresponding GR-S gum stocks.

Natural rubber vulcanizates compounded with sulfur varying from 15 to 25 parts by weight (13 to 20%) were examined by Gibbons and Cotton (*9*) as possible substitutes for leather and compounded soft rubber soling stocks. Their work showed that accelerated compounds containing 17.5 parts by weight of sulfur exhibit the highest original physical properties, and that unaccelerated compounds cured with 22.5 to 25.0 parts of sulfur have the best aging properties but are not sufficiently stable under accelerated aging conditions to warrant their use. No marked improvements are obtained by the use of antioxidants.

Rubber-sulfur vulcanizates were shown by Kemp (*12*) and later by Scott, McPherson, and Curtis (*19*) to vary widely in dielectric

TABLE VII. DIELECTRIC PROPERTIES OF GR-S INTERMEDIATE VULCANIZATES AT 25° C.

Sulfur		Vulcanization[b]		Dielectric Constant (1 Kc.)	Power Factor, % (1 Kc.)	D.C. Vol. Resistivity (400 Volts)
Parts[a]	%	Hr.	° C.			
6	5.7	12	148	3.09	0.56	$>10^{16}$
12	10.7	12	148	3.46	4.78	$>10^{16}$
14	12.3	12	148	3.38	6.18	$>10^{16}$
16	13.8	12	148	3.19	6.06	$>10^{16}$
18	15.3	12	148	3.05	4.59	$>10^{16}$
20	16.7	12	148	3.03	4.35	$>10^{16}$
20	16.7	8	153	3.02	4.17	10^{16}
20	16.7	24	153	2.84	0.87	6×10^{16}

[a] By weight to 100 of whole polymer.
[b] 1/16-inch calendered sheets, tin-plated and vulcanized under water in open steam.

Table VIII. Physical Properties of Intermediate Vulcanizates of GR-S and Smoked Sheet Rubber

Composition	Vulcanization Time	Vulcanization ° C.	Tensile Strength, Lb./Sq. In.	Elongation, %
GR-S 100, sulfur 20	8 hr.	148	2100	115
	12 hr.	148	2200	110
	16 hr.	148 orig.	2900	85
	16 hr.	148 aged[a]	2930	76
	24 hr.	148	3740	65
	36 hr.	148	5060	28
GR-S 100, sulfur 20, Altax 1, Zimate 1	4 min.	200 orig.	1500	100
	4 min.	200 aged[a]	2100	76
	6 min.	200	2225	70
	8 min.	200	2900	67
Smoked sheet 100, antioxidant 2, sulfur 21	16 hr.	148 orig.	2920	205
	16 hr.	148 aged[a]	525	0[b]
	36 hr.	148	2950	200

[a] Specimens aged 48 hr. in oxygen bomb at 70° C. and 300 lb./sq. in. O_2 pressure.

[b] Oxidized surfaces developed cracks immediately upon application of load.

properties at 25° C. and 1 kilocycle in the intermediate ranges of combined sulfur. Kemp's data indicated a maximum in dielectric constant (3.95) at 10% combined sulfur, as compared to 3.2 at 5% in the soft rubber range and 2.7 when 19% sulfur is combined with the rubber. The power factor reached a maximum of 0.098 at 13% combined sulfur and a value of 0.005 at 19%, as compared to 0.014 at 5%.

From the information given on the intermediate products of natural rubber and sulfur it appears that their rapid deterioration on aging is the main objection to their commercial use. Although our investigation of GR-S–sulfur vulcanizates below the ebonite range was limited, there is evidence that some of these materials may be of interest in applications where their specific properties are advantageous. The effect of sulfur content on the dielectric properties of flexible GR-S vulcanizates (Table VII) indicates that the 1 kilocycle dielectric constant and power factor reach maximum values with 12 and 14 parts of combined sulfur, respectively. The power factor remains high throughout the range of flexible products, but upon conversion of the 100:20 composition to a hard product by prolonged heating at 153° C., the power factor drops to 0.87% and the dielectric constant to 2.84.

Table VIII contains physical test data for intermediate products of GR-S and smoked sheet rubber vulcanized at 148° C. and for an accelerated GR-S and sulfur mixture cured at 200° C. A significant difference in the natural and GR-S compositions may be seen in the data for the 16- and 36-hour cures. The tensile strength and elongation of the natural rubber composition undergo practically no change, whereas the extended cure converts the GR-S vulcanizate from a flexible to a hard product of high tensile strength and relatively low elongation. However, the GR-S product cured 16 hours exhibited little change in physical properties or appearance after 2 days of aging in an oxygen bomb. The corresponding natural rubber was converted to an unextensible product of exceedingly brittle surface and visibly deteriorated internal structure.

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LITERATURE CITED

(1) Alexandrov, A. P., and Lazurkin, Y. S., *J. Tech. Phys.* (U.S.S.R.), 9, 1249–60 (1939).
(2) Am. Soc. for Testing Materials, Standards on Rubber Products, D15–41 (1944).
(3) *Ibid.*, D530–39T (1944).
(4) Ariano, R., *Rubber Chem. Tech.*, 10, 778–86 (1937).
(5) Cheney, La V. E., and Robinson, A. L., Ind. Eng. Chem., 35, 976–79 (1943).
(6) Church, H. F., and Daynes, H. A., *Rubber Chem. Tech.*, 17, 923–28 (1944).
(7) Gartner, E., *Kautschuk*, 16, 109–16 (1940).
(8) Garvey, B. S., Jr., and Sarbach, D. V., Ind. Eng. Chem., 34, 1312–15 (1942).
(9) Gibbons, P. A., and Cotton, F. H., *Trans. Inst. Rubber Ind.*, 11, 354–76 (1935–36).
(10) Houwink, R., "Elasticity, Plasticity and Structure of Matter", p. 196, London, Cambridge Univ. Press., 1937.
(11) Kashin, *J. Rubber Ind.* (U.S.S.R.), 10, 521 (1936).
(12) Kemp, A. R., U. S. Patent 1,656,737 (1928).
(13) Kemp, A. R., and Herrmann, D. B., *Proc. Rubber Tech. Conf.*, 1938, 893–909; *Rubber Chem. Tech.*, 12, 317–31 (1939).
(14) Kemp, A. R., and Malm, F. S., "Chemistry and Technology of Rubber", ACS Monograph 74, Chap. 18, pp. 635–55, New York, Reinhold Pub. Corp., 1937.
(15) Kemp, A. R., and Peters, Henry, Ind. Eng. Chem., Anal. Ed., 15, 453–9 (1943).
(16) Kitchin, D. W., Ind. Eng. Chem., 24, 549–55 (1932).
(17) Morris, R. E., Mitton, P., Seegman, I., and Werkenthin, T. A., *Rubber Age* (N. Y.), 54, 129–33 (1943).
(18) Roelig, H., *Chem. Fabrik*, 12, 481–82 (1939).
(19) Scott, A. H., McPherson, A. T., and Curtis, H. L., *Bur. Standards J. Research*, 11, 173–209 (1933).
(20) Scott, J. R., *Rubber Chem. Tech.*, 15, 826–34 (1942).
(21) *Ibid.*, 17, 719–30 (1944).
(22) Stöcklin, P., *Trans. Inst. Rubber Ind.*, 15, 51–66 (1939–40).
(23) Tinius Olsen Testing Machine Co., *Bull.* 11 (1939).
(24) Webster, D. M., and Porritt, B. D., *India-Rubber J.*, 79, 239–43 (1930).
(25) Wolesensky, E., *Bur. Standards J. Research*, 4, 501–13 (1930).
(26) Yager, W. A., *Trans. Electrochem. Soc.*, 74, 113–34 (1938).

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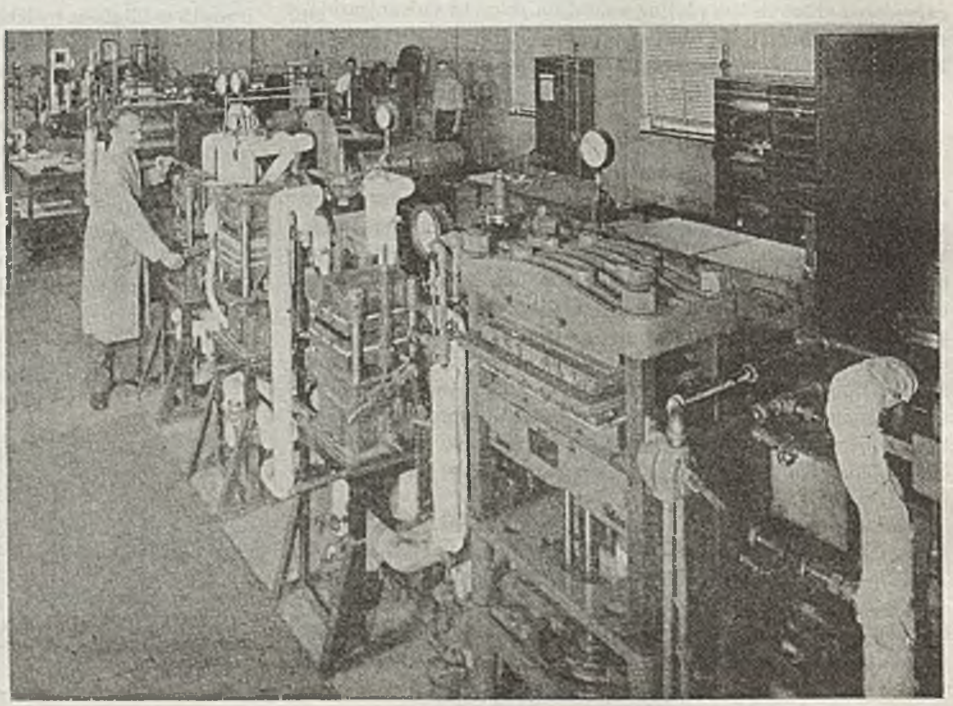

Water Immersion Testing of Metal Protective Paints

ROLE OF OSMOSIS IN WATER ABSORPTION AND BLISTERING

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A paint system consisting of one coat of zinc chromate primer and one coat of low gloss, alkyd hull paint was applied to various substrate materials and immersed for varying periods of time in distilled water and in solutions of sodium chloride and sucrose with osmotic pressures of 6 to 30 atmospheres. The rate and degree of water absorption and blistering were determined by extensive measurements of weight and volume changes, and by visual examination. Regardless of the nature of the substrate and immersion bath, water absorption and blistering increased with increasing immersion time but decreased markedly with increasing osmotic pressure of the bath. Factual evidence developed here establishes that water is transferred through the face of the paint film under the influence of, and at a rate determined by, the difference in osmotic pressure of the bath solution and of the solution formed within the paint system by the water absorbed. If osmotic pressure of the external solution is high enough, blistering does not take place. The minimum osmotic pressure of the external solution required to prevent blistering varies with the nature of the substrate, and is suggested as a basis for measuring the adhesion level of the test coating for the substrate material. Some evidence is presented which indicates that water absorption does not take place by way of pores but by a process related to actual solution.

ONE of the major types of coating failure when painted metal articles are immersed in fresh or sea water is blistering and peeling. Some progress has been made in overcoming blistering by formulation; but it is doubtful that this problem can be solved satisfactorily until more is known about the fundamental mechanism by which blisters are formed when paint films are intermittently or continuously immersed in water.

In the course of work on the development of metal protective pigments and primers, extensive use was made of water immersion tests, and consideration was given to the variables involved in this type of exposure. Some evidence was uncovered which indicated that the blistering of paint films immersed in fresh water is largely due to osmotic effects, whereas blistering in salt water is a combination of osmotic and electroendosmotic effects (*5*). This evidence, however, was insufficient to furnish a measure of the relative importance of osmotic and electroendosmotic influences and to formulate a valid theory of blister formation. Subsequent experiments have furnished the necessary data, and the results obtained in a study of osmotic influences are described and discussed in this paper.

For the purpose of this report osmosis is defined as the transfer of water through a paint film under the influence of a solute concentration gradient; electroendosmosis applies to the movement of water through a film under the influence of an electrical potential gradient.

This investigation dealt with the behavior of a paint system under purely osmotic influences. Electroendosmotic influences may be avoided by eliminating, as far as possible, highly corrosive environments or corroding substrates which could set up electrical potential gradients across the paint film and thus cause electroendosmosis. Both of these schemes were employed to make certain that the conclusions drawn were justified.

Three series of tests were conducted. In the first series a paint system was applied to glass panels and immersed in sodium chloride solutions of varying solute content and, hence, of varying osmotic pressures. In the second series the same paint system was applied to glass panels and immersed in sugar solutions covering the same range of osmotic pressures as the salt solutions in the first test series. This served to determine whether there is any difference in principle in the behavior of paint systems immersed in solutions which had the same osmotic pressures or escaping tendencies but contained different solutes. In the third series the same paint system was applied to steel, duralumin, zinc, and glass panels, and immersed in the same sugar solutions employed in the second series. This permitted a study of the influence exerted by the substrate and helped to strengthen the general concepts derived from the results of the first two test series.

PANEL TESTS

The paint system used in this work consisted of one coat of zinc chromate primer (Navy specification 52-P-18) and one coat of low gloss, gray alkyd hull paint (made from 52-P-25 base). Although this particular paint system is not intended for use under water, it was chosen because a considerable amount of data is available from previous water immersion tests with it, and because it is relatively easy to prepare and handle.

The panels were approximately 3.3 × 2.6 inches in size; they varied in thickness depending upon the panel material. The glass panels were cut from used spectrographic plates and were approximately 0.05 inch thick. After the photographic emulsion had been removed, the plates were cleaned in chromic acid solution, thoroughly rinsed first in tap and then in distilled water, and finally dried by dipping in alcohol and ether. The metal panels were buffed to a high degree of polish several days before being coated and stored in a desiccator over calcium chloride. On the day before the application of the test paint, they were lightly buffed and then thoroughly cleaned in trichloroethylene vapor. All of the panels were then weighed in both air and distilled water in order to permit their volumes to be calculated. The edges and corners of all panels were well rounded.

The test paints were applied by dip coating at such a rate as to yield primer and finish coats about 1.25 mils thick each. The

TABLE I. WATER ABSORPTION OF COATING ON DIFFERENT SUBSTRATES

Osmotic Pressure of Sugar Soln., Atm.	Water Absorption, %, 48-hr. immersion				192-hr. immersion				840-hr. immersion			
	Fe	Al	Zn	Glass	Fe	Al	Zn	Glass	Fe	Al	Zn	Glass
0	11.9	...	11.0	11.2	16.0	15.3	15.7	15.9	20.6	27.2	30.5	27.2
6	8.4	8.0	7.5	7.7	14.0	12.0	13.1	....	16.6	13.7	17.5	14.8
12	5.4	5.3	5.0	5.0	10.0	8.5	8.6	9.2	13.8	11.9	12.7	....
18	4.5	3.9	3.9	3.9	7.3	6.3	6.1	6.5	9.9	8.5	8.1	8.9
24	4.1	3.3	2.8	3.0	5.4	4.9	4.7	4.8	7.4	6.4	6.5	6.4
30	3.0	2.8	2.4	2.7	4.3	3.9	3.7	4.0	5.9	5.0	5.0	5.3

TABLE II. WATER ABSORPTION OF COATING IN SALT AND SUGAR SOLUTIONS

Osmotic Pressure of Soln., Atm.	% Water Absorption after Immersion for: 24 hours		48 hours		96 hours		192 hours		384 hours		840 hours	
	NaCl	Sugar	NaCl	Sugar	NaCl	Sugar	NaCl	Sugar	NaCl	Sugar	NaCl	Sugar
0	7.2	5.9	10.6	9.6	12.9	11.8	16.0	14.0	19.7	18.4	29.9	26.3
6	4.6	4.6	6.3	6.4	8.9	8.5	10.1	10.5	11.3	11.5	12.3	11.9
12	3.4	3.5	4.5	4.6	5.9	5.7	7.1	6.9	8.4	8.4	8.2	9.7
18	3.0	2.9	3.6	3.7	4.4	4.6	5.3	5.3	5.5	6.2	6.5	7.0
24	2.4	2.5	2.8	3.0	3.2	3.6	3.6	4.1	4.0	4.5	4.7	5.1
30	2.1	2.1	2.3	2.7	2.6	2.9	2.7	3.6	3.1	3.8	3.3	4.3

paint coats were dried in a well ventilated glass-walled cabinet maintained at about 32° C. Each test panel was weighed on an analytical balance before and after application of each coat. The finished panels were also weighed submerged in the proper salt or sugar solution, to permit calculation of initial specimen volumes. The edges of the coated panels were given additional protection by two dippings in molten ceresin wax. A tiny hook of Nichrome wire was partially embedded in the wax edging at the center of one edge of each panel to provide a means of support for the weighing of specimens submerged in liquid. The panels were again weighed after the edges had been waxed and the small hooks attached.

It seemed desirable to have the test solutions cover a range of osmotic pressures from that of distilled water to slightly above that of sea water. Since the osmotic pressure of a 3.5% sodium chloride solution, as calculated from vapor pressure data (*4*), is 27.74 atmospheres, it was decided to carry out the immersion tests in solutions of approximately 0, 6, 12, 18, 24, and 30 atmospheres osmotic pressure.

The experiments were so designed that one test panel would be utilized for each set of measurements. In other words, six specimens were immersed in each test solution to provide for the necessary measurements after six different periods of immersion. Thus the experiments were begun with thirty-six test specimens, contained in eighteen wide-mouth pint jars (three sets filled with six different solutions), each of which held two panel specimens. The jars and their contents were held at constant temperature by immersion to the lids in a water bath maintained at 25° C. The test specimens were examined 1, 2, 4, 8, 16, and 35 days after the start of the immersion. In order to allow for accidents, extra specimens were tested in some cases.

During these immersion exposures, the test films absorbed water, increased in volume, blistered, and either gained or lost in dry weight. The magnitude of all these changes was determined by measuring weight and volume changes. All weighings were carried out to the nearest tenth of a milligram and converted to weight in vacuum. Depending upon the nature of the substrate, the panels weighed between about 15 and 30 grams. Volume was determined by weighing the panels in two media of known but different densities. The media selected were air and the particular solution in which the panel was immersed. Since the temperatures of the solutions and inside the balance case could not be controlled within sufficiently narrow limits, the necessary temperature readings were made, and weight and volume corrections calculated. The specific gravity of the solution used as the denser medium in volume determinations was checked from time to time with the aid of a clean glass panel of known weight and volume. Independent measurements were made of the density and thermal expansion of the ceresin wax used on the panel edges in order to obtain correct values for paint coating volumes. The glass test panels were assumed to have the same density as that of a measured blank specimen cut from the same lot of photographic plates. Since the thermal expansion of this type of glass is relatively low, a published value for this property (*3*) was considered sufficiently accurate for this work. Published values were also accepted for the density and thermal expansion of the Nichrome wire (*2*) used in the panel hooks and suspension rig employed in weighing. Immediately after a panel was removed from the test solution and wiped with a soft sponge to remove adherent moisture, it was weighed repeatedly over a measured period of time, usually 6 to 10 minutes. The resultant weights were plotted as weight loss-time curves and extrapolated to zero time in order to obtain the superficially dry weights of the specimens. This appeared to be the most accurate method available for determining the specimen weight which changed rapidly as a result of evaporation of water. Next the panels were graded for blistering with the aid of A.S.T.M. Tentative Blistering Standards (*1*), but the assigned numerical values were reversed so that 0 stood for no blistering and 10 for very bad blistering. The panels were placed in a desiccator in which a relative humidity of 50% was maintained with the aid of sulfuric acid (specific gravity, 1.327) and allowed to come to equilibrium at room temperature. After a minimum of 10 days they were again weighed to determine final dry weight. It seemed desirable to present some of the experimental data on a percentage basis; consequently it was necessary to determine what portion of the total weight of the coating was actually subjected to the influence of the test solutions, because some of it had been protected by the wax edgings. After soaking in water for a short time, the paint films could be cleanly removed from the actual test areas within the boundaries of the wax edges. Six of the specimens were treated in this manner and, after being conditioned at 50% relative humidity, were reweighed. This final dry weight subtracted from the initial weight of coated and waxed specimens gave the initial weight of coatings on test areas. The area of coating actually under exposure on each test panel was derived from the dimensions of the areas within the boundaries of the waxed edges. Photographs of test panels were used for this purpose, and corrections were made for deviations from life size.

STUDY OF VARIABLES

The independent variables studied were nature of substrate, nature of solute, concentration of solute or osmotic pressure of bath, and length of time of immersion in test solution. The investigation was primarily a determination of the influence of the four independent variables upon the following five dependent variables: increase in weight or water absorption of coating, increase in volume or swelling, loss of coating substance by leaching, density of material responsible for volume increase, and degree of blistering of paint film. The data obtained are recorded and discussed on the basis of this outline. Typical sets of experimental results have been chosen to illustrate the relationships outlined.

Table I illustrates the effect of variations in the nature of the substrate material upon degree and rate of water absorption by the organic coating. A comparison of corresponding values for

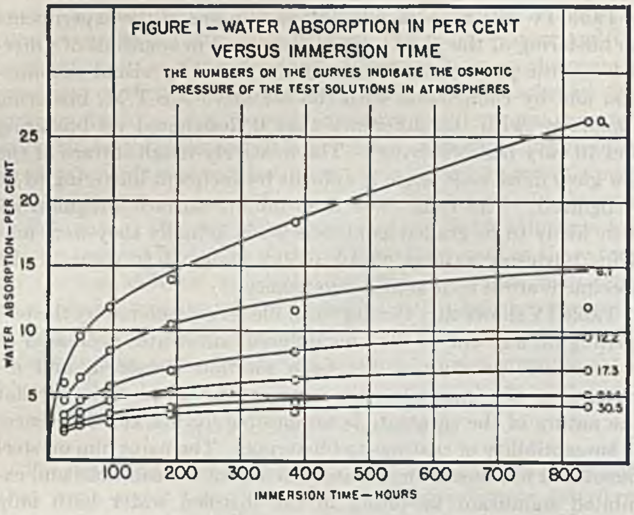
FIGURE I – WATER ABSORPTION IN PER CENT VERSUS IMMERSION TIME

THE NUMBERS ON THE CURVES INDICATE THE OSMOTIC PRESSURE OF THE TEST SOLUTIONS IN ATMOSPHERES

various metal and glass panels reveals that the effect upon both rate and degree of water absorption is relatively slight. It must be remembered that water absorption is a property of the coating which is not expected to be altered materially by contact with the substrate. The effect of the nature of the substrate upon blistering, however, is of a different order and is discussed in detail later in this paper.

Table II compares the percentage water absorbed by the paint coating, after various immersion periods, from the salt and sugar solutions of corresponding osmotic pressures. The data show that the nature of the solutes used does not exert any significant influence and that the osmotic pressure of the solution is the controlling factor determining both rate and amount of water taken into the film. Therefore, mention of the nature of substrate and solute is eliminated from the discussion as far as possible, and observations are interpreted in terms of length of immersion and osmotic pressure of the immersion solution.

Regardless of the nature of the substrate or the immersion bath, water absorption increased with immersion time. These observations are illustrated by the curves in Figure 1. After an initial high rate of water absorption lasting 100 to 150 hours water was taken up at a steady rate. Attention should be called to the marked difference in behavior of the test film in distilled water and its behavior in all other solutions, including the one having the lowest osmotic pressure. Although films immersed in various solutions approached saturation rather quickly, the film immersed in distilled water continued to absorb water; the corresponding curve gives no indication that saturation might ever have been reached. When the same data were plotted against osmotic pressures of the test solutions, the curves of Figure 2 were obtained. Water absorption decreased sharply as osmotic pressure of the bath increased without, however, quite reaching zero. It is likely that the paint system used in this investigation would absorb a small quantity of water (about 1%) even from saturated solutions of salt or sugar.

As the typical results plotted in Figures 1 and 2 show, the force responsible for the absorption or imbibition of water by the paint coating is the difference in the osmotic pressures of the solutions inside and outside of the film. However, although the experimental data are presented here in terms of osmotic pressures, the relative vapor pressures or escaping tendencies of the solutions would have served as well or better.

In the case of water transfer from the external to the internal solution, the osmotic pressure difference or gradient can be increased either by increasing the internal or decreasing the external osmotic pressure. Therefore, as the water solubility of a paint coating increases (other properties remaining the same) water should be absorbed in increasing amounts from a particular immersion solution. Lowry and Kohman (*6*) demonstrated that, for rubber, water absorption increases with increasing content of water soluble materials. The paint coating with which our tests were carried out appeared to behave in exactly the same manner as the rubber samples studied by Lowry and Kohman. Water absorption should cease only when the osmotic pressure gradient between the internal and external solutions becomes zero. In the case in question, this equilibrium was most quickly reached with the most highly concentrated external solution. With distilled water as the external liquid, however, it was impossible to achieve equilibrium by diluting the internal solution with absorbed water; nevertheless, a state of equilibrium could be reached even in this case if the mechanical pressure, exerted on the internal solution and resulting from the film's resistance to swelling and deformation, becomes equal to the osmotic pressure. This condition is a function of the mechanical and cohesive properties of the particular paint system under test; although it does not materially alter the water absorption of most common paint systems, it does tend to play a role in blistering as will be shown later.

NATURE OF THE FILM

The data so far presented indicate that osmotic pressure causes water to enter the film; this would require that the film act as a semipermeable membrane, as a source of soluble material to form a solution with a substantial osmotic pressure, and as a holder for that solution. Some circumstantial evidence regarding behavior of the film in certain of these respects merits discussion.

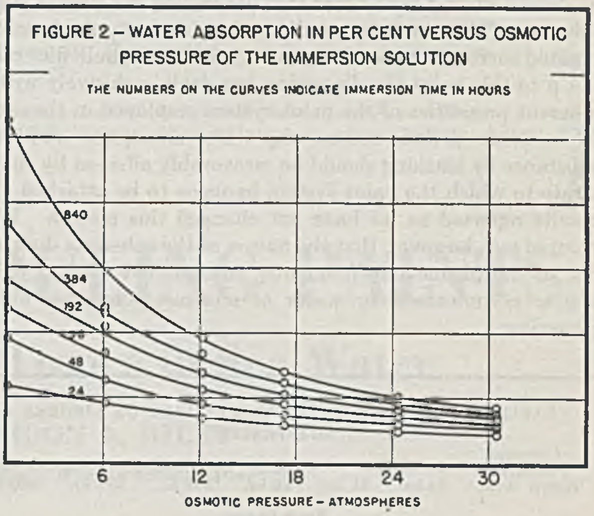
FIGURE 2 – WATER ABSORPTION IN PER CENT VERSUS OSMOTIC PRESSURE OF THE IMMERSION SOLUTION

THE NUMBERS ON THE CURVES INDICATE IMMERSION TIME IN HOURS

Calculations based on weight and volume increases of test films immersed in various salt solutions showed that the material responsible for these increases had an average specific gravity of 0.9956 gram per cc. at 25° C. Although the individual density values ranged from 0.9600 to 1.0500 grams per cc., they showed no trend which appeared to be related to the concentration of sodium chloride in the test solutions. This would seem to indicate that little or no sodium chloride, but only pure water (specific gravity 0.9970 at 25° C.), was absorbed by this coating during immersion in salt solutions. This conclusion has been supported by subsequent measurements of the electrical resistance of similar paint systems exposed to the same conditions.

When the paint films were dried and reweighed after immersion tests had been completed, a major difference was found between those which had been immersed in salt solutions and those immersed in corresponding sugar solutions (Table III); the former lost weight as the result of leaching, whereas the latter gained weight. The gain in weight shown in the last column is not large, but the value represents the difference between amount of material lost from the film by leaching and that of the material (other than water) absorbed from the sugar solution. It seems reasonable to assume that the weight of material lost from the film by leaching was of the order of that lost in the distilled water; consequently the total weight of the material absorbed from the sugar solution was about 1.5%. There is no doubt that the material responsible for this gain in weight was sucrose.

Table III. Change in Dry Film Weight Due to Leaching during 840-Hour Immersion

Osmotic Pressure of Soln., Atm.	Change in Film Weight, % Salt soln.	 Sugar soln.
0	−1.93	−1.02
6	−1.69	−0.13
12	−1.27	+0.40
18	−1.17	+0.34
24	−1.04	+0.28
30	−1.02	+0.26

It was observed that a paint system immersed in salt solutions of different osmotic pressures absorbs water but no sodium chloride, whereas a system immersed in sugar solutions of the same osmotic pressures absorbs some sugar in addition to water. This phenomenon cannot be explained by the assumption that absorption takes place by way of pores in the paint system; it is difficult to visualize pores of such size or nature that the relatively large sugar molecules could enter whereas the sodium and chloride ions could not. The observations reported are more easily explained when it is assumed that absorption is a process akin to solution. Thus inorganic sodium chloride is insoluble whereas organic sucrose is measurably soluble in the organic film binder.

Up to this point the discussion has dealt exclusively with the inherent properties of the paint system employed in these tests. There is no obvious reason why water absorption and loss of substance by leaching should be measurably affected by the substrate to which the paint system happens to be attached. The results reported so far have not changed this picture. It was pointed out, however, that the nature of the substrate does affect one of the phenomena frequently encountered when a painted article is immersed in water or aqueous solutions—namely, blistering.

Table IV. Effect of Immersion Time on Degree of Blistering

Osmotic Pressure of Batch, Atm.	Grades for Blistering 24 hr.	 48 hr.	 96 hr.	 192 hr.	 384 hr.	 840 hr.
			Steel Panels			
0	0	0.4	0.3	0.3	1.1	2.2
6	0	0.2	0.3	0.3	0.2	0.2
12	0	0.2	0	0.3	0.2	0.2
18	0	0	0	0	0	0
24	0	0	0	0	0	0
30	0	0	0	0	0	0
			Duralumin			
0	0	0.2	0.4	2.7	3.8	4.5
6	0	0	0.2	0.2	0.9	1.8
12	0	0	0	0.2	0.4	0.5
18	0	0	0	0	0	0
24	0	0	0	0	0	0
30	0	0	0	0	0	0
			Zinc			
0	0.2	0.6	0.8	3.0	3.7	3.8
6	0	0.2	0.2	2.2	2.9	3.2
12	0	0	0	0.4	2.0	2.2
18	0	0	0	0	0	0.4
24	0	0	0	0	0	0.3
30	0	0	0	0	0.2	0.3
			Glass			
0	0.3	0.4	1.5	2.8	3.9	4.4
6	0	0.2	0.5	1.3	1.7	2.4
12	0	0.2	0.4	0.6	1.3	1.0
18	0	0	0.2	0.3	0.5	0.5
24	0	0	0	0.2	0.4	0.3
30	0	0	0	0	0.2	0.2

Table IV shows the results obtained in one of the experiments on blistering of the paint system immersed in solutions of different osmotic pressures. Blistering was rated by visual examination and by comparison with the tentative A.S.T.M. blistering standards (with the difference that 0 designated no blistering and 10 very bad blistering). The relatively rough surface of the low gloss finish coat made it difficult for incipient blistering to be recognized. The result was that minute surface irregularities were likely to be graded as blisters when actually they were not. Thus blistering ratings of 0.1 or 0.2 assigned to some of the specimens are of no practical significance.

Table IV shows that the degree of blistering suffered by the test coating on any one of the four different substrates decreased as the osmotic pressure of the bath solution increased, and increased as the immersion time increased. It also shows that the nature of the substrate is responsible for marked differences in susceptibility of coatings to blistering. The paint film on steel panels did not blister significantly in any of the solutions and exhibited significant blistering in the distilled water bath only after 16 days of immersion; the same paint system applied to the other substrate materials, however, blistered quite severely even in the 6- and 12-atmosphere solutions.

The relative resistance to blistering exhibited by this paint system on four different substrate surfaces follows practical experience and may be explained on the basis of differences in adhesion of the paint coating to the substrates tested. It should therefore be possible to base upon this phenomenon a method for determining relative levels of adhesion of a given coating to various substrate materials. The determination of relative adhesion levels of different paint systems to the same substrate material, however, is more complicated.

ANALYSIS OF BLISTER FORMATION

The forces responsible for blistering must be large enough to overcome the film's resistance to swelling and deformation, as well as its adhesion to the substrate before blistering can result. An analysis of these forces is simplified if we assume the condition in which the first trace of liquid water has penetrated through the film to the substrate. We assume further that the paint film acts as a semipermeable membrane and that the external liquid is a salt solution. Under these initial conditions, if the water in the incipient blister between the paint film and the substrate were pure, the transfer tendency due to osmotic pressure would be outward from the incipient blister through the film. It appears necessary, therefore, to premise the presence of a solute in the water of the blister derived either from the paint film or from the substrate. It is necessary to premise further that the amount and character of this solute are sufficient to raise the osmotic pressure of the solution forming the blister to a value greater than that of the external solution. When such a condition exists, osmotic pressures tend to result in the transference of water from the outside of the paint film, through the paint film, and into the blister, and thus cause it to grow; therefore, the maximum osmotic pressure causing growth of the blister will be the amount by which the osmotic pressure of the solution in the blister exceeds that of the external solution. If P_B is the osmotic pressure of the solution in the blister, P_E the osmotic pressure of the external solution, and P_M the total mechanical force resisting blistering,

$$P_B - P_E = P_M, \text{ or } P_E = P_B - P_M$$

P_E, the osmotic pressure of the external solution necessary to just inhibit blistering, may therefore be considered the difference between the osmotic pressure within the blister, which tends to cause growth, and the mechanical forces of adhesion and film strength, which resist growth. In the particular case described, resistance to swelling or deformation was the same in all specimens because the same coating was employed; the opposing forces were, on the one hand, attraction between the paint system and the substrate and, on the other hand, difference between the osmotic pressures of the internal solution and the external solution (immersion bath). This osmotic pressure gradient was greatest when the bath contained distilled water, and blistering resulted in all cases. It was smallest when the bath had an osmotic pressure of 30 atmospheres, and no significant blistering was observed in any case. The osmotic pressure of the bath solutions just able to prevent blistering of the paint system used in these tests on the four different substrate materials, therefore, may serve as a relative measure of the attractive forces between the paint system and the substrates employed. (This assumes that the substrate does not influence the internal osmotic pressure of the blisters, P_B.)

MECHANISM OF PROCESS

The preceding analysis of forces involved in blistering assumed that some water had reached the coating-substrate interface; no mention was made, however, of the mechanism of this process. The observations made in the course of this investigation furnish an adequate explanation of the forces causing transfer of water through the face of the film, but fail to explain why, under certain conditions, water passes entirely through the film and becomes concentrated in blisters at the interface. Since a definite force exists, which is represented in most cases by an escaping tendency gradient drawing water into the coating, a still greater force would seem to be required to draw it out again into blisters at the interface with the substrate, especially since the forces of adhesion must also be overcome in the process. However, it is possible that the blisters do not form exactly at the interface, but that a thin, perhaps monomolecular layer of the coating remains attached to the substrate. In this case absorbed water would not have to leave the coating to cause blistering. It is likely that the concentration of dissolved film substance in the absorbed water would increase as water moves from the face of the film toward the layer next to the substrate. This concentration gradient should keep the water moving through the film to the interface, or to the last layer next to the interface. There it should form blisters as soon as the pressure becomes high enough to overcome the cohesive strength at the interface between monomolecular layer and film. This assumption, however, makes it more difficult to understand why there are such marked differences in blistering properties of a given coating system on different substrate materials, unless it is assumed that the character of this monomolecular layer is greatly modified by the nature of the substratum.

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LITERATURE CITED

(1) Am. Soc. for Testing Materials, Standards, Spec. D714-43T, pp. 1559-62 (1944).
(2) Handbook of Chemistry and Physics, p. 1207, Cleveland, Chem. Rubber Pub. Co., 1942.
(3) *Ibid.*, p. 1655.
(4) International Critical Tables, Vol. III, p. 297 (1928).
(5) Kittelberger, W. W., Ind. Eng. Chem., 34, 943-8 (1942).
(6) Lowry, H. H., and Kohman, G. T., *J. Phys. Chem.*, 31, 23-57 (1927).

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ACTION OF ANTIFOULING PAINTS

Solubilities of Antifouling Toxics in Sea Water

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The solubilities in sea water of various copper and mercury compounds which have been proposed as antifouling toxics cover a very wide range, from 10^{-3} to over 10^5 micrograms of metal per cc. Cuprous oxide, the toxic which has been most widely used, has a solubility of 5.4 micrograms of copper per cc., high enough to be effective but not so high that its leaching rate from antifouling paints is too difficult to control.

THE most commonly used antifouling toxics are compounds of copper and mercury. Salts of the latter metal were employed very early in the development of antifouling coatings; the use of mercuric oxide was patented in 1857 (*14*), mercuric chloride in 1864 (*3*), and mercurous chloride in 1885 (*4*). The use of cuprous oxide was described in 1863 (*13*), and this substance has found wide application in antifouling paints ever since. In many early formulations "copper oxide" was specified without distinguishing between the cuprous and the cupric compound.

The solubility and rate of solution of cuprous oxide in sea water were reported in the first paper of this series (*5*). Although no other toxic substance has been studied in such detail, it is possible to summarize here data on the sea water solubilities of a number of these compounds. Some of the data are based on experimental measurements and some on calculations from thermodynamic data in the literature.

COPPER COMPOUNDS

Experimental measurements of the solubilities of copper compounds in sea water were carried out at 25° C. After equilibration, the filtered solutions were analyzed for copper by the method of Coulson (*2*, *8*), and pH measurements were taken with a Beckman glass electrode.

Cuprous Oxide. The solubility of cuprous oxide in air-free sea water was shown (*5*) to be proportional to the hydrogen ion concentration and unaffected by carbonate ions. In normal sea water at pH 8.1, the solubility is 8.6×10^{-5} moles copper per liter, or 5.4 micrograms per cc. The measured values are in

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TABLE I. ANALYSES OF END PRODUCTS OF REACTION BETWEEN SEA WATER AND COPPER AND CUPROUS OXIDE

Source	Cu, %	CO_2, %	Cl, %	Investigators
Copper	67	11	4	Sexton (*11*)
Copper	50–55	7–12	3–6	Bengough & May (*1*)
Copper	51–58	11	3	Authors
Cuprous oxide	51	...	2	Authors

TABLE II. SOLUBILITIES OF COPPER AND MERCURY COMPOUNDS IN SEA WATER AT pH 8.1

Compound	Soly., µg./cc.	Source
Cupric citrate	>170,000	Exptl.
Cuprous chloride[a]	3,100	Calcd.
Cuprous oxide[a]	5.4	Exptl.
"Basic cupric carbonate"	0.5	Exptl.
Aged "b.c.c."[b]	<0.1	Exptl.
Cupric hydroxide	0.013	Calcd.
Cupric oxide	0.001	Calcd.
Mercuric chloride	200,000	Exptl.
Mercuric oxide	80,000	Calcd.
Mercurous chloride	0.3	Calcd.

[a] In oxygen-free sea water.
[b] "Basic cupric carbonate" aged in sea water for one year.

good agreement with those calculated (*5*) from thermodynamic data obtained with simple chloride solutions, and on this basis it is concluded that the cuprous copper exists in sea water solution largely as the complex ions $CuCl_2^-$ and $CuCl_3^{--}$.

In the presence of air, cuprous copper dissolved from cuprous oxide in sea water is oxidized to the cupric form, and is partially reprecipitated as a mixture of basic cupric carbonate and oxychloride.

CUPROUS CHLORIDE. From the same thermodynamic data used to calculate the solubility of cuprous oxide (*5*), the solubility of cuprous chloride in air-free sea water is computed to be 5.1×10^{-2} *M*. While there are no experimental measurements, this value may be taken with some confidence in view of the agreement between measured and calculated solubilities of cuprous oxide. As in the case of cuprous oxide, copper dissolved from cuprous chloride in sea water in the presence of air is oxidized and partly reprecipitated.

CUPRIC OXIDE AND HYDROXIDE. In contrast to cuprous oxide, cupric oxide has been found to have a negligible solubility in sea water within the limits of the analytical method employed ($<10^{-6}$ *M*). The value calculated from thermodynamic data in the literature is very small. Latimer (*9*) gives the ion product $(Cu^{++})(OH^-)^2$, in equilibrium with cupric hydroxide, as 5.6×10^{-20}; at pH 8.1, if the activity coefficient of cupric ion in sea water (ionic strength 0.63) is taken as 0.17, the corresponding copper concentration is 2.1×10^{-7} *M*. Using Latimer's value (*9*) of 1590 calories for the free energy of hydration of cupric oxide to hydroxide, the corresponding solubility of cupric oxide is calculated to be 1.4×10^{-8} *M*.

BASIC CUPRIC CARBONATE. Although basic cupric carbonate has not been widely suggested as an antifouling toxic, it is of interest in this connection because of its formation in the reaction of sea water with either cuprous oxide or metallic copper in the presence of air. When the supply of oxygen is ample, the end product of either reaction is a bluish precipitate whose composition, according to Bengough and May (*1*), corresponds to a mixture of basic cupric carbonate and oxychloride, in which the former predominates. The results of analyses of such precipitates derived from copper, by these authors (*1*) and also by Sexton (*11*), are compared in Table I with our analyses of precipitates from copper and cuprous oxide. The data show considerable variation, but the results of the different investigators are in fair agreement. The average chlorine content of 3% corresponds to a content of about 20% of atacamite, $Cu_4(OH)_6Cl_2 \cdot H_2O$, a salt which was identified by Rooksby and Chirnside (*10*) in the corrosion products of copper.

Just as the composition of this precipitate shows variations, so also does its solubility in sea water. A large number of experimental determinations has given values lying between 5 and 10×10^{-6} mole of copper per liter. These solutions would appear to be supersaturated with respect to cupric hydroxide.

A sample of basic cupric carbonate precipitate which had aged for one year under sea water was found to have a negligible solubility by the analytical method employed ($<10^{-6}$ *M*). The chloride content of this material was 14% as compared with 16% for pure atacamite, which suggested that conversion of carbonate to oxychloride had occurred during aging.

CUPRIC CITRATE. This substance is of interest in experimental studies of antifouling action because its solubility in sea water is enormously greater than those of the other copper compounds discussed here. By mixing 1 mole each of cupric carbonate and citric acid with 1.6 moles of sodium hydroxide in aqueous solution and precipitating the reaction product with ethanol, a dark blue crystalline salt is obtained whose copper content corresponds to the formula $NaCuC_6H_5O_7$. This material is hygroscopic and has an enormous solubility in sea water; solutions of concentrations as high as 2.7 *M* have been prepared. Evidently a very stable complex ion is formed which prevents the precipitation of the copper as basic carbonate.

MERCURY COMPOUNDS

Experimental measurements of the solubilities of mercury compounds in sea water were carried out by equilibrating at 25° C. and analyzing the filtered solutions by titration with dithizone in chloroform (*15*).

MERCUROUS CHLORIDE. This compound is decomposed in the presence of other chlorides and, therefore, presumably in sea water, with the formation of mercuric chloride and metallic mercury. The equilibrium constant for the reaction, $Hg + Hg^{++} = Hg_2^{++}$, is given by Latimer (*9*) as 81, and the solubility product of Hg_2Cl_2 as 1.1×10^{-18}. The dissociation constant of the weak salt $HgCl_2$ is given by Sherrill (*12*) as 10^{-14}. From these data and the concentration of chloride ion in sea water (0.48 *M*), neglecting activity coefficients, the concentration of dissolved mercuric mercury in sea water in equilibrium with mercurous chloride and metallic mercury is calculated to be 1.4×10^{-6} *M*. The amounts dissolved as determined experimentally are of this order of magnitude, but depend upon the amount of solid phase present in a complicated manner which requires further study.

MERCURIC OXIDE. The solubility of mercuric oxide has been measured only at a pH considerably alkaline to that of normal sea water. At pH 9.7 it is about 2×10^{-3} *M*. The solubility at pH 8.1 calculated from the ionic product as given by Latimer (*9*), 2.7×10^{-26}, and the dissociation constant of $HgCl_2$, quoted in the preceding paragraph, neglecting activity coefficients, is 0.39 *M*.

MERCURIC CHLORIDE. The solubility of mercuric chloride in sea water has been found experimentally to be approximately 1.0 *M*.

DISCUSSION

The solubility data, summarized in Table II, give the values in micrograms of metal per cc. of sea water. A wide range of solubilities is represented by the compounds listed.

The extremely low solubilities of such compounds as cupric oxide and hydroxide suggest a priori that these substances can never function effectively as antifouling toxics. The very high solubilities of cupric citrate and mercuric chloride, on the other hand, suggest that it might not be easy to utilize such compounds in antifouling paints because of the difficulty of controlling the leaching rate to prevent premature exhaustion of toxic.

The solubility of cuprous oxide is intermediate in the range covered by Table II, although it is quite low compared with those of inorganic salts in general. As stated in the preceding paper (*5*), this moderately low solubility facilitates control of the leaching rate from a paint in which it is compounded.

The leaching rate of toxic from a paint, which determines the antifouling effectiveness, depends upon many factors in addition to the solubility of the toxic. The proportion of toxic in the paint formulation, and the composition of the matrix, both influence the leaching rate profoundly, as Tables V, VI, and VII of an earlier article (*8*) indicated. These variables will be discussed in the succeeding papers of this series (*6*, *7*).

LITERATURE CITED

(1) Bengough, G. D., and May, R., *J. Inst. Metals*, 32, 81 (1924).
(2) Coulson, E. J., *J. Assoc. Official Agr. Chem.*, 19, 219-28 (1936); 20, 178-88 (1937).
(3) Dannatt, J., Brit. Patent 2645 (1864).
(4) Dorr, H. C., U. S. Patent 331,383 (1885).
(5) Ferry, J. D., and Carritt, D. E., Ind. Eng. Chem., 38, 612-17 (1946).
(6) Ferry, J. D., and Ketchum, B. H., *Ibid.*, 38, to be published.
(7) Ketchum, B. H., Ferry, J. D., and Burns, A. E., Jr., *Ibid.*, 38, to be published.
(8) Ketchum, B. H., Ferry, J. D., Redfield, A. C., and Burns, A. E., Jr., *Ibid.*, 37, 456-60 (1945).
(9) Latimer, W. M., "Oxidation States of the Elements", New York, Prentice-Hall, 1938.
(10) Rooksby, H. P., and Chirnside, R. C., *J. Soc. Chem. Ind.*, 53, 33T (1934).
(11) Sexton, A. H., "Corrosion and Protection of Metals", 1906.
(12) Sherrill, M. S., *Z. physik. Chem.*, 47, 103 (1904).
(13) Tarr, J. G., and Wonson, A. H., U. S. Patent 40,515 (1863).
(14) Wall, A., Brit. Patent 2198 (1857).
(15) Winkler, W., *J. Assoc. Official Agr. Chem.*, 22, 341 (1939).

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Fungicidal Activity of Bisphenols as Mildew Preventives on Cotton Fabric

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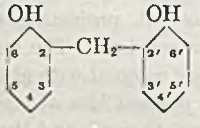
Biological tests have been made to determine the fungicidal potency as mildew preventives on cotton fabric of a group of bisphenols and related compounds. Substitution of two chlorine or two bromine atoms for hydrogens in the positions para to the phenolic hydroxyls invariably increased fungicidal potency over that observed with the unhalogenated diphenols; further symmetrical halogen substitution resulted in compounds which were generally, and in certain cases distinctly, less potent than the dihalogen derivatives. 2,2′-Methylenebis(4-nitrophenol) was completely lacking in measurable fungicidal potency at any of the concentrations tested; the same was also true of chlorine-substituted derivatives of 2,2′-methylenediphenol in which both phenolic hydroxyls had been blocked by formation of ether linkages. Three- and four-ring compounds containing *p*-cresol or *p*-chlorophenol units joined by —CH₂— were distinctly less effective than the corresponding bisphenols. No compound was found to be more fungicidal per unit weight on the fabric than 2,2′-methylenebis(4-chlorophenol). Methods for testing fabric mildew preventives are discussed.

MANY new fungicidal compounds were investigated as prospective mildew preventives for fabrics during World War II. The present paper reports biological tests on an experimental series of bisphenols and related materials of commercial origin, samples of which were made available to the Department of Agriculture with the suggestion that they be tested for fungicidal activity on fabric.* The tests were carried out primarily during the spring of 1944. Certain new information is presented concerning fungicidal activity as related to chemical structure within this group of compounds, together with observations and comments on biological test methods for use in the selection of new fungicides.

The compounds studied were largely included in four different series whose parent compounds were:



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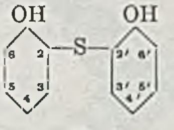

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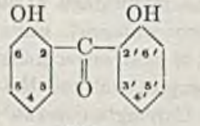

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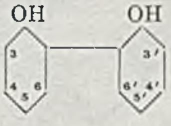


IV

Test results showed that substitution of two chlorine or two bromine atoms for hydrogens in the positions para to the phenolic hydroxyls invariably increased fungicidal potency over that observed with the unhalogenated diphenols; however, further symmetrical halogen substitution resulted in compounds which were quite generally, and in certain cases distinctly, less potent than the dihalogen derivatives. Considering the results as a whole, compound No. 11, 2,2′-methylenebis(4-chlorophenol), was equal and probably superior in activity to any of the other compounds tested. The related compound, 2,2′-methylenebis(4-nitrophenol), was completely lacking in measurable fungicidal potency at any of the concentrations tested; the same was also true of chlorine-substituted derivatives of 2,2′-methylenediphenol in which both phenolic hydroxyls had been blocked by formation of ether linkages.

Three- and four-ring compounds containing *p*-cresol or *p*-chlorophenol units joined by —CH₂— were distinctly less effective than the corresponding bisphenols.

TEST METHODS

Each of the compounds was dissolved in acetone and applied to 8-ounce cotton duck, the fabric being dipped into the solution and run through a household clothes wringer fitted with metal

Table I. Fungicidal Activity of Analogs of 2,2′-Methylenediphenol as Measured by the Rating of Treated Fabrics in Various Tests[a]

Compound No.	Substituents on Carbons Numbered:					Per Cent Strength Loss in:														
						Soil burial		Soil suspension				Metarrhizium test				Chaetomium test			Growth of *A. niger*	
	1 1	3 3′	4 4′	5 5′	6 6	Compost, 0.8%	Carrington, 0.8%	0.025%	0.05%	0.1%	0.2%	0.025%	0.05%	0.1%	0.2%	0.1%	0.2%	0.4%	0.1%	0.2%
1	OH	..	..	..	..	93	100	..	..	..	..	..	..	..	..	97	24	0	3	3
11	OH	..	Cl	..	..	17	38	91	8	0	0	17	14	0	0	0	0	0	0	0
13	OH	..	Cl	..	Cl	100	100	100	2	0	0	0	0	0	0	0	0	0	2	1
15	OH	Cl	Cl	..	Cl	63	88	100	10	6	0	49	0	0	0	0	0	0	3	2
17	OH	Cl	Cl	Cl	Cl	100	100	..	..	..	..	..	..	..	..	96	39	46	3	3
25	OH	..	Cl	..	CH_3	72	100	100	97	79	97	..	..	..	..	11	0	0	2	1
18	OCH_3	..	Cl	..	..	100	100	100	100	100	100	100	100	100	100	100	100	100	3	3
19	OCH_3	..	Cl	..	Cl	100	100	100	100	100	100	100	100	100	43	100	100	100	3	3
20	OCH_3	Cl	Cl	..	Cl	100	100	100	100	100	100	100	100	100	100	100	100	100	3	3
12	OH	..	Br	..	..	48	43	100	14	0	2	12	0	0	0	0	0	0	1	0
14	OH	..	Br	..	Br	100	100	100	100	100	66	21	4	0	0	98	91	65	3	2
16	OH	Br	Br	..	Br	98	100	100	100	88	3	37	3	1	2	29	4	0	3	3
42	OCH_3	..	Br	..	..	100	100	100	100	100	100	..	..	..	..	100	100	100	3	3
30	OH	..	NO_2	..	..	100	100	100	100	100	100	100	100	100	17	100	98	100		

[a] In all cases concentration on the fabric is expressed as percentage of the pure compound on the dry fabric.

rolls. The quantity of compound applied per unit weight of fabric was fixed at certain desired dosages by calculation from the known wet-weight pick-up of the fabric with a standard pressure on the rolls of the wringer. The fabric was then cut into 6 × 1.5 inch strips with the long dimension parallel to the warp and was subjected to biological tests. Tests *A*, *C*, and *D* were carried out with a fabric designated as M-2 duck and having an original breaking strength in the warp direction of 123 pounds; tests *B* and *E* were carried out on a similar 8-ounce fabric designated as Q duck and having an original breaking strength in the warp direction of 119 pounds. The biological tests were carried out as follows:

A. Chaetomium globosum (Culture Bottle). The experimental strips were raveled to exactly 1 inch in width, wet in water containing 0.002% of the nontoxic wetting agent Gardinol, planted without sterilization on mineral salts-agar in flat-sided 16-ounce culture bottles, inoculated with 1 cc. of a spore suspension of the fungus *Chaetomium globosum* (USDA isolate 1042.4), incubated at 30° C. for 12 days, and then washed, dried, conditioned in a desiccator over saturated sodium nitrite solution, and broken on a Scott tester to determine residual strength. With the exception of tests on compounds 4 and 17, which involved only three replicates, each strength loss figure reported for the *Chaetomium globosum* test is an average obtained from six replicate samples. The bottle tops used were provided with glass cloth air vents as described by Greathouse, Klemme, and Barker (4). The culture medium in the bottles contained the following quantities per liter: 1.90 grams NH_4NO_3, 1.43 grams $MgSO_4.7H_2O$, 1.31 grams K_2HPO_4, 1.75 grams KH_2PO_4, 20 grams agar.

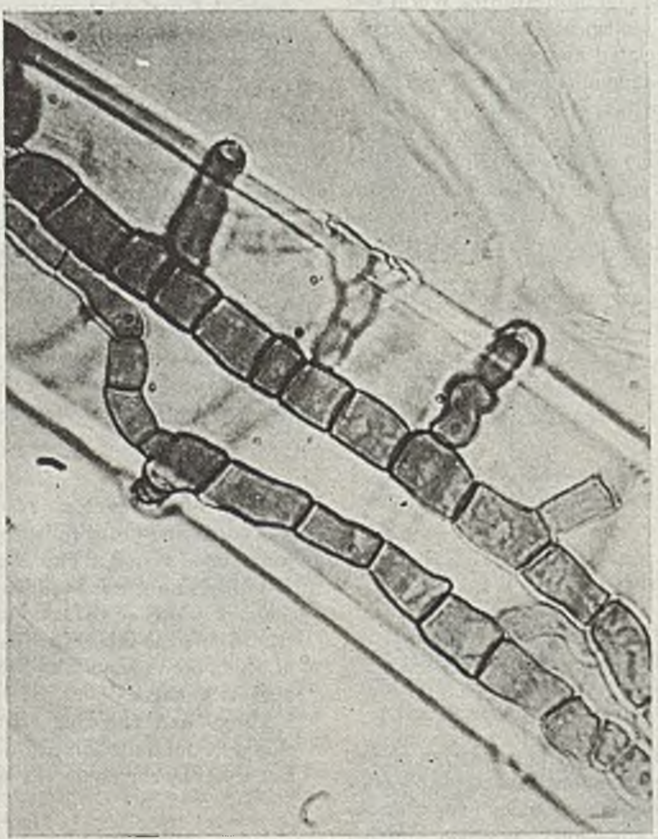


PHOTO BY M. JAEGER

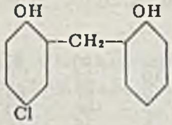
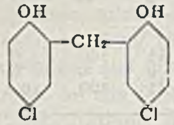
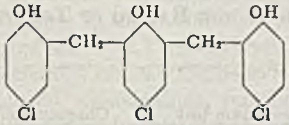
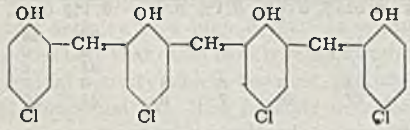
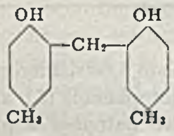
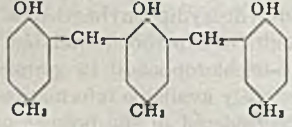
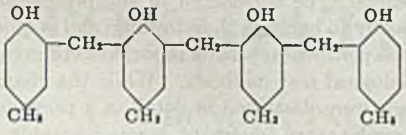
Photomicrograph of Mildew Organism (Unidentified) Growing in Naturally Infected Cotton Fiber

B. Metarrhizium glutinosum (Culture Bottle). This test was carried out with *Metarrhizium glutinosum* 1334.2 following the same procedure as that for *Chaetomium globosum* except that the incubation period was reduced to 8 days, and three replicate strips were used.

C. Aspergillus niger (Culture Bottle). Three unraveled experimental strips for each fungicide concentration were wetted in water, planted in culture bottles without sterilization on a glucose-mineral salts-agar medium of the same composition as that described under *A* except for the addition of 0.5% glucose, inoculated with 1 cc. of a suspension of spores of *Aspergillus niger* (USDA isolate TC-215-4247), incubated at 30° C. for 5 days, and rated for fungus growth by visual observation. The numerical system of recording these experimental results was as follows: 0 = no growth, 1 = slight growth, 2 = medium growth, 3 = heavy growth.

D. Soil Burial Test. Test strips raveled to one inch in width were wet in water containing 0.002% Gardinol WA and planted in a vertical position in rectangular glass aquaria, 12 × 12 × 30 inches, containing a layer of soil 6 inches deep. About 3/4 inch of the sample marked for identification was left projecting above the soil line. The aquaria were covered with glass lids to prevent loss of moisture from the soil, and the temperature of the soil room was maintained at 30° C. Two different soil types were used, one a greenhouse compost soil and the other a Carrington series loam from Lincoln, Nebr. The Carrington soil had a pH of 6.0 and an organic matter content by the hydrogen peroxide method of 4.4%. Upon mechanical analysis it was found to contain 1.3% of particles with a diameter between 2.0 and 0.2

Table II. Fungicidal Activity of Two-, Three-, and Four-Ring Compounds Related to 2,2′-Methylenediphenol, as Measured by the Rating of Treated Fabric in Soil Burial and *Chaetomium globosum* Tests

Compound No.	Formula	Per Cent Strength Loss after Exposure to:								
		Soil burial (9 days)						*Chaetomium globosum* (14 days)		
		Carrington			Compost					
		0.1%	0.2%	0.4%	0.1%	0.2%	0.4%	0.1%	0.2%	0.4%
70		99	96	67	100	98	90	5	0	0
11		99	39	6	100	90	22	8	3	0
74		100	100	100	100	100	100	77	33	23
75		100	100	100	100	100	100	77	79	87
67		99	97	92	100	100	100	0	5	5
68		100	100	100	100	100	100	100	100	100
69		100	100	100	100	100	100	100	100	100

mm., and 48.3, 23.5, and 26.9% particles in the lower diameter classes of 0.2-0.02, 0.02-0.002, and <0.002 mm., respectively. Three replicate samples were used for each dosage of each treatment. The samples were removed from the soil at the end of 12 days of incubation, washed, dried at room temperature, conditioned, and broken as described. Both soils were high in biological activity, as shown by the fact that incubation in them resulted in complete loss of strength by untreated 8-ounce duck in 5 to 8 days.

E. Soil Suspension Test. The experimental strips were raveled to one inch in width, wet in water, planted without sterilization on mineral salts-agar of the composition described under *A*, and inoculated with 1 cc. of a fine suspension of biologically active soils in water. Three replicate samples were used for each concentration of each treatment. The soil suspension was made by mixing 1 gram of each of five sifted soils with 500 cc. of water. The five soils included a greenhouse compost, one loam soil from each of three states (Maryland, Nebraska, and California), and a muck from Michigan.

RESULTS WITH VARIOUS SERIES OF COMPOUNDS

I, Parent Compound 2,2′-Methylenediphenol. Experimental results on this series of compounds are shown in Table I. The fungicidal activity per unit weight on the fabric of parent compound 1 is relatively low. The fungicidal effectiveness increases markedly on substitution of two chlorine atoms for hydrogens in the two positions para to the phenolic hydroxyl groups (compound 11). Further substitution of chlorine for hydrogen results in decreases in activity, manifested in the soil burial and Aspergillus tests in the tetrachloro, hexachloro, and octachloro analogs (compounds 13, 15, and 17), in the Metarrhizium test in compound 15, and in the Chaetomium test only in compound 17. Blank spaces in Table I represent absence of data due to exhaustion of the sample of experimental compound. Formation of methyl ethers at the phenolic hydroxyl groups consistently reduced fungicidal effectiveness to zero in all tests (compounds 18, 19, and 20).

Bromine derivatives of compound 1 (Table I) showed trends between structure and activity similar to those found with the chlorinated compounds. The dibromo derivative (compound 12) showed increased activity as compared with compound 1, as had the dichloro derivative (compound 11). The tetrabromo and hexabromo compounds (14 and 16), however, showed distinctly lower activity than compound 12, and a methyl ether (compound 42) was again very low in activity in all tests.

Substitution of two nitro groups for hydrogens yielded compound 30, analogous to halogenated compounds 11 and 12, but it failed to show similar fungicidal activity.

Soil burial and *Chaetomium globosum* experiments (Table II) revealed that compounds containing three or four *p*-chlorophenol units joined by methylene bridges (74 and 75) were distinctly lower in protective value than bisphenol compound 11. Compound 70, however, differing from compound 11 only by the absence of one chlorine atom, showed moderately good fungicidal

TABLE III. FUNGICIDAL ACTIVITY OF ANALOGS OF 2,2′-THIODIPHENOL AND 2,2′-DIHYDROXY BENZOPHENONE, AS MEASURED BY THE RATING OF TREATED FABRICS IN VARIOUS TESTS

Compound No.	Substituents on Carbons Numbered:					Per Cent Strength Loss in: Soil burial		Soil suspension				Metarrhizium test				Chaetomium test			Growth of *A. niger*	
	1 1′	3 3′	4 4′	5 5′	6 6′	Compost, 0.8%	Carrington, 0.8%	0.025%	0.05%	0.1%	0.2%	0.025%	0.05%	0.1%	0.2%	0.1%	0.2%	0.4%	0.1%	0.2%
								THIODIPHENOL SERIES												
5	OH	..	..	..	..	100	94	..	..	..	..	..	..	..	..	100	85	0	3	2
57	OH	..	Cl	..	..	0	65	100	2	0	0	6	0	3	10	15	0	0	0	0
59	OH	..	Cl	..	Cl	85	100	95	24	5	13	43	0	0	0	97	83	63	0	0
63	OH	CH_3	Cl	CH_3	..	100	100	100	100	100	100	..	..	..	..	100	100	100	3	3
58	OH	..	Br	..	..	36	77	100	25	0	0	0	0	3	3	46	11	0	0	0
								BENZOPHENONE SERIES												
43	OH	..	..	..	..	100	100	100	100	94	21	100	100	50	21	100	0	0	2	2
45	OH	..	Br	..	..	41	100	73	16	45	0	5	0	0	0	0	0	0	1	1
47	OH	..	Br	..	Br	98	100	100	100	100	100	60	20	22	41	100	100	98	2	2

TABLE IV. FUNGICIDAL ACTIVITY OF ANALOGS OF *o,o′*-BIPHENOL AS MEASURED BY THE RATING OF TREATED FABRICS IN VARIOUS TESTS

Compound No.	Substituents on Carbons Numbered					Per Cent Strength Loss in: Soil-burial		Soil suspension				Metarrhizium test				Chaetomium test			Growth of *A. niger*	
	2 2′	3 3′	4 4′	5 5′	6 6′	Compost, 0.8%	Carrington, 0.8%	0.025%	0.05%	0.1%	0.2%	0.025%	0.05%	0.1%	0.2%	0.1%	0.2%	0.4%	0.1%	0.2%
4	OH	..	..	..	..	100	100	..	..	..	..	..	..	..	..	92	44	15	3	3
50	OH	..	..	Cl	..	20	59	..	..	..	..	..	..	..	..	0	0	0	0	0
52	OH	Cl	..	Cl	..	33	43	100	100	0	19	..	..	..	..	93	1	0	2	1
51	OH	..	..	Br	..	5	72	100	65	23	3	34	3	6	3	0	0	0	1	0
53	OH	Br	..	Br	..	85	100	100	100	100	2	87	26	7	0	95	66	29	2	2

capacity. In similar fashion compounds containing three and four *p*-cresol units joined by methylene bridges (68 and 69) were less effective in a *Chaetomium globosum* test than bisphenolic compound 67.

II. PARENT COMPOUND 2,2′-THIODIPHENOL. In this series Table III shows that substitution of two hydrogens para to the phenolic hydroxyls by chlorine (compound 57) increased the fungicidal effectiveness as compared with parent compound 5; further substitution to form the tetrachloro derivative (compound 59) resulted in a general decrease in activity. Compound 63, with methyl groups in the 3, 5, 3′, and 5′ positions, was inactive. Dibromo-substituted compound 58, analogous to compounds 57, 11, and 12, showed relatively high effectiveness in all tests, in line with the behavior of the other dihalogenated compounds.

III, PARENT COMPOUND 2,2′-DIHYDROXYBENZOPHENONE. In this series the introduction of two bromine atoms into the parent molecule brought about the usual increase in fungicidal effectiveness while a tetrabromo derivative (compound 47) was less effective in all tests than the dibromo derivative (compound 45). These results are shown in Table III.

IV, PARENT COMPOUND *o,o′*-BIPHENOL. Table IV indicates the same general trends as those of the previous series. The dichloro and dibromo derivatives (compounds 50 and 51) were much more active than parent compound 4. Tetrachloro compound 52 showed a decrease in effectiveness in the Chaetomium and Aspergillus tests as compared with compound 50; the tetrabromo derivative (compound 53) showed a decrease in activity in all five tests as compared with the dibromo derivative (compound 51).

DISCUSSION

Several patents have been issued and a few papers published which deal with germicidal halogenated hydroxydiphenylmethanes and closely related materials. Klarmann and Von Wowern (*9*) described the chemical preparation and bacteriocidal properties of certain chloro and bromo derivatives of 2,4-dihydroxydiphenylmethane and -ethane, and Klarmann and Gates (*8*) claimed disinfectant properties for several halogenated monohydroxydiphenylmethanes. Britton and Bryner (*1*) attributed strong germicidal action to 3-chloro- and 5-chloro-2-hydroxybiphenyl and their salts. Patents have been issued in the names of Gump and others describing the use of 3,3′,5,5′-tetrachloro-*o,o′*-biphenol (*6*), 2,2′-thiobis(3,4,6-trichlorophenol) (*10*), and 2,2′-methylenebis(3,4,6-trichlorophenol) (*5*), as active agents in germicidal soaps. Gump also patented a process for making halogenated 2,2′-dihydroxydiphenylmethanes (*7*). Traub *et al.* (*14*) presented results of experiments related to the use of 2,2′-methylenebis(3,4,6-trichlorophenol) in germicidal soaps. It is seen that the previously available information on compounds of the general type considered in the present paper applies more specifically to bacteria than to fungi and is quite limited.

The experimental results reported here involved several different biological test methods. While the characteristics of these methods were described in detail in a previous publication (*12*), some explanatory comment seems desirable here. In general, the *Chaetomium globosum* test follows the technique of Thom, Humfeld, and Holman (*13*). The Metarrhizium test utilizes the organism *Metarrhizium glutinosum* which was introduced as a fabric mildew-resistance test organism by Greathouse, Klemme, and Barker (*4*). The *Aspergillus niger* test is generally similar to the other two except that glucose is included in the medium and the test results are judged by the amount of visible fungus growth rather than by fabric breaking strength. All three of the culture tests were carried out on unsterilized fabric in order to avoid the complicating factor of partial volatilization or decomposition of the mildew preventives during autoclaving. The samples were examined after incubation and determined to be essentially free of contaminating microorganisms other than the intended test fungus.

The soil burial test is similar in principle to tests described previously from this (*11*, *12*) and other (*2*) laboratories. According to the results reported here, the severity of the test is more nearly approximated by the *Aspergillus niger* test than by the two other culture-bottle procedures. The soil suspension test is a somewhat simplified procedure patterned after a test described by Furry and Zametkin (*3*).

The choice of a suitable test for mildew resistance of fabrics is complicated by the fact that a wide variety of fungi are involved in fabric deterioration in actual service. This situation, coupled with the fact that microorganisms differ widely in sensitivity to fungicidal agents, has argued strongly in favor of tests involving a heterogeneous mixture of organisms such as is commonly found in soils. Contact with warm, moist soil is undoubtedly one of the most severe conditions for biological fabric deterioration, and certain military agencies have stressed the point that many of their fabric items must be able to withstand this condition. Although quantitative differences do exist among soil burial results determined on identical fabrics under different conditions with various soils, experience in many laboratories indicates that certain fabric treatments are consistently poor in all or essentially all tests and that other treatments are consistently much better.

The soil suspension test represents an attempt to retain the heterogeneous microflora of the soil but to bring the environmental conditions under closer control than in the soil burial test. Although a heterogeneous microflora is retained in actual practice, the writers cannot defend the thesis that soil suspension tests are merely simplified soil burial tests. The population of organisms which grow on the fabric in soil suspension tests is qualitatively and quantitatively different from the population found on the same fabric in soil burial tests in the same soil.

Previously reported tests of 2,2′-methylenebis(4-chlorophenol), number 11 (commercially called "compound G-4"), in parallel with pentachlorophenol, salicylanilide, tetrabromo-*o*-cresol, and other phenols (*12*) had already established that the former compound has fungicidal activity of a high order. It is apparent from the data presented here that other closely related compounds also have high fungicidal activity which, however, probably does not exceed that of compound 11. The possible uses for these compounds have not been thoroughly explored, and it might be found that for specific uses certain of them would have distinct advantages over compound 11. Compound 57, for example, might be superior to compound 11 as a spray or dust to prevent "late blight" of potatoes or other plant diseases, etc.

Although compound 11 has been used commercially as a fabric preservative on an extensive scale in the last three years, data from service trial and outdoor exposure tests are still rather limited. Data of this type on various materials are being accumulated in several laboratories. Any complete evaluation of compound 11 as a fabric preservative will be possible only after a careful analysis of these data.

ACKNOWLEDGMENT

The authors are indebted in particular to W. S. Gump, of Givaudan-Delawanna, Inc., who synthesized the compounds used in this study, and to E. Kunz, R. Horsey, and Thomas Wallace of the same concern for advice and interest during the course of the work.

LITERATURE CITED

(1) Britton, E. C., and Bryner, F., U. S. Patent 1,969,963 (1934).
(2) Dean, J. D., Strickland, W. B., and Berard, W. N., *Am. Dyestuff Reptr.*, 34, 195–201 (1945).
(3) Furry, M. S., and Zametkin, M., *Ibid.*, 32, 395–8 (1943).
(4) Greathouse, G. A., Klemme, D. E., and Barker, H. D., Ind. Eng. Chem., Anal. Ed., 14, 614–20 (1942).
(5) Gump, W. S., U. S. Patent 2,250,480 (1941).
(6) *Ibid.*, 2,353,724 (1944).
(7) *Ibid.*, 2,354,012 (1944).
(8) Klarmann, E., and Gates, L., *Ibid.*, 1,967,825 (1934).
(9) Klarmann, E., and Von Wowern, J., *J. Am. Chem. Soc.*, 51, 605–10 (1929).
(10) Kunz, E. C., Luthy, M., and Gump, W. S., U. S. Patent 2,353,735 (1944).
(11) Marsh, P. B., Greathouse, G. A., Bollenbacher, K., and Butler, M. L., Ind. Eng. Chem., 36, 176–81 (1944).
(12) Marsh, P. B., Greathouse, G. A., Butler, M. L., and Bollenbacher, K., U. S. Dept. Agr., *Tech. Bull.* 892, 1–22 (1945).
(13) Thom, C., Humfeld, H., and Holman, H. P., *Am. Dyestuff Reptr.*, 23, 581–6 (1934).
(14) Traub, E. F., Newhall, C. A., and Fuller, J. R., *Surgery, Gynecol. Obstet.*, 79, 205–16 (1944).

AUTOXIDATION OF FURFURAL

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Color and acid formation in furfural at room temperature are shown to be due to autoxidation, the course of which is different from that of benzaldehyde. It occurs at a considerably lower rate and the reaction is interrupted at a much lower level of acidity. A mixture of acids is formed from furfural, not merely acetic acid or solely furoic acid as had been speculated previously. The changes may be prevented by storing furfural in an oxygen-free atmosphere, or effectively inhibited by adding to furfural a small quantity of a variety of basic substances such as tertiary amines or alkali metal soaps or phenolic antioxidants. Water causes a partial inhibition of the autoxidation.

IN NORMAL storage, furfural slowly darkens in color; a change accompanied by formation of acid. The magnitude of these changes with reference to the amount of furfural is small even after relatively long periods of time. Nevertheless, it was considered desirable to find some means of preventing or retarding the reactions responsible, and to accomplish this it was necessary to have some knowledge of the cause.

Previous to this work, it was known that the color bodies in aged furfural were left behind as a residue on distillation, and that the yield of recovered furfural was generally high. In addition, stabilizers such as hydroquinone and pyrocatechol had been found to inhibit color formation. There had been considerable speculation regarding the nature of the formed acid. For example, acetic acid was postulated, a view originating in plant data since acetic acid and also acetaldehyde are by-products of the furfural manufacturing process. Another hypothesis attributed the development of acidity to the formation of furoic acid, a belief based largely on the known behavior of benzaldehyde. This was not unreasonable, since it is true that furfural parallels benzaldehyde in a number of well known reactions. Some of these reactions are illustrated in Figure 1, where R denotes the furyl or phenyl radical. Under the influence of sodium cyanide, furfural condenses with itself to form furoin, the furan analog of benzoin. Both aldehydes undergo the Cannizzaro reaction in the presence of strong alkalies to give the corresponding alcohol and acid in equimolecular proportions. With ammonia, complex aldimines are formed: hydrofuramide from furfural, and hydrobenzamide from benzaldehyde. Under appropriate conditions both can be oxidized to the carboxy derivatives or reduced to furfuryl or benzyl alcohols, respectively. The usual aldehyde derivatives can be prepared from either, as illustrated in this case by the oximes.

OXYGEN IN COLOR AND ACID FORMATION

Preliminary studies soon showed that, when technical furfural was stored with free access to air at room temperature, it darkened in color and developed acidity much more rapidly than

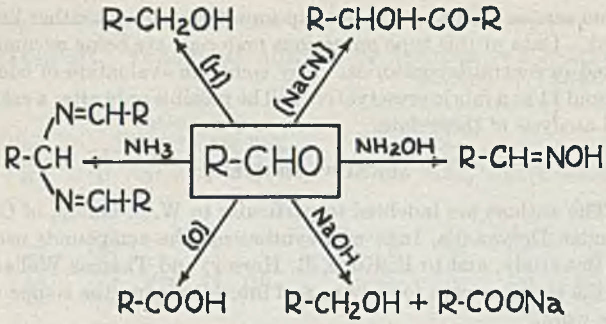

Figure 1. Reactions of Furfural

similar samples in tightly stoppered flasks. Difficulty was experienced, however, in checking the rates of acid formation in supposedly duplicate experiments. Table I demonstrates that this was due to variations in the surface/volume ratio.

In this experiment differing volumes of distilled furfural were exposed to air in Petri dishes of equal area, and the increase in acidity was measured. The results show that the rate of acid formation is a function of the surface/volume ratio. Recognition of this fact made it possible to obtain reliable and reproducible results. The surface/volume ratios employed in our studies were as much as a hundredfold greater than that obtaining in normal storage of furfural—that is, in 55 gallon drums. By accelerating the rate in this manner, we were able to obtain results in a reasonable time.

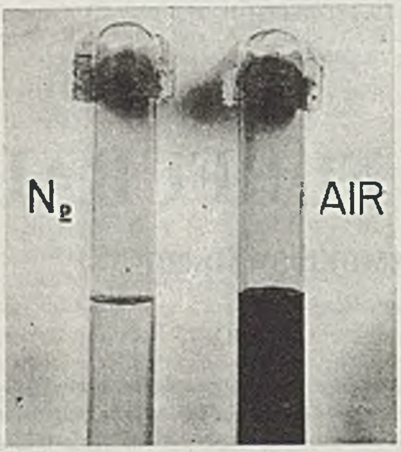

Figure 2. Effect of Storage Atmosphere on Furfural

The results in Table I indicate that the development of acidity in furfural is brought about by autoxidation. Conversely, then, by providing an oxygen-free atmosphere it should be possible to prevent these changes. Accordingly, duplicate samples of freshly distilled furfural were stored, one in contact with air and the other in an atmosphere of nitrogen. Over a period of 9 weeks the air sample (Figure 2) deepened in color and exhibited an increase in acidity of 0.24 equivalent per liter. In the same period the nitrogen sample showed only a slight change in color and no measurable acid formation. Apparently then, color and acidity are interrelated, and oxygen is necessary for their development.

AUTOXIDATION OF FURFURAL

Up to this point it was not clear whether the formed acid had its origin in furfural or in an impurity in the technical product. Therefore comparative tests were made to determine the relative rates of acid formation on storing technical furfural and pure furfural at room temperature with free access to air.

The results in Figure 3 show that technical furfural, on exposure to air at room temperature, exhibits an induction period which is not apparent in the autoxidation of pure furfural. In each case, however, the rate of acid formation reaches a maximum and then the curves slope off quite abruptly, although at different levels. At this stage of the investigation it was reasoned that the formed acid had its origin in a readily oxidizable impurity, a theory which would explain why the autoxidation of pure furfural practically ceases at a relatively low level of acidity. In others words, it was indicated that, in preparing the sample of pure furfural, the concentration of acid precursor had been decreased.

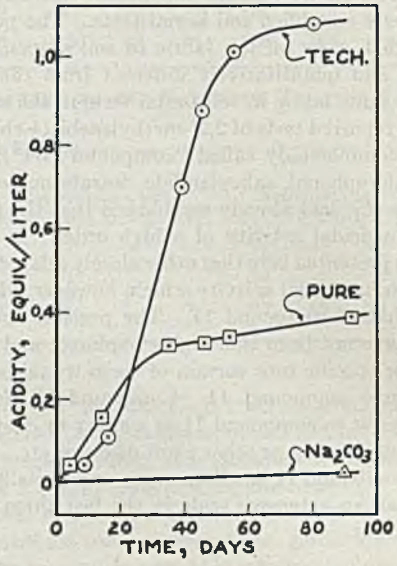

Figure 3. Acid Formation in Furfural, with Free Access to Air

To check the validity of this theory, a sample of technical furfural was allowed to oxidize as before until the acidity curve sloped off; then it could be assumed that all of the postulated impurity had been oxidized. The formed acids were removed, and the furfural was purified by distillation and then exposed to air at room temperature. No diminution in the tendency to form acid could be detected, a result entirely at variance with the "impurity" theory. On the contrary, the experiment established furfural itself as the acid precursor.

Inhibition of autoxidation is strikingly shown by the curve at the bottom of Figure 3. This result was obtained by washing technical furfural with dilute, aqueous sodium carbonate, dehydrating under vacuum, and exposing the product to air as in the previous experiments. Similar results have been obtained by addition of small quantities of tertiary amines to technical furfural.

CHARACTER OF ACID FORMED

As mentioned previously, acid formation in furfural has been attributed to acetic acid, according to one hypothesis, and to furoic acid, according to another. During this investigation the data obtained precluded the possibility that the formed acid was solely acetic or solely furoic acid.

Autoxidized furfural is very dark in color, the intensity varying directly with the concentration of formed acids. On titrating aqueous solutions of such furfural, an indicator effect has been noted. Neither furoic acid nor acetic acid, added to furfural in the concentrations considered here, impart such an indicator effect.

At various intervals during the autoxidation of technical furfural (room temperature, free access to air), the distribution ratio

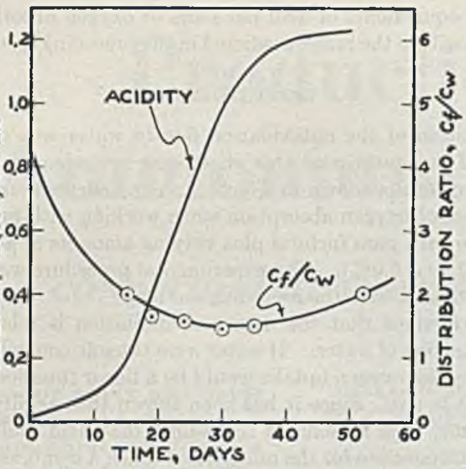

Figure 4. Distribution of Acids between Furfural and Water during Formation

of the formed acid between furfural and water was measured. The results are shown in Figure 4. The distribution ratio of the small initial acidity in technical furfural was 4.1; as autoxidation proceeded, the acid distribution ratio decreased, went through a minimum value of 1.5, and then showed an upward trend. The distribution ratio of furoic acid between furfural and water is 5.8; hence it is evident that the formed acid is not solely furoic. Although the distribution curve in the early stages of autoxidation approaches a value reasonably close to that for acetic acid, 1.1, it then shows an upward trend. This indicates that, whereas acetic acid may be one of the products of the autoxidation of furfural, it is not the sole acid formed.

These conclusions are further substantiated by the results shown in Table II. It is evident that acetic acid is almost entirely removed from furfural in a 60% overhead distillate. On the other hand, furoic acid remains almost completely in the residue in a similar distillation. Autoxidized furfural exhibits an entirely different distillation characteristic, since it is apparent that a mixture of volatile and nonvolatile acids is present.

COMPARISON WITH AUTOXIDATION OF BENZALDEHYDE

The autoxidation of furfural appears to be different from that of benzaldehyde. The latter proceeds rapidly and almost completely, with benzoic acid as virtually the sole end product. Furfural, on the other hand, oxidizes much more slowly, and the reaction is interrupted at a much lower level of acidity. For instance, under our highly accelerated conditions only 7% of the furfural was destroyed before auto-inhibition occurred. In addition, the end result with furfural is a mixture of acidic products and not one single acid.

Table I. Effect of Surface/Volume Ratio on Acid Formation

(Distilled furfural exposed 7 days to air at room temperature; surface of samples, 63.5 sq. cm.)

Volume, ml.	10	20	40
Acidity, equivalent/liter			
Initial	0.006	0.006	0.006
Final	0.100	0.076	0.059
Increase	0.094	0.070	0.053

Table II. Volatility Distribution of Acids in Furfural

Condition of Furfural	Initial Acidity, Equivalent/L.	% of Initial Acidity in: 60% dist.[a]	% of Initial Acidity in: 40% still bottoms
Autoxidized	0.265	31.5	68.5
Pure + acetic acid	0.270	97.4	2.6
Pure + furoic acid	0.245	6.6	93.4

[a] Engler flask, atmospheric pressure.

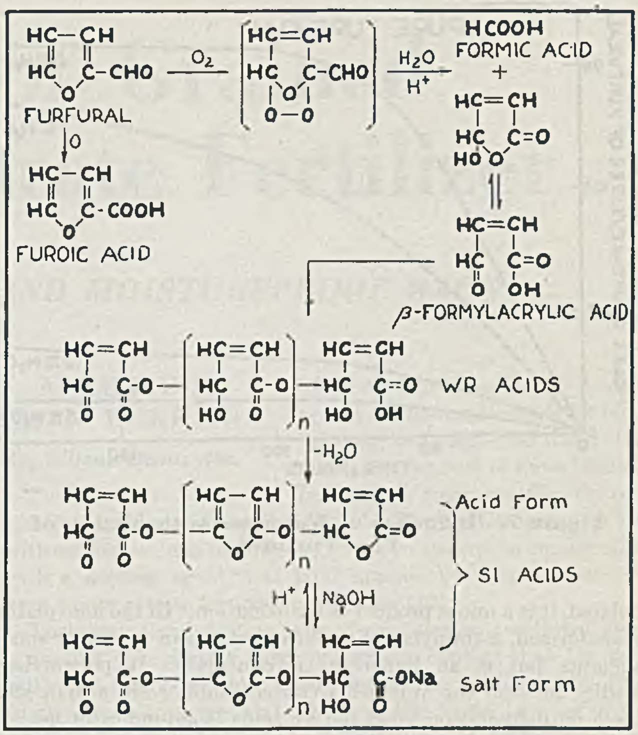

Figure 5. Summary of Furfural Autoxidation

Differences between the two aldehydes on autoxidation can be seen further in previously published work. For example, Swerne *et al.* (*3*) demonstrated that under conditions which gave a 40% yield of perbenzoic acid from benzaldehyde, no perfuroic acid was obtained from furfural. Milas and McAlevy (*2*) showed that the small amount of peroxide formed on autoxidation of furfural was not identical with authentic perfuroic acid synthesized from furoyl peroxide.

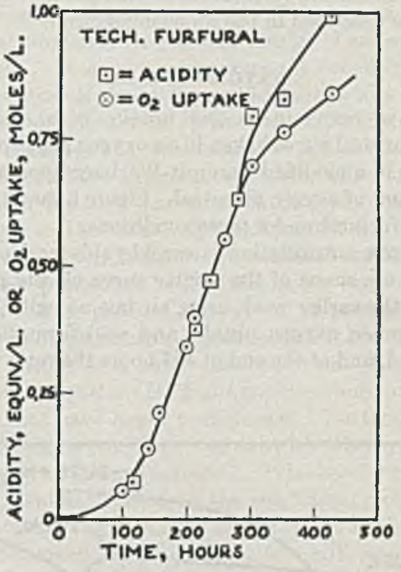

Figure 6. Relation of Autoxidation and Acid Formation

A study is reported elsewhere (*1*) on the nature of the products of autoxidation of furfural, and a mechanism is postulated to account for their formation. Figure 5, which summarizes that work, shows that the only volatile acid produced is formic acid. No acetic acid was found, and although some furoic acid was

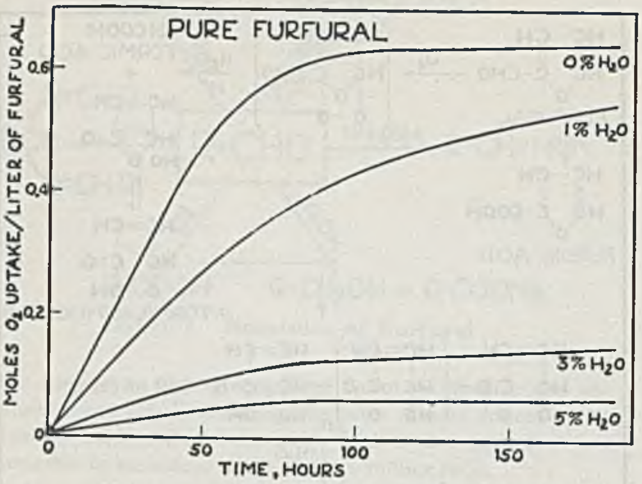

Figure 7. Influence of Water on Autoxidation of Pure Furfural

isolated, it is a minor product of autoxidation. Of the nonvolatile acids formed, β-formylacrylic acid is isolated in relatively small amounts but is an important intermediate. It polymerizes readily to form the WR acids (water-soluble resin acids), and these on dehydration yield the SI acids (solid-indicator acids). The latter two acid fractions are dark resinous materials, and constitute the polymer which develops in furfural during normal storage. The SI acids are responsible for the indicator effect previously noted.

The differing solubilities and volatilities of the various acids formed explain the results shown in Figure 4 and Table II. In addition, this scheme of oxidation predicts that more than 1 but less than 2 equivalents of acid should be formed per mole of oxygen consumed. A verification of this prediction is apparent in the results described in the following section.

OXYGEN UPTAKE

In order to correlate oxygen uptake with acid formation, samples of furfural were shaken in an oxygen atmosphere at room temperature in a modified Barcroft-Warburg apparatus to measure the amount of oxygen absorbed. Figure 6 shows the behavior of technical furfural under these conditions.

Although the autoxidation is considerably accelerated in this experiment, the shape of the acidity curve closely parallels that obtained in the earlier work using air but no agitation. A relationship between oxygen uptake and acid formation is clearly demonstrated, and at the end of 427 hours the ratio was found to be 1.17 equivalents of acid per mole of oxygen absorbed. This value is within the range predicted in the preceding section.

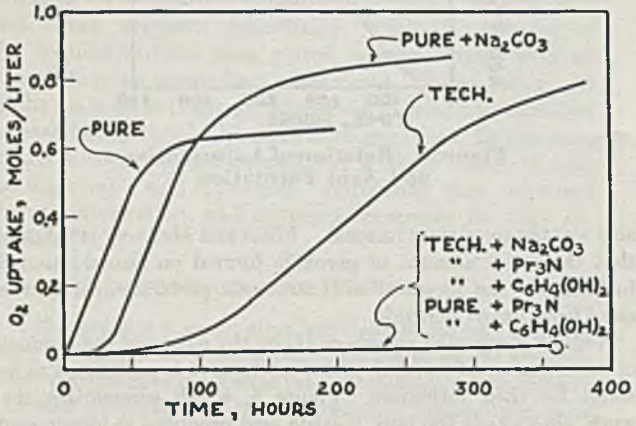

Figure 8. Effect of Inhibitors on Furfural Autoxidation

EFFECT OF WATER

Inhibition of the autoxidation due to water was observed in some of our tests, and this effect was investigated more fully with the results shown in Figure 7. The curves show the relative rates of oxygen absorption when working with pure furfural and also with pure furfural plus varying amounts of added water (1.0, 3.0, and 5.0%). The experimental procedure was the same as that described in the preceding section.

It is obvious that the degree of inhibition is related to the concentration of water. If water were the sole controlling factor, however, the oxygen uptake would be a linear function of time—which it is not. Since it has been shown that acidity increases with time, it is reasonable to assume that acid and water are jointly responsible for the inhibition. Such a combination would imply that hydrogen ion is the controlling factor, a possibility which is not inconsistent with the results obtained in this experiment. For example, as the concentration of water decreases, an increasing amount of formed acid will be required to attain a hydrogen ion concentration sufficient to inhibit autoxidation effectively. Such a hypothesis offers an explanation as to why these curves slope off at different levels.

EFFECT OF INHIBITORS

The technique previously described was used to study the effect of various inhibitors on the autoxidation of furfural. The results are illustrated in Figure 8. The induction period in the technical furfural curve is apparent, whereas pure furfural exhibits no such induction period. Tripropylamine as an example of a tertiary amine and hydroquinone as an example of a phenolic antioxidant are effective inhibitors for either technical or pure furfural. Sodium carbonate treatment, on the other hand, is effective in inhibiting the autoxidation of technical but not of pure furfural. In the latter case a short induction period is noted. Apparently treatment of pure furfural wtih sodium carbonate has caused the formation, though to a lesser degree, of a type of substance which occurs naturally in technical furfural and which causes a long induction period. Such a substance might be a soap of a high-molecular-weight acid. Since furfural, when distilled for purification, would be virtually free of such acids, only a minute amount of furfural-soluble soap could be formed on sodium carbonate treatment, and a short induction period would result. Technical furfural, with a greater amount of soap, would have a longer induction period, and sodium carbonate treatment might form enough additional soap to cause an indefinitely long induction period. Tripropylamine is completely soluble in furfural and is available for soap formation in either pure or technical furfural, and thus is an effective hibibitor in either.

The quantities of base required for inhibition of autoxidation need not be sufficient to make the furfural alkaline.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Dunlop, A. P., and Swadesh, S., to be published.
(2) Milas, N. A., and McAlevy, A., *J. Am. Chem. Soc.*, **56**, 1219, 1221 (1934).
(3) Swern, D., Findley, T. W., and Scanlan, J. T., *Ibid.*, **66**, 1926 (1944).

PRESENTED before the Organic Chemistry session at the Technical Conference of the Chicago Section, AMERICAN CHEMICAL SOCIETY, Evanston, Ill., November 16, 1945.

Production of Grained Ammonium Nitrate Fertilizer

CONDITIONING TREATMENTS AND MOISTUREPROOF BAGS

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A plant-scale study was made of the conditioning of granular ammonium nitrate produced in batch graining kettles. The conditioning treatments consisted either of 1% of a coating agent, 4% of a dust, or a combination of both. The behavior of the conditioned ammonium nitrate during prolonged bag storage and in fertilizer distributors indicated that the combination treatment gives a satisfactory product for direct use, whereas a dust used alone is much less satisfactory and a coating treatment used alone is quite unsatisfactory. The multiwall moistureproof paper bags were more effective than were asphalted burlap bags in protecting ammonium nitrate from atmospheric moisture during storage.

IN April, 1943, when the War Department suddenly curtailed its demand for ammonium nitrate then being produced in the graining plant of the Tennessee Valley Authority, the plant output became available for use as fertilizer. In view of the well known tendency of ammonium nitrate to cake and to absorb moisture from the atmosphere, it was evident that its physical properties would have to be improved to assure a satisfactory fertilizer material. Studies were undertaken immediately to develop a conditioning treatment that would make possible prompt diversion of the ammonium nitrate plant output to help meet the pressing demand for nitrogen fertilizer. As a result of these studies, production of conditioned ammonium nitrate was started; meanwhile, research was continued on developing and evaluating improved conditioning methods. This paper is based on these studies.

Ammonium nitrate has long been recognized as an excellent source of nitrogen for all crops, and it is also one of the most concentrated forms of nitrogen fertilizer (35% N for the pure salt). Prior to World War II it was employed extensively as an ingredient of solutions used to ammoniate superphosphate; substantial quantities of the solid salt also were used commercially in fertilizers but generally in admixture with considerable proportions of other materials that modified its physical properties. In Europe granulated mixtures of ammonium nitrate with limestone or dolomite, known as Cal-Nitro or Nitro-Chalk and containing 16 to 20% nitrogen, have been marketed for some time, and considerable amounts were exported to the United States (*9*). Recently a similar material has been produced in this country (*9*). Ammonium nitrate and ammonium sulfate in the form of mechanical mixtures or of the double salt have also been widely used abroad.

Coating of ammonium nitrate with petrolatum or paraffin to reduce moisture absorption, with or without addition of small amounts of various dusts to minimize caking, has long been practiced in the explosives industry and has been proposed for fertilizer conditioning. Following World War I, the Fixed Nitrogen Laboratory (*6*) made tests of rosin-paraffin mixtures, petrolatum, and paraffin as coating agents for the grained salt for fertilizer use, and concluded that petrolatum was the best of those studied. In 1940 a rosin-paraffin-coating treatment, developed by the Hercules Powder Company for use with explosives, was patented (*1*); the treatment, in combination with a dusting agent, was later applied by this company to ammonium nitrate fertilizer production (*10*).

The coating and dusting type of conditioning treatment gives a product only slightly lower in nitrogen content than the pure salt; this kind of product was therefore selected for use by TVA in preference to a material similar to Cal-Nitro, because of the savings in bags, labor, and transportation. A recent paper by Ross and co-workers (*7*) describes the results of small-scale studies of coating and dusting treatments applied to spray-granulated ammonium nitrate produced in Canada, and of large-scale storage tests of Canadian and TVA ammonium nitrate, carried out during the same period as the present work. Ross and Yee (*8*) studied the suitability of various types of paper and burlap bags for storing ammonium nitrate.

Up to a certain point, both the storage and drillability properties of ammonium nitrate improve with increased particle size, and material produced in graining kettles is somewhat smaller than optimum. Ross and co-workers (*7*) concluded from their tests that, because of its smaller particle size, grained ammonium nitrate is less drillable than spray-granulated material. Spray granulation is carried out continuously and, like other continuous processes proposed for ammonium nitrate, will almost certainly give a cheaper product than does batch graining. Because of the higher cost and the relatively small particle size of the grained product, it is likely that future installations for ammonium nitrate fertilizer production will utilize some continuous process that gives a coarser product. However, at present virtually all of the solid ammonium nitrate produced in this country is made in graining kettles in a batchwise operation. Effective conditioning is more important for grained ammonium nitrate than for other types that have larger particle size. Furthermore, the results of conditioning studies carried out with other types cannot be applied directly to grained material. It is therefore believed that a report of plant-scale tests on the conditioning of grained ammonium nitrate, along with information on the application of conditioning treatments in plant operation, will serve a practical need.

In the present investigation a number of conditioning treatments employing a variety of coating and dusting agents were applied to grained ammonium nitrate in plant-scale graining kettles, and the products were evaluated for caking under commercial storage conditions and for drillability under simulated field conditions, using a commercial distributor.

GRAINING AMMONIUM NITRATE

The ammonium nitrate plant at Muscle Shoals was described by Fairlie (*3*) in 1919; it has since been modified considerably to comply with revised Ordnance safety regulations, but the process is essentially unchanged. The graining process will be de-

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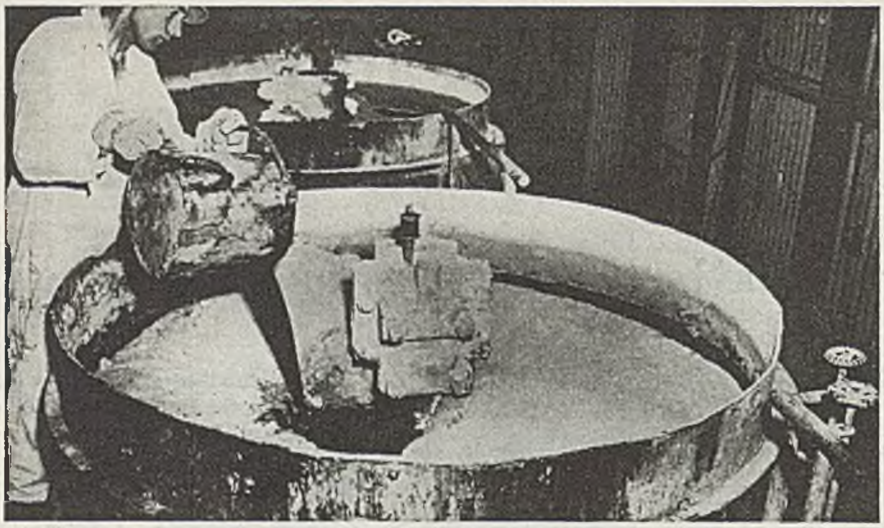

Figure 1. Adding *PRP* Coating Mixture to Grained Ammonium Nitrate

scribed here only in sufficient detail to make evident the method of applying the conditioning treatment.

A 1-ton batch of molten ammonium nitrate, at about 320° F. and containing about 1.5% water, is charged to a jacketed graining kettle in which it cools slowly while being agitated by slow-moving plows. As cooling progresses and the water is evaporated, crystallization begins and the material changes from a pasty mixture to large soft lumps and finally into grains. These grains can be seen under the microscope as large numbers of fine crystals cemented together to form a rounded granule; they are fully formed by the time the temperature falls to 260° F. At this point the moisture content has been reduced to a constant value of 0.05%, and the cooling rate is increased by admitting water to the kettle jacket. The batch is discharged from the kettle at about 200° F. onto a belt conveyor; each graining cycle requires 2.5 to 3 hours. The ammonium nitrate is screened to remove the +12 mesh material and is bagged in 100-pound bags: the ammonium nitrate temperature at the time of bagging is about 190° F. The +12 mesh material, mostly lumps and irregular fragments, is crushed and recycled to another kettle batch.

The conditioning treatment was incorporated into the above cycle in the following manner: Molten coating agent was poured in at a point behind the plows near the center post (Figure 1) when the batch was at 230-240° F. Tests showed that addition of the coating material by pouring was as effective as spraying in obtaining satisfactory distribution. After 10 to 15 minutes, when the batch temperature was 210-220° F., the dusting agent was dumped into the kettle. Samples were taken from ten points in the kettle just before the dust was added and were composited; a similar composite was obtained just before the kettle was discharged.

The proportion of fines in ammonium nitrate produced in a graining kettle can be varied over a wide range by changes in the graining cycle and technique; a discussion of these changes is beyond the scope of this paper. For fertilizer use the product is made as coarse and as free from fines as is practical. TVA ammonium nitrate contains a small amount (less than 0.1% total) of ferric and aluminum hydroxides (from the ceramic nitric acid absorption towers) which has been found to aid in the production of coarse grains. The usual particle size range of the grained conditioned product follows:

Screen Size	Per Cent
−12 +35 mesh	60 to 85
−35 +100 mesh	10 to 35
−100 mesh	1 to 5

In the studies reported here the particle size, within these limits, was a constant factor. The bulk density of this material is about 62 pounds per cubic foot; it is approximately the same for the unconditioned material.

Three types of conditioning treatments were investigated: a water repellent coating material, a water repellent coating plus a dusting agent, and a dusting agent used alone. In general, the coating has the effect of reducing the rate at which ammonium nitrate absorbs moisture and of improving its drillability under humid conditions, whereas the dust reduces the caking tendency. The two-step treatment is inherently more effective than the coating or the dust alone, since each improves the product in a different respect; however, in view of the lower cost and greater simplicity of the one-step treatments, it was desirable to determine whether either step would be satisfactory by itself.

CONDITIONING MATERIALS

A large number of materials were considered for use as coating and dusting agents. Many of them were eliminated because of unfavorable results in exploratory tests or because of excessive cost. Among the materials eliminated as coatings were lubricating oil, oleic acid, petrolatum-rosin-clay mixture, alumina gel, and silica gel; among those eliminated as dusts were limestone, whiting, calcium silicate slag from phosphorus electric furnaces, tripoli, common clay, gypsum asphalt rock, cyanamide, and seawater magnesia. Because of its availability, low cost, and wide use in agriculture, limestone was studied rather extensively before being eliminated. In addition to providing poor protection against caking, it caused some loss of ammonia when added to the hot ammonium nitrate. After exploratory tests, the following materials were tested thoroughly on a plant scale.

Coating Ingredient[a]	Dust
Petrolatum	Kaolin
Rosin	Kieselguhr
Paraffin	Plaster of Paris ($CaSO_4 \cdot {}^1/_2H_2O$)
Gilsonite	Soapstone

[a] In the text these materials are given the symbols *P*, *R*, *P*, and *G*, and are always referred to in the order given here. For example, *PR* means petrolatum-rosin mixtures and *RP* rosin-paraffin mixtures.

The rosin generally used in this work was FF grade wood rosin. The suitability of the various grades of rosin as coating ingredients appeared to be governed by the "oxidized rosin" content (determined analytically as the fraction insoluble in petroleum ether). Excessive contents of oxidized rosin resulted in unstable *PRP* mixtures and also decreased the resistance of the coating to water vapor penetration. The oxidized rosin content of FF grade wood rosin (about 4%) was sufficiently low so that stable mixtures were obtained. Although the more highly refined grades of wood rosin and the various grades of gum rosin contained even less oxidized rosin, they did not offer sufficient advantage to compensate for their higher price. On the other hand, B grade wood rosin (the lowest grade), which is much cheaper than the FF grade, contained 40 to 60% of material insoluble in petroleum ether and would not form homogeneous *PRP* mixtures. Because of the occasional shortage of FF grade wood rosin, experiments were made on the compatibility of *PRP* (1-3-1) mixtures in which one third or one half of the rosin was B grade wood rosin and the remainder was K grade wood rosin. B grade rosin obtained from different vendors, unlike the higher grades, varied widely in properties; however, all three brands tested in the manner described proved incompatible.

TABLE I. PHYSICAL PROPERTIES OF DUSTING AGENTS

Dust	Source	Bulk Density, Lb./Cu. Ft.	Oil Absorption[a], G. Oil per 100 G. Dust	Screen Analysis, % +200 mesh	Screen Analysis, % −200 +325 mesh	Screen Analysis, % −325 mesh
Kaolin	Thomas Kaolin Co., Hackleburg, Ala.	48	49	2.5	5.5	92.0
Kieselguhr (Celite 379)	Johns-Manville Corp., New York, N. Y.	15	176	1.8	3.9	94.3
Plaster of Paris[b]	International Minerals and Chemical Corp., Wales, Tenn., and Armour Fertilizer Co., Columbia, Tenn.	60	40	22.3	13.7	64.0
Soapstone	Southern Talc Co., Atlanta, Ga.	49	43	1.3	7.4	91.3

[a] Gardner-Coleman method (*4*).

[b] Purchased as wet by-product calcium sulfate, obtained in the wet-process manufacture of phosphoric acid; dehydrated and ground at Wilson Dam.

Two grades of paraffin, specified as "light yellow crude scale" (melting point, 124-126° F.) and "semirefined 128 AMP white crude scale", respectively, proved equally satisfactory.

Petrolatum from a number of sources and varying widely in specifications, appearance, and cost was used with no appreciable difference in results. The material used included both "commercial amber" and "dark crude" grade, varied in color from amber to black, and ranged in melting point from 118-155° F.

Some consideration was given to the possibility of substituting a single petroleum product for the petroleum constituents of the *PRP* mixture or for the entire mixture. However, after exploratory tests with a few high melting waxes and consultation with the research department of a leading petroleum refiner, it was concluded that neither possibility was promising.

Gilsonite, one of the asphaltites of petroleum origin, is a naturally occurring hard black material of high melting point, mined in Utah. The gilsonite used in the present work was all of the grade known as selects and had a melting point of about 330° F.

Except for plaster of Paris, which was prepared by TVA from by-product calcium sulfate, the dusts were purchased under specifications of 97% −200 mesh particle size, no extraneous gritty material, and not more than 1% moisture. The particle size was determined by a wet screen method. The grit test was made by rubbing a linseed oil-dust paste across a smooth glass plate with a spatula. Measurements of the apparent bulk density and the oil absorptivity were made to obtain a preliminary evaluation of the effectiveness of a dust; usually, although not always, low bulk density and high oil absorptivity indicated good conditioning properties. Table I contains these data for some dusts.

BEHAVIOR OF MATERIALS

Following are some qualitative and semi-quantitative observations on the behavior of the conditioning materials during and after application. While the molten *PRP* coating mixture was normally added at ammonium nitrate temperatures of 230-240° F., satisfactory application was also obtained when the mixture (at 200° F.) was added to the graining kettle at an ammonium nitrate temperature as low as 120° F. Addition of the coating mixture at ammonium nitrate temperatures above the crystal transformation temperature of 258° F. resulted in a less effective coating. The effectiveness of the coating and its uniformity of distribution throughout the batch were evaluated by comparing the moisture absorption rate of a number of random samples. Coating mixtures containing appreciable amounts of gilsonite were much more viscous and had higher melting points than other mixtures, and in general had to be added at ammonium nitrate temperatures above 220° F. for satisfactory application. On the other hand, when more viscous mixtures containing gilsonite were used as the second of two coatings (the first being a softer mixture), best results were obtained when the mixture was added at the lowest grain temperature (about 220° F.) at which good distribution could still be obtained. These results can be explained by the fact that this procedure would be expected to give the least degree of mixing of the two coatings.

Microscopic examination of coated grains indicated that the bulk of coating material was utilized in forming a protective shell around the grains; but with the softer materials, such as petrolatum or *PRP* mixtures of low rosin content, there was some penetration into the cracks and fissures in the grain. When the ammonium nitrate was dissolved from grains that had been coated with a *PRP* (1-1-1) mixture but not dusted, a continuous shell was left behind which enclosed a varying amount of coating material of a spongelike cellular structure. If a dust had been added also, particles of dust were found embedded in the coating, lowering its cohesive strength, with the result that the coating fell into fragments when the ammonium nitrate was dissolved. Harder coatings such as *PRPG* mixtures resisted the abrasive action of the dust to a considerable degree but failed to penetrate the interior of the grain.

This behavior was reflected in the rates at which ammonium nitrate absorbed moisture when conditioned by various methods. The rate of moisture absorption was determined by a simplified modification of the method described by Keenen (*5*), in which air of controlled temperature and humidity flowed over 2-gram samples exposed on watch glasses. This rate proved to be of limited significance in the final evaluation of the effectiveness of conditioning; it proved helpful, however, in obtaining some insight into the specific behavior of the conditioning agents when different procedures were used. The rate at which the grains absorbed moisture was reduced to about 8-10% of its original value (relative hygroscopicity[2] 8-10%) by applying a coating of 1% by weight of petrolatum. When 4% kaolin dust was added on top of the petrolatum coating, the relative rate increased to about 20%. A *PRP* coating (1%) used alone was more effective than petrolatum, giving a relative hygroscopicity of 2-5%; however, addition of the dust increased the value to 40-60%. Evidently the semifluid nature of the petrolatum maintained a continuous coating even after penetration by the dust particles, whereas the *PRP* coating, with a more skinlike structure, was ruptured by the dust, which provided gaps for the entrance of moisture. Varying the amount of dust from 1 to 4% made no difference in the extent to which the moisture absorption rate was increased by dust addition. Ammonium nitrate grains with a *PRPG* coating, which was much harder than the *PRP*, had a relative hygroscopicity of about 20%. This comparatively high initial rate was attributed to failure of the coating to penetrate the interior of the grain; thereby a large internal area of ammonium nitrate was left exposed to water vapor, which penetrated the outer shell. On the other hand, the greater resistance of the outer coating to abrasion reduced somewhat the increase in moisture absorption rate which was caused by the addition of dust.

On the basis of this behavior a two-step coating treatment was tried. A small amount of a soft material (0.2 to 0.4% petrolatum or *PRP*) was added first to penetrate the interior of the grains and to form a thin surface coating. This was followed by addition of a larger amount (0.6 to 1.0%) of a harder coating (*RPG* or B grade rosin) to offer protection against the dust or to make it feasible to dispense with the dust entirely. When this treatment was used, the relative hygroscopicity was about 10% after the first coating, about 12 to 20% after the second coating, and about 40 to 70% after adding kaolin dust.

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[2] Hygroscopicity is used here to designate the rate of moisture absorption. The conditioning treatment did not change the equilibrium concentration of water vapor at the hygroscopic point but did affect the rate of moisture absorption. Relative hygroscopicity is expressed as per cent of the hygroscopicity of unconditioned grains.

TABLE II. MOISTURE ABSORBED BY GRAINED AMMONIUM NITRATE[a] STORED IN VARIOUS TYPES OF BAGS AT 80 (±4)° F. AND 80 (±1)% RELATIVE HUMIDITY.

Description of Bag	History of Bag Prior to Exposure	No. of Days Bag Was Exposed	No. of Days Bag Remained Dry	Moisture Content of Ammonium Nitrate, %				Moisture Held by Burlap or Paper at End of Test, Lb.	Total Moisture Absorbed during Test, Lb.	Av. Rate of Absorption, Lb./Day	
				Before exposure	After exposure: Edge	Center	Composite			Filled hot	Filled cold
BURLAP AND COTTON BAGS LINED WITH PAPER CEMENTED WITH ASPHALT											
7.5-oz. burlap, 1-ply paper, source F	Filled with hot NH_4NO_3	16	..	0.10	2.12	0.86	1.58	0.23	1.71	0.11	...
7.5-oz. burlap, 1-ply paper, source F	Filled with hot NH_4NO_3	35	20	0.07	1.48	0.99	1.78	0.50	2.21	0.06	...
7.5-oz. burlap, 1-ply paper, source F	Filled with cold NH_4NO_3	20	20	0.06	1.45	0.43	0.75	0.26	0.95	...	0.05
7.5-oz. burlap, 1-ply paper, source F	Filled with cold NH_4NO_3	35	20	0.08	2.02	1.06	1.85	0.45	2.22	...	0.06
10-oz. burlap, 1-ply paper, lot 1, source E	Filled with hot NH_4NO_3	16	11	0.06	2.22	0.87	1.71	0.80	2.45	0.15	...
10-oz. burlap, 1-ply paper, lot 1, source E	Filled with hot NH_4NO_3	35	11	0.05	1.90	1.61	1.84	0.80	11.09[b]	0.32	...
10-oz. burlap, 1-ply paper, lot 1, source E	Filled with cold NH_4NO_3	20	13	0.10	2.37	0.89	1.85	0.80	2.55	...	0.13
10-oz. burlap, 1-ply paper, lot 1, source E	Filled with cold NH_4NO_3	35	13	0.06	2.60	2.12	2.14	0.86	9.84[b]	...	0.28
10-oz. burlap, 1-ply paper, lot 2, source E	Filled with hot NH_4NO_3	20	11	0.08	2.13	0.76	1.49	0.48	1.89	0.09	...
10-oz. burlap, 1-ply paper, lot 2, source E	Filled with hot NH_4NO_3	25	11	0.04	1.79	0.85	1.73	0.48	2.17	0.09	...
8-oz. burlap, double asphalted liner, source E	Filled with cold NH_4NO_3	35	18	0.06	1.90	0.73	1.49	0.58	2.01	...	0.06
10-oz. burlap, double asphalted liner, source E	Filled with cold NH_4NO_3	25	18	0.07	2.26	1.00	1.34	0.42	1.69	...	0.07
3.3-yd. cotton, 1-ply paper, source F	Filled with cold NH_4NO_3	12[c]	7	0.15	..	..	1.05	0.48	1.38	...	0.11
10-oz. burlap, 1-ply paper, source G	Filled hot and stored in freight car-18 hr.	12[c]	7	0.03	..	..	0.93	0.75	1.65	0.14	...
10-oz. burlap, 1-ply paper, source G	Filled with cold NH_4NO_3	12	7	0.15	0.25	..	0.55	0.44	0.84	...	0.07
10-oz. burlap, 1-ply paper, source H	Filled with hot NH_4NO_3	14	..	0.07	..	..	0.48	0.17	0.58	0.041	...
10-oz. burlap, 1-ply paper, source H	Filled with hot NH_4NO_3	35	..	0.05	..	..	1.38	0.27	1.60	0.046	...
10-oz. burlap, 1-ply paper, source H	Filled cold with unconditioned NH_4NO_3	14	..	0.07	..	..	0.40	0.10	0.43	...	0.031
10-oz. burlap, 1-ply paper, source H	Filled cold with NH_4NO_3 conditioned with 1% *PRP* coating only	14	..	0.22	..	..	0.59	0.10	0.47	...	0.034
MULTIWALL PAPER WITH ONE OR TWO MOISTUREPROOF (MP.) PLIES											
5-ply paper (1 mp.), source A	Filled with hot NH_4NO_3	35	34	0.06	0.69	0.46	0.74	0.19	0.87	0.025	...
5-ply paper (1 mp.), source A	Filled with hot NH_4NO_3	51	34	0.08	..	..	1.22	0.22	1.36	0.026	...
5-ply paper (1 mp.), source A	Filled with cold NH_4NO_3	35	34	0.04	1.08	0.44	0.84	0.29	1.09	...	0.031
5-ply paper (1 mp.), source A	Filled with cold NH_4NO_3	51	34	0.12	..	..	1.43	0.32	1.63	...	0.032
5-ply paper (1 mp.), source D	Filled with hot NH_4NO_3	35	..	0.08	..	..	0.74	0.11	0.77	0.022	...
5-ply paper (1 mp.), source D	Filled with hot HN_4NO_3	35	..	0.02	..	..	0.91	0.16	1.05	0.030	...
3-ply paper (1 mp.), source E	Filled with cold NH_4NO_3	35	...	0.07	0.50	0.75	0.82	0.13	0.78	...	0.022
5-ply paper (2 mp.), source C	Filled with cold NH_4NO_3	35	..	0.13	0.25	0.28	0.45	0.22	0.54	...	0.015
5-ply paper (2 mp.), source C	Filled with cold NH_4NO_3	51	48	0.05	..	..	0.68	0.17	0.80	...	0.016
6-ply paper (2 mp.), source B	Filled with cold NH_4NO_3	12[c]	..	0.15	..	..	0.23	0.09	0.17	..	0.014
6-ply paper (2 mp.), source B	Filled hot and stored in freight car 18 hr.	12	..	0.07	..	..	0.23	0.12	0.28	0.023	..

[a] Conditioned with 1% *PRP* plus 4% kaolin, except where otherwise noted.

[b] Sufficient ammonium nitrate had dissolved from bags to cause an appreciable loss in weight. The moisture equivalent of the dissolved ammonium nitrate, calculated as 70% solution of NH_4NO_3, is included in this total.

[c] These bags were received in time to permit only a 12-day test.

In agreement with the results reported by Ross and co-workers (7), the effectiveness of *PRP* coatings in reducing moisture absorption did not vary much with wide variations in the proportions of the three ingredients. However, the stability of the mixtures, which is of considerable importance to the plant operator, varied considerably with the composition. In semiquantitative tests, like those described earlier for B grade rosin, mixtures of various compositions containing FF grade wood rosin were stored in open beakers at 230° F. (approximately the temperature used in plant operation). The tests indicated that in a few days a gummy material settled out of mixtures containing less than about 60% rosin; mixtures containing more than this amount showed little or no separation after 10 days or longer. The dividing line was quite marked and was practically unaffected by changes in the relative proportions of the other two ingredients, petrolatum and paraffin. These beaker tests were confirmed by a few tests in small tanks and by subsequent plant experience with the 1-3-1 *PRP* mixture. It was found that *PR* or *RP* mixtures gave less satisfactory coatings than the *PRP* mixtures.

Dusting agents varied in the extent to which they neutralized the protection against moisture absorption which was provided by a *PRP* coating. Of the dusts tested extensively, soapstone caused the least increase in moisture absorption rate of the coated grains; the effect of plaster of Paris was slightly greater, the effect of kaolin was considerably greater, and kieselguhr resulted in the highest absorption rate of all. The same general behavior was observed by Ross and coworkers (7), but their tests indicated that kaolin gave a higher absorption rate than Dicalite (a commercial kieselguhr). In tests made with clay from various sources, it was observed that clay containing palpably gritty particles resulted in a higher absorption rate than did clay free of grit. In an attempt to avoid the deleterious action of dust on the coating, experiments were run in which the coated ammonium nitrate was allowed to cool; this permitted the *PRP* coating to harden before addition of the dust. This procedure had a beneficial effect initially; for example, material freshly conditioned with 1% *PRP* and 4% kaolin had a relative moisture absorption rate of 20% when kaolin dust was added at a grain temperature of 150° F., compared with a rate of 50% when the temperature of addition was 220° F. However, after a week of storage the two batches had approximately the same absorption rate, and similar behavior was observed even when the coated ammonium nitrate was cooled to room temperature before dust addition. By comparison, the moisture absorption rate of ammonium nitrate coated with *PRP* and that undusted remained unchanged over a long period.

EVALUATION OF STORAGE PROPERTIES

The storage properties of ammonium nitrate fertilizer were evaluated by storage tests made with 100-pound bags in stacks twelve bags high. The tests were carried out in a large unheated warehouse of hollow tile construction with a concrete floor. Test stacks rested on wooden platforms, and usually two or more stacks supported each other. In these tests average warehouse conditions were fairly well duplicated.

Two types of storage test were carried out; they differed in duration and in the method of evaluating the extent of caking. The first was exploratory; it lasted 4 weeks, a period representing a compromise between the 6 to 12 months of storage encountered in practice, and the practical need of obtaining preliminary indications as quickly as possible. This test was given to all products. For evaluation, the ninth bag from the top was removed and cut open for inspection after 1 week, the tenth bag after 2 weeks, the eleventh bag after 3 weeks, and the twelfth bag after 4 weeks. The bags removed were replaced with dummy bags to maintain constant pressure on the lower bags. The degree of caking was rated on the basis of estimated amount and hardness of cake formed; these tests obviously gave a relative measure of the amount of caking rather than an absolute value. The rating system consisted of an arbitrary scale, ranging from 1, which indicated complete absence of caking, to 10, which indicated the same amount of caking as was observed in unconditioned ammonium nitrate after 4 weeks of storage; in this case the bag contents formed a solid cake, most of which broke up when the bag was dropped several times on the concrete floor. The 1-month tests proved very useful, but in some cases the results were not confirmed by subsequent long term tests, and it was concluded that the 1-month test is not sufficient for a final evaluation.

The more promising experimental products were given long bag storage tests in which inspections usually were made at intervals of 3 months. Evaluation of the degree of caking in the long term tests was made by the drop test, which consisted of dropping the bag of fertilizer four times from a height of 3 feet to a concrete floor, and then weighing the amount of material that would not pass a 2-mesh screen. This test is considered to be a practical method that approximates the amount of handling given a fertilizer between storage and application to the soil.

Most of the long-term storage tests were made with ammonium nitrate packed in burlap bags that had an asphalted creped-paper lining and were closed by wire ties. However, after these tests were under way, experience with commercial shipments of ammonium nitrate sent to particularly humid regions indicated that these bags did not afford satisfactory protection against water-vapor penetration. A study was therefore made to compare the effectiveness of various multiwall moistureproof paper bags and asphalted burlap bags, from different sources, in protecting ammonium nitrate against moisture.

STUDY OF BAGS

Tests were carried out on the absorption of water vapor by bagged ammonium nitrate exposed in an air-conditioned room maintained at 80 (±4)° F. and 80 (±1)% relative humidity (*2*). These conditions provided a difference of about 5 mm. mercury between the water vapor pressure in the air and that of a saturated solution of ammonium nitrate; this difference is slightly greater than the maximum to be expected in highly humid southern coastal regions[3]. Air was circulated at a rate of 800 cubic feet per minute through the storage room, which had a volume of 560 cubic feet. Bags of ammonium nitrate, stacked vertically and resting on brick platforms, were arranged in two rows perpendicular to the direction of air flow. Tests lasted from 2 to 7 weeks, depending on the rate at which moisture was absorbed. A final sample of ammonium nitrate, obtained by riffling the entire contents of the bag, was analyzed for water. Water held by the bag material was determined by loss of weight on drying; this water was 20 to 40% of the total amount absorbed. In a few cases where the rate of moisture absorption was particularly high, there was a net decrease in the weight of the filled bag caused by leakage of dissolved ammonium nitrate. In such cases it was assumed that the ammonium nitrate had been lost as a 70% solution (saturation at about 80° F.), and the corresponding amount of water was included in calculating the total amount absorbed. Tests were in duplicate, with one test in each pair generally extending longer than the other. In plant practice the temperature of the ammonium nitrate when it is bagged is close to the melting point of asphalt. The effect of filling with hot and room-temperature ammonium nitrate, respectively, was therefore tested for each type of bag.

Table II presents the results of tests made with four brands of burlap bag and one brand of cotton bag all having a single asphalted-paper liner, a burlap bag with a double asphalted-paper liner, three brands of multiwall paper bag with one moistureproof ply, and two brands of multiwall paper bag with two moistureproof plies. It was concluded that the multiwall moistureproof paper bags had higher resistance to water vapor penetration than did the asphalted burlap or cotton bags. Filling with hot ammonium nitrate (at 185-190° F.) decreased the resistance of burlap bags considerably and had less effect on paper bags. A paper bag with two moistureproof plies had 1.5 to 2 times the resistance of a bag with one moistureproof ply. These results agree with the data of Ross and Yee (*8*) as to the superiority of multiwall paper bags, having either one or two moistureproof plies, over most burlap bags having a single asphalted-paper liner, of the type ordinarily available. These workers also found that some types of burlap bags with double asphalt layers were virtually as resistant to water vapor penetration as multiwall paper bags with two moistureproof plies. This was not confirmed for the single brand of double-asphalted burlap bag tested in the present work; in any case, these double-asphalted burlap bags presumably would cost considerably more than the paper ones.

Apparently the rate of moisture penetration was the same whether the ammonium nitrate in the bag was coated or uncoated; this indicated that the protection provided by conditioning treatment against moisture absorption during storage was negligible by comparison with that provided by the bag. However, the coating was important in protecting the ammonium nitrate during exposure to humid atmospheres after removal from the bag. Other tests indicated that the wire-tie closure provided a satisfactory seal against moisture penetration, that moisture penetration was generally highest along seams, and that wax-dipped seams were not effective when the bags were filled with hot (180-190° F.) ammonium nitrate.

The storage tests and shipments of TVA ammonium nitrate in both paper and burlap indicated that the mechanical strength of the two types of bag was approximately the same. To obtain further information, a series of dropping tests was made with

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[3] Ross and co-workers (7) discuss the relation of temperature to the relative humidity above which ammonium nitrate absorbs moisture from the atmosphere and present data for the range 0-44° C. (32-111° F.). At 26.7° C. (80° F.) ammonium nitrate absorbs moisture at relative humidities exceeding 61%.

several makes of paper and burlap bags. The bags were filled with hot ammonium nitrate, closed by sewing or tying, cooled to room temperature, and dropped eight times (or until prior failure) in turn on each of the four long faces, from a height of 3 feet onto a flat surface. In general, with sewed closure, both paper and burlap bags showed few failures. Bag failure was much more frequent with tied bags than with sewed bags. This result was to be expected because, in addition to elimination of the failures caused by slipping off of the wire ties or tearing of the bag, the sewed bags afforded a larger internal volume, and the stresses on the sewed bags were therefore less than those on the wire-tied bags.

As a result of the bag tests, multiwall moistureproof paper bags were adopted for shipment of the TVA product starting in the spring of 1944. Steps were also taken to provide facilities so that the wire ties could be eliminated and sewed or valve-packed bags could be used.

Since most of the bag storage tests were made with burlap bags, which were later shown to be inferior to multiwall moistureproof paper bags in providing moisture protection, it is desirable to compare the storage properties of variously treated material in these two types of bags before the main body of the storage test results are given. Table III shows the results of 6-, 9-, and 12-month storage tests in both paper and burlap bags. In judging the number of bags in the stack that were in satisfactory condition after the drop test, the following conditions were used as a standard: (*a*) less than 10 pounds of +2-mesh lumps, (*b*) less than 1 pound of hard lumps, and (*c*) free-flowing material. Lumps found only near the seams of the bags were discounted, since their occurrence was found to be related to the condition of the bag seams rather than to the conditioning treatment.

The tests in paper bags were not all made concurrently with those in burlap bags; therefore, the two tests were not directly comparable. Continuous records of atmospheric temperature and humidity at Wilson Dam showed that relative humidity rose above the hygroscopic point of ammonium nitrate on about one day out of four during the summer months, and one day out of three during the winter months; the records showed also that the average differential between vapor pressure of the air and of saturated ammonium nitrate solution was greater in summer than in winter. Although the storage season apparently had some effect on the results, attempts to correlate temperature and humidity with caking were unsuccessful. However, all differences in caking were clearly in favor of paper bags. For Wilson Dam climatic conditions, conditioned ammonium nitrate in burlap bags remained in good condition for about 6 months and caked badly in about 9 months, whereas it was in excellent condition in paper bags after 12 months.

Table III. Comparison of Paper and Burlap Bags in Long-Term[a] Storage Tests of Conditioned Ammonium Nitrate

Bag	Ammonium Nitrate Conditioners	Storage Period, Months	Moisture Content, %	Number of Bags in Satisfactory Condition
Paper	1% *PRP* (1-3-1) + 4% kieselguhr	6	0.3	12
Burlap	1% *PRP* (1-3-1) + 4% kieselguhr	6	0.4	12
Paper	1% *PRP* (1-3-1) + 4% kaolin	6	0.2	12
Burlap	1% *PRP* (1-3-1) + 4% kaolin	6	0.2	12
Burlap	1% *PRP* (1-3-1) + 4% kaolin	6	0.3	12
Paper	0.5% *PRP* (1-3-1) + 4% kaolin	6	0.2	12
Burlap	0.5% *PRP* (1-3-1) + 4% kaolin	6	0.4	8
Paper	1% *PRP* (1-3-1) + 4% plaster of Paris	6	0.3	12
Burlap	1% *PRP* (1-3-1) + 4% plaster of Paris	6	0.5	5
Paper	1% *PRP* (1-3-1) + 4% kieselguhr	12	0.5	12
Burlap	1% *PRP* (1-3-1) + 4% kieselguhr	9	1.1	7
Paper	1% *PRP* (1-3-1) + 4% kaolin	12	0.4	12
Burlap	1% *PRP* (1-3-1) + 4% kaolin	9	1.5	2
Burlap	1% *PRP* (1-3-1) + 4% kaolin	9	1.7	5

[a] The tests in paper bags and those in burlap bags were made in different periods.

The lesser amount of moisture absorbed and lost by the ammonium nitrate in paper bags during alternate humid and dry periods evidently was responsible for the lesser degree of caking. This point was also brought out in long term bag-storage tests at various locations made by the U. S. Department of Agriculture (*7*); the TVA materials (in burlap bags) included in those tests showed greater variations in moisture content from one inspection period to the next than did the materials of other producers which were packed in paper bags, and the caking seemed to parallel the moisture changes, especially in periods in which moisture was lost. The data in Table III suggest that the caking of TVA conditioned ammonium nitrate observed in the Department of Agriculture tests would have been absent if the ammonium nitrate had been packed in suitable paper bags.

RESULTS OF STORAGE TESTS

The results of 6- and 9-month storage tests, made on the materials that showed promise in the 4-week storage tests, are shown in Table IV. Burlap bags were used in these tests; therefore, although the relative results would probably remain the same, it should be kept in mind that in paper bags a longer storage period would have elapsed before an equivalent amount of caking occurred.

A number of the conditioning treatments in which dust was used gave good protection against caking. Treatments in which kieselguhr was used generally showed the least caking: Kaolin, plaster of Paris, and soapstone were not far apart in effectiveness, with possibly a small margin in favor of kaolin. As long as the moisture content of the ammonium nitrate remained low, the effectiveness of the dusts in preventing caking was the same whether the dusts were used alone, with petrolatum, or with *PRP*. However, after an appreciable amount of moisture absorption had occurred, caking increased rather rapidly for material conditioned with petrolatum and a dust, less rapidly where dust alone was used, and least where *PRP* plus dust was used. There was some indication that 0.5% *PRP* plus 4% dust gave better protection than 1% *PRP* plus 4% dust, but the results were too limited to be conclusive. The use of *PGP* in place of *PRP* resulted in slightly increased caking.

Treatments in which coatings were used without a dust proved unsatisfactory against caking. Caking became severe after about 3 months and progressively worse thereafter. In this case the long-term storage results were in poor agreement with the 4-week tests, which were favorable for some of the harder coatings containing gilsonite or B grade wood rosin. Visual observation indicated that the caking mechanism might be different in the case of coating treatments than in other cases, and that caking might be caused largely by cementing together of the coatings of adjacent grains rather than by recrystallization of dissolved ammonium nitrate. Many different combinations of the coating ingredients were tried, but none gave results better than those shown in Table IV.

Several other points may be noted from the data in Table IV. Unconditioned ammonium nitrate caked badly in all cases. While there was some erratic variation, caking in general grew proportionally more severe from top to bottom of the twelve-bag stacks with all materials. Most of the tests were continued for a total of 12 months, but the data are not reported because some of the stacks were given only a one-drop test as part of another program. In general, however, the increase in caking between 9 and 12 months was severe for material in burlap bags, while the relative evaluation of different treatments shown by the 6- and 9-month results was confirmed.

TABLE IV. RESULTS OF LONG-TERM STORAGE TESTS OF TVA EXPERIMENTAL FERTILIZER AMMONIUM NITRATE IN BURLAP BAGS

Conditioning Treatment	Weight of +2 Mesh Lumps after Four-Drop Test in Pounds[a], with Position of Bag from Top of Stack as Follows: 1	2	3	4	5	6	7	8	9	10	11	12	Moisture Content, %	Number of Bags in Satisfactory Condition
SIX-MONTH TESTS[b]														
1% *P-RP*[e] (20, 64-16) + 4% kieselguhr	....	0.5S[c]	....	0.5S[c]	....	0.5S[c]	....	0	....	0.5S[c]	....	0.5S[c]	0.4	12
1% *PRP* (1-3-1) + 4% kieselguhr	1H[c]	....	1H[c]	....	1H[c]	....	1S[c]	....	1S[c]	....	0.5S[c]	....	0.4	12
0.5% *PRP* (1-3-1) + 4% kieselguhr	2S[c]	....	2H[c]	....	1H[c]	....	2H[c]	....	3H[c]	....	3H[c]	....	0.4	12
1% *PRP* (1-3-1) + 4% kaolin	....	2S	....	1S	....	3S	....	7S	....	4S	....	6S	0.3	12
5% kieselguhr	3H[c]	....	3H[c]	....	3H[c]	....	3H[c]	....	3H[c]	....	3H[c]	....	0.5	12
5% kaolin	....	4H[c]	....	2S[c]	....	5H[c]	....	3H[c]	....	4H[c]	....	4H[c]	0.7	12
1% petrolatum + 4% kieselguhr	4H[c]	....	4H[c]	....	3H[c]	....	2H[c]	....	2H[c]	....	2S[c]	....	0.5	12
1% *PRP* (1-3-1) + 4% kaolin	1H	....	2S	....	4S	....	6S	....	3S + 2H	....	0.5S	....	0.4	8
0.5% *PRP* (1-3-1) + 4% kaolin	0.5S	....	0.5S	....	2S	....	4S + 1H	....	2S + 7H	....	2S + 11H	....	0.6	7
1% *PRP* (1-3-1) + 4% soapstone	0.5S	0.5S	2S	2S	4S	13S	9S	17FH	18FH	....	18FH	25H	...	5
1% *PRP* (1-3-1) + 4% by-product plaster of Paris	....	0	....	2S	....	7S + 3H	....	8S + 8H	....	7S + 10H	....	10S + 4H	0.5	5
1% *PGP* (1-3-1) + 4% kaolin	....	....	7FH	....	....	13FH	....	....	....	13FH	....	....	...	5
0.2% petrolatum + 0.8% *RP* (9-1)	....	....	8FH	....	40H	37VH	40VH	....	....	....	....	85HT	1.2	3
1% petrolatum + 4% kaolin	....	3S + 5H	....	3S + 5H	....	9S + 2H	....	10S + 15H	....	20S + 12H	....	20S + 12H	0.6	1
0.2% petrolatum + 1% *RPG* (2-1-2)	....	15FH	12FH	27FH	18FH	40VH	32VH	....	50VH	....	80HT	....	0.8	1
None	....	34H	....	50H	....	35H	....	95H	....	95H	....	100H	0.9	0
NINE-MONTH TESTS[d]														
0.5% *PRP* (1-3-1) + 4% kaolin	0	....	1S	....	1S	....	4S	....	2S	....	6S	....	1.0	12
1% *P-RP*[e] (20, 64-16) + 4% kieselguhr	0.5S	....	0.5S	....	0.5S	....	2S	....	10S	....	9S	....	1.8	12
0.5% *PRP* (1-3-1) + 4% kieselguhr	2FH	....	2FH	....	4FH	....	2S	....	3S	....	3FH	....	1.3	12
1% *PRP* (1-3-1) + 4% kieselguhr	1S	....	1S	....	2S	....	4S	....	30FH	....	30FH	....	1.1	8
1% petrolatum + 4% kieselguhr	....	3S	....	4FH	....	3FH	....	4FH	....	3S + 9FH	....	20FH + 30H	1.5	8
5% kieselguhr	....	5FH	....	10FH	....	8FH	....	25FH	....	15FH	....	45FH	1.2	6
1% *PRP* (1-3-1) + 4% kaolin	0	0	1S	5S	5S	26S	11S	34FH	44FH	38FH	50H	30H	1.7	5
1% *PRP* (1-3-1) + 4% by-product plaster of Paris	....	1S	....	4S + 2FH	....	6S + 10FH	....	5S + 12FH	....	5S + 15FH	4S + 18FH + 10H	....	1.8	5
1% *PRP* (1-3-1) + 4% soapstone	1S	2S	2S	5S	5S	20S	22S	26FH	30FH	37FH	40H	46H	1.6	5
1% *PRP* (1-3-1) + 4% kaolin	....	....	6FH	....	17FH	....	60FH	....	95FH	....	90H	....	1.4	4
1% *PRP* (1-3-1) + 4% kaolin	1FH	....	10FH	....	50FH	....	66FH	....	66FH	....	70FH	....	1.5	3
1% *PRP* (1-3-1)	3S	5S	7S	35FH	49FH	37FH	59FH	55H	52H	75H	60H	60H	2.0	3
5% kaolin	....	12H	....	18H	....	40H	....	60H	....	90VH	....	90VH	0.5	1
1% petrolatum + 4% kaolin	3S + 7FH	....	20FH + 10H	....	30FH + 15H	....	15FH + 60H	....	90H	....	95VH	....	1.6	1
None	....	30H	....	50H	....	90H	....	95VH	....	95HT	....	95HT	2.0	0

[a] Numbers indicate the weight in pounds of +2 mesh lumps, and letters indicate physical condition of lumps (S, soft; FH, fairly hard; H, hard; VH, very hard; and HT, hardest) remaining after the four-drop test.
[b] Stored from November, 1943, to May, 1944.
[c] Lumps found near the seams of the bags. These were discounted in estimating the number of bags in satisfactory condition.
[d] Stored from November, 1943, to August, 1944.
[e] 1% *P-RP* (20, 64-16) signifies that a total of 1% coating material was applied in two steps, consisting of 0.2% petrolatum, followed by 0.8% of a mixture of rosin and paraffin in the proportions 64:16.

DRILLABILITY

Unconditioned ammonium nitrate in dry, uncaked condition can be distributed readily with ordinary farm equipment. However, when exposed to the atmosphere at humidities higher than about 60%, it absorbs moisture rapidly, becomes sticky, and is difficult to distribute; the presence of fine particles increases the difficulty. One function of the conditioning treatment is to maintain the fertilizer in a drillable condition for the period after it is removed from the bag until it is applied to the soil. The severity of the exposure encountered during this period will vary with climate, weather, and individual farm practice. Consequently it must be realized, even more than in the case of storage tests, that drillability tests provide a relative and not an absolute measure, and that several factors must be weighed in evaluating the results.

Drilling rates were measured in a screw-type fertilizer distributor (John Blue No. 30), a type used extensively for application of nitrogenous side dressing. The test procedure consisted of first measuring the rate of drilling of the dry product after breaking up any caked material, and then exposing the ammonium nitrate to a humid atmosphere and making drilling tests after 24 and 48 hours of exposure. In the exposure cycle 50 pounds of ammonium nitrate, contained in a layer 2.5 inches deep in an open wooden box 2 feet square, were placed in an air-conditioned room through which air at 80 (±4)° F. and 80 (±1)% relative humidity was passed (as previously described under testing of bags). The ammonium nitrate was mixed by shovel just prior to each drilling. Each drilling test included three consecutive 6-minute drilling periods during which the amount of product delivered was weighed. The drill speed was set to deliver dry ammonium nitrate at a rate of about 1.7 pounds per minute, which corresponded to an estimated application of 100 pounds per acre.

In initial tests with the distributor installed in the laboratory and motor-driven, bridging occurred in the hopper and caused irregular delivery. In comparable tests made in the field with the distributor horse-drawn, delivery was uniform; it was evident that the irregularities of the ground caused enough jarring to eliminate most of the bridging. Equivalent results were obtained in laboratory tests by jarring the hopper at 30-second intervals by the single rotation of a hand-operated attachment, and this operation was made part of the standard test procedure.

Table V. Summary of Drillability Results for Grained Ammonium Nitrate Conditioned by Various Treatments

Conditioning Treatment	No. of Tests Averaged	Drilling Rate, Amt. Delivered in 6 Min., Lb. (Av. for 3 Periods)		Av. Deviation from Av. Rate, %		Moisture Content, as Drilled, %		Relative Hygroscopicity, % (Lab. Detn.)	Relative Drillability, % (after 24-Hr. Exposure)
		Before exposure	After 24-hr. exposure	Before exposure	After 24-hr. exposure	Before exposure	After 24-hr. exposure		
Chilean sodium nitrate (Champion brand)[a]	4	13.9	10.0	3	3	0.57	1.88	...	72
Ammonium sulfate[a]	1	8.2	1.8	7	24	0.45	1.55	...	21
NH_4NO_3 (unscreened) conditioned with:									
1% *PRP*[b] + 2% kaolin	2	11.1	7.2	2	3	0.10	1.28	35	66
0.2% petrolatum, 0.8% B-rosin	4	11.0	6.9	5	5	0.16	1.10	35	65
0.2% petrolatum, 1% *RPG*[c]	4	10.7	6.9	4	8	0.07	1.35	15	64
1% *PRP* + 2% mica	3	10.7	6.6	6	8	0.05	1.50	20	62
1% *PRP* + 4% soapstone	4	12.2	7.4	11	8	0.16	1.12	20	61
1% *PRP*	4	8.4	5.0	2	18	0.06	0.84	5	60
1% *PRP* + 4% plaster of Paris	4	11.2	6.2	1	9	0.20	1.54	25	56
1% *PRP* + 4% kaolin	4	11.0	6.0	5	15	0.14	1.64	50	55
1% *PRP* + 4% kieselguhr	3	11.5	6.1	3	8	0.21	1.95	60	53
1% *PGP* + 4% kaolin	4	10.8	5.0	4	15	0.16	1.50	75	46
0.5% *PRP* + 4% plaster of Paris	3	11.5	5.1	4	20	0.20	1.67	35	45
1% *PGP* + 4% plaster of Paris	2	10.6	4.1	3	32	0.14	1.50	35	40
5% kaolin	2[d]	7.7	3.1	3	32	0.17	2.48	80	39
0.5% *PRP* + 4% kaolin	3	10.7	3.6	1	45	0.15	1.87	60	34
None	4	10.6	3.5	5	21	0.12	1.86	100	32
5% kieselguhr	2	7.9	1.2	2	50	0.26	2.22	90	15
1% *PRP* + 4% bentonite	1	11.8	2.6	2	28	0.27	2.72	60	22
1% *PRP* + 4% Diluex[e]	1	8.4	0.6	3	105	0.20	4.25	65	7
NH_4NO_3 (screened) conditioned with:									
1% *PRP* + 4% kaolin, +20 mesh grains	3	9.9	6.7	4	11	0.11	1.35	...	68
1% *PRP* + 4% kaolin, −20 mesh grains	1	12.7	3.0	2	22	0.31	2.85	...	23

[a] Screen analyses: Champion brand sodium nitrate: +12 mesh, 38%; −12 +35 mesh, 59%; −35 +100 mesh, 1%; −100 mesh, 2%. Ammonium sulfate: −12 +35 mesh, 3%; −35 +100 mesh, 85%; −100 mesh, 12%.

[b] *PRP* = 1 part petrolatum, 3 parts rosin, 1 part paraffin.

[c] *RPG* = 2 parts rosin, 1 part paraffin, 6 parts gilsonite.

[d] The two tests showed poor agreement, giving relative drillabilities of 21 and 56, respectively The second value seems out of line with other results.

[e] Diluex is the trade name for a mineral mined in Florida.

The simplest and probably most useful basis for comparing the results of different tests is the relative drillability; this is defined as the percentage ratio of the drilling rate, after a given period of exposure at controlled conditions of high humidity, to the rate obtained with the dry material as taken from the bag. A second criterion is the uniformity with which the ammonium nitrate is delivered by the drill after exposure; this was evaluated by comparing the rates for three successive 6-minute periods. The absolute delivery rate, in pounds per minute, is also of practical importance. However, the delivery rate of fertilizer distributors can generally be varied over a wide range by changes in the size of opening or drill speed, so that uniformity of delivery at a given setting is more important than absolute rate.

The results obtained in duplicate drillability tests with a material conditioned by a given treatment varied appreciably; three or four separate tests were therefore made for each treatment that showed promise, and different treatments were compared on the basis of average results (Table V). Table VI presents detailed results of individual tests for two materials to indicate the degree of variation encountered. It includes results of drilling tests after 48-hour as well as 24-hour exposure, as an illustration of the behavior obtained. Forty-eight-hour tests were made in most cases, but upon review it was concluded that this length of exposure was much more severe than would be expected in practice. It was so severe as to obscure relative behavior; consequently 48-hour results are not presented in Table V.

Table V summarizes the averaged results of drillability tests for materials conditioned by the various treatments. Data for Champion brand Chilean sodium nitrate and by-product ammonium sulfate are shown for comparison. The results for ammonium nitrate (unscreened) are arranged in order of decreasing values of relative drillability after 24-hour exposure; however, differences of less than five percentage units in the relative drillability value may not be significant; the order of listing should be interpreted accordingly. It is not feasible to state a value above which the drillability is satisfactory and below which it is unsatisfactory. However, it is believed that the drillability of all the materials listed with values above 50 was satisfactory and that the drillability of all those with values below about 30 was unsatisfactory.

The following general conclusions can be drawn from the data of Table V. Drillability was best on materials to which only a coating had been applied and was almost as good as that of Champion brand sodium nitrate for such materials, in spite of their much smaller particle size. Application of a dust in addition to the coating decreased the relative drillability somewhat;

Table VI. Detailed Results of Drillability Tests on Ammonium Nitrate and Chilean Sodium Nitrate

	Period of Exposure, Hr.[a]	Chilean Sodium Nitrate, Champion Brand					Grained NH_4NO_3, Conditioned with 1% *PRP* (1-3-1) + 4% Kaolin				
		No. 1	No. 2	No. 3	No. 4	Av.	No. 1	No. 2	No. 3	No. 4	Av.
Drilling rate, amt. delivered in 6 min., lb. (av. of 3 periods)	0	14.4	13.2	12.7	15.2	13.9	10.7	12.0	10.5	10.7	11.0
	24	11.2	9.3	8.9	10.8	10.0	6.0	6.7	6.8	4.5	6.0
	48	6.8	8.7	7.6	9.8	8.2	1.8	2.6	1.1	1.3	1.7
Av. deviation from av. rate, %	0	2.0	8.1	3.1	0.0	3.3	2.6	1.4	3.2	13.6	5.2
	24	2.3	2.6	3.1	4.7	3.2	5.5	4.2	38.3	10.9	14.7
	48	20.6	8.8	22.7	3.4	13.9	38.0	17.2	87.4	53.3	49.0
Relative drillability[b], %	0	100	100	100	100	100	100	100	100	100	100
	24	78	70	70	71	72	56	56	65	42	55
	48	47	67	60	64	60	16	22	10	12	15
Moisture content, as drilled, %	0	0.61	0.85	0.43	0.38	0.57	0.05	0.14	0.22	0.14	0.14
	24	2.05	2.60	1.68	1.20	1.88	1.44	1.62	1.79	1.70	1.64
	48	3.47	3.25	2.94	1.77	2.86	2.38	2.06	2.94	2.51	2.47

[a] Exposed at 79° to 81° F. and 79 to 81% relative humidity.

[b] Relative drillability is the ratio $100 \times \left(\frac{\text{rate after exposure}}{\text{rate before exposure}}\right)$

4% dust caused a greater decrease than did 2%. A decrease in the amount of coating used with a dust also caused a decrease in relative drillability. Materials conditioned with a dust alone showed rather poor drillability, not much different from that of unconditioned ammonium nitrate. On the other hand, Ross and co-workers (7) found that spray-granulated ammonium nitrate of large particle size had satisfactory drillability when conditioned with a dust only, which indicates the important effect of particle size on drillability.

Four treatments in which 1% *PRP* and 4% dust were used appeared quite satisfactory. Of these, the treatment using soapstone showed up somewhat better than the other three (with plaster of Paris, kaolin, and kieselguhr) which were very close together. On the other hand, when bentonite or Diluex was the dust, moisture absorption was rapid and drillability was very poor. Use of 1% of a *PGP* mixture (gilsonite substituted for rosin) resulted in somewhat poorer drillability than corresponding treatments using *PRP*.

The effect of the particle size of ammonium nitrate on drillability is shown by data for the last two tests in Table V. Ammonium nitrate was screened to give +20 and −20 mesh portions, and these were conditioned with 1% *PRP* and 4% kaolin. The +20 mesh material showed the best drillability of any of the ammonium nitrate materials tested; the −20 mesh material was not far from the poorest and gave lower relative drillability than unconditioned and unscreened ammonium nitrate. These results indicate the beneficial effect on drillability of large particle size and freedom from fines.

A special test was made which threw some light on the significance of the relative drillability value. When some of the +20 mesh material, exposed 48 hours and giving a relative drillability of 39%, was run through the drill again after the drill speed had been tripled, the actual drilling rate was nearly tripled. When the same test was made with the −20 mesh material, which had a relative drillability of 15% after 48 hours, the actual drilling rate increased only about 50%. These results suggest that relative drillability values above 40% show the exposed material to be still drillable at controlled rates, whereas values under 20% show the opposite.

In addition to actual and relative drilling rates, Table V contains data on the moisture content of the material, as drilled, and on the relative hygroscopicity. One of the chief points is the poor correlation between relative hygroscopicity and drillability. In the early stages of this work and in work by others, considerable emphasis was placed on relative hygroscopicity as an indication both of storage and of drillability properties to be expected. The final results of the present work showed that this measurement can often be misleading. Thus, material treated with 1% petrolatum plus 4% kaolin (data not shown in Table V) had a relative hygroscopicity of only 20%; it was thought for a time that this treatment would be effective because of its simplicity and because of promising results in preliminary storage tests. It was found, however, that the drillability of material conditioned by this treatment decreases sharply with absorption of moisture. The treatment was concluded to be unsatisfactory.

Tied in with this behavior is the fact that the amounts of moisture absorbed by the 50-pound samples do not agree well with the relative hygroscopicity values determined in the laboratory. While the causes for the difference were not investigated, it appeared that there were significant differences in the wettability of the differently conditioned materials, which depended chiefly on the coating material used but also on the nature of the dust. Apparently, in the case of less wettable materials the moisture remained largely on the surface and actually formed pools of clear liquid in some cases, whereas with more wettable materials the moisture penetrated readily into the interior of the 50-pound samples. This was particularly noteworthy in the case of the petrolatum-kaolin treatment, wherein the entire sample appeared to become wet and sticky after the absorption of a relatively small amount of moisture. This behavior also influenced storage test results, in which the petrolatum-kaolin treatment gave relatively poor protection against caking after prolonged storage. This reversed the short-time storage results. With certain treatments the relative hygroscopicity of the freshly conditioned material was lower than that of material which had been stored several days. Laboratory determinations of hygroscopicity on small samples are useful chiefly as an indication of (*a*) the effectiveness with which a treatment is applied to a given batch and (*b*) the uniformity of the batch.

Comparison of the relative drillability values and the moisture content of the materials at time of drilling, after 24 hours of exposure, shows reasonably good concordance. The results should be viewed with reservations since, in practice, fertilizer materials will be subjected to fluctuating rather than uniform humidity conditions, and the degree of exposure is unpredictable. Nevertheless, the behavior of the 50-pound samples may be taken as a fair indication of what to expect in practice.

CONCLUSIONS

On the basis of storage and drillability test results, supplemented by experience with commercial shipments, it was concluded that ammonium nitrate produced in graining kettles can be effectively conditioned with 1% of a petrolatum-rosin-paraffin mixture plus 4% of one of several dusts; with this treatment it should remain in satisfactory condition for direct application when stored in suitable moistureproof paper bags in stacks twelve bags high for a year, under the fairly unfavorable climatic conditions prevalent at Wilson Dam. The treatment adopted for plant use consisted of 1% *PRP* (1-3-1) plus 4% kaolin. This treatment was used also, under the technical supervision of TVA, in four Ordnance graining plants that produced ammonium nitrate fertilizer in 1943 and 1944. Several hundred thousand tons of grained ammonium nitrate conditioned by this treatment have been used successfully both in mixed fertilizer and for direct application during the past two years.

Water repellent coatings, without a dust, do not afford adequate protection against caking. The use of dusts alone for conditioning grained ammonium nitrate is not recommended; although caking in storage is effectively reduced, the drillability of the material under humid conditions is not good. It seems likely that a dusting treatment would be satisfactory for grained ammonium nitrate from which the −20 mesh material had been screened.

In the two-step treatment kaolin, plaster of Paris, and soapstone are about equally effective as dusts. Kieselguhr is definitely superior in preventing caking, but its superiority is not considered sufficient to compensate for its higher cost, which for eastern United States is caused partly by the long haul required from California. To avoid sludge formation during storage and handling, petrolatum-rosin-paraffin mixtures should contain at least 60% rosin; grade FF wood rosin or higher grades should be used. Elimination of one of the three components gives less satisfactory coating mixtures. Gilsonite could probably be substituted for rosin, with some increase in the difficulty of applying the coating mixture and some sacrifice in the effectiveness of the conditioning treatment. Reduction in the amount of coating applied decreases the caking tendency but has an unfavorable effect on drillability; an amount smaller than 1% might prove optimum. Some reduction in the amount of dust might also prove feasible, particularly if the ammonium nitrate particle size were increased or the fines were removed.

The moistureproof quality of bags is one of the chief factors in keeping ammonium nitrate fertilizer in good condition during prolonged storage in humid climates. Of a number of commercially available bags tested, multiwall paper bags with one or two moistureproof plies gave better protection than asphalted burlap bags. Sewed or valve-type closure was superior to wire-tied closure.

Storage tests of bagged material for 6 to 12 months under factory conditions are recommended for final evaluation of the storage properties of ammonium nitrate fertilizer. For material to be applied directly, relative drillability as determined in the present work is believed to be a useful guide. Laboratory determinations of rate of moisture absorption, in small samples of conditioned ammonium nitrate, are of limited significance in indicating the potential value of the conditioning treatment used.

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LITERATURE CITED

(1) Cairns, R. W., U. S. Patent 2,211,738 (1940).
(2) Chenevey, J. E., *Chem. & Met. Eng.*, 52, No. 8, 115 (1945).
(3) Fairlie, A. W., *Ibid.*, 20, No. 1, 8–17 (1919).
(4) Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquer and Colors", 7th ed., pp. 541–5, Washington, Inst. of Paint and Varnish Research, 1935.
(5) Keenen, F. G., Ind. Eng. Chem., 31, 903–8 (1939).
(6) Krase, H. J., Yee, J. Y., and Braham, J. M., *Chem. & Met. Eng.*, 32, No. 2, 241–3 (1925).
(7) Ross, W. H., Adams, J. R., Yee, J. Y., and Whittaker, C. W., Ind. Eng. Chem., 36, 1088–95 (1944).
(8) Ross, W. H., and Yee, J. Y., *Am. Fertilizer*, 102, No. 7 (April 7, 1945).
(9) Titlestad, N. N., *Ibid.*, 101, No. 10, 9 (1944).
(10) War Production Board, Chemicals Div., private communication, April 26, 1943.

Uncatalyzed Reaction of Natural Gas and Steam

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The uncatalyzed reaction of natural gas with steam has been studied between 1225° and 1516° C. with steam-natural gas ratios of 1.5 and 5, and time of contact between 0.21 and 4.6 seconds. Even at high temperatures, long contact times, and steam-natural gas ratio of 5 there is some carbonization of the natural gas. The extent of carbonization is shown to be a function of the ratio of steam to natural gas, and to vary erratically with temperature and time of contact. As the temperature is increased, the percentages of natural gas undecomposed in one pass through the furnace become less dependent on contact time (in the range of contact times studied), until at about 1500° C. there is little or no effect. At any temperature the percentage of undecomposed gas shows little if any dependence on the ratio of steam to natural gas.

THE catalyzed reaction between steam and natural gas has been studied by a number of investigators (*1*, *2*), and industrial processes are being used to produce a mixture of hydrogen and carbon monoxide by this reaction at 750° to 900° C. Nickel seems to be the best catalyst; it is usually supported on some refractory with a promoter such as magnesium oxide, aluminum oxide, or chromium oxide.

Cheap and efficient heat transfer in gas systems, obtainable by the use of pebble furnaces, furnishes an attractive industrial possibility for carrying out the uncatalyzed natural gas-steam reaction. Temperatures up to 1500° C. may be used with Alundum pebbles. The uncatalyzed reaction has been studied by Karzhavin (*3*) who states: "The rate of reaction of methane with steam is very low and only at temperatures above 1300° C. does it become sufficiently high for industrial use." No data are supplied to support this statement. To obtain data which can be used for design of pilot plant installations, a laboratory investigation of this reaction at high temperatures was undertaken, and the reaction conditions were limited to those significant for industrial conditions.

Figure 1 is a schematic drawing of the apparatus. Natural gas is admitted to the system through flowmeter *A*, and then goes into water saturator *B*, which consists of a glass distilling flask with a heating coil resting inside and at the bottom of the bulb. The current to the coil is controlled by a variable voltage transformer (Variac). The gas is admitted to the base of the asbestos lagged column, which is packed with a tightly rolled coil of stainless steel screening to increase the contact surface of water with gas. From temperatures read on a thermometer placed with the bulb at the height of the exit tube, the water vapor pressure of the reactant gases is determined. The total pressure is one atmosphere. The difference between atmospheric pressure and the vapor pressure of the water gives the pressure of the natural gas. In operation the exit temperature is controlled by the current supplied to the heating coil. The saturator is similar to the one used by Hawk, Golden, Storch, and Fieldner (*1*).

The degree of saturation of the gas by water vapor was determined by trapping a known volume of the natural gas-steam mixture in a boiling-water thermostat, displacing the water vapor into a drying tube, and determining its weight. This method showed that the gas was saturated with water vapor within experimental error, even at the highest flow rates of natural gas used in this research. Some of the data are included in Table I. The flow rates of the gases were measured with a capillary flowmeter.

TABLE I. TEST FOR SATURATION OF NATURAL GAS BY WATER VAPOR

Temp. at Exit Tube, ° C.	Total Pressure, Mm.	Flow Rate of Natural Gas, Cc./Sec.	Ratio, Steam/Natural Gas	
			Theoretical	Observed
85.6	740	1.14	1.50	1.47
85.8	745	1.30	1.50	1.20
85.8	745	1.30	1.50	1.25
94.2	739	1.23	5.00	4.31
94.2	739	1.18	5.00	5.37

From the saturator the gases are led into the reaction vessel through tubing heated by resistance wire. In the earliest experiments this vessel was quartz, with quartz-Pyrex graded seals in the cold portion at each end. Quartz was not used because it devitrifies rapidly at temperatures over 1000° C. and is permeable to hydrogen; consequently a porcelain vessel was substi-

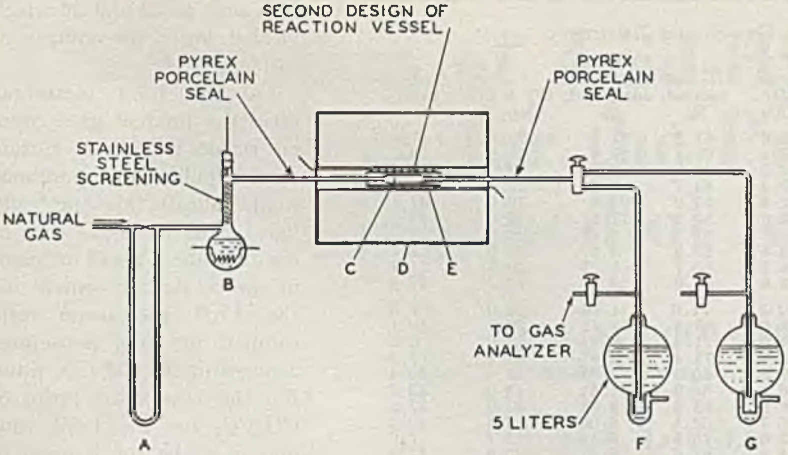

Figure 1. Diagram of Reaction Apparatus

tuted. The first porcelain vessel was a 30-inch McDanel combustion tube of $^3/_4$-inch inner diameter and 1-inch outer diameter, with two Alundum-filled porcelain tubes slipped inside, which left an annular space of about $^1/_{32}$ inch. The reaction vessel was formed by spacing these porcelain tubes. For a reaction vessel 2 inches long the ratio of linear velocities in the annular and reaction spaces was about 40. In the latest design, *C*, a $^7/_{64}$-inch-bore porcelain tube was sealed to each end of a $2^1/_4$-inch porcelain tube of $^3/_4$-inch inner diameter and 1-inch outer diameter. In this arrangement the ratio of linear velocities was about 50. Pyrex was sealed directly to porcelain in either type of vessel to make a butt rather than a lap seal, according to the method outlined by Strong (*4*).

Furnace *D* is a heavily insulated Alundum cylinder, in which is placed another Alundum tube wound with platinum-rhodium wire *E*. A platinum, platinum-rhodium thermocouple rests on the outside of the reaction vessel. The temperature gradient from the center of the reaction vessel to either end is less than 10° C.

The reacted gases were collected in one of two gas sampling bottles, *F* and *G*, filled with a saturated solution of sodium chloride in water. These bottles were constructed in such a way that the gas was delivered at atmospheric pressure. One of the bottles was employed while the correct temperature of the water vapor was established, and served to seal the system from air. After a steady state was reached, the gas was led to the second sampling bottle by turning a three-way stopcock. It took 5 to 30 minutes to reach a steady state. The time necessary to displace 100 cc. of the liquid was measured. The gases were analyzed in a Fisher-Orsat gas analyzer for carbon dioxide, carbon monoxide, hydrogen, oxygen, unsaturates, and unreacted natural gas. All the gases were analyzed in duplicate, and the average values are reported. Hydrogen and carbon monoxide analyses almost always checked within 0.5%, whereas methane and carbon dioxide checked within 0.2% on an absolute basis.

CALCULATIONS

The experiments were run in pairs, with no cleansing of carbon deposits unless a carbon block developed in the first run of a pair. Between pairs of runs the carbon deposits were removed by steam. The results of analyses of the exit gases together with the contact time, percentage hydrogen calculated, percentage carbonization, and percentage carbon monoxide plus carbon dioxide (corrected) are included in Table II. Contact times were calculated from the volume of the reaction vessel divided by the volume of reactant gases (at the temperature of the reaction cell) passing through the cell per second.

The percentage hydrogen calculated was obtained from a mass spectrometer analysis of the entrant gas and the carbon monoxide and carbon dioxide content of the exit gas. From the equation of the reaction with steam, the percentage hydrogen may be readily calculated if no carbon is formed. It was assumed that all the hydrocarbon gases reacted in the same ratio as their percentage composition in the original gas. This introduces a small error in the results. The percentage carbonization was calculated from the difference between the calculated percentage and the observed percentage of hydrogen. This figure is divided by the number of moles of hydrogen generated from each mole of gas which carbonizes, and is then corrected to the original volume. A sample calculation for run 24 follows: CO_2 = 6.5%, CO = 14.9%. Assuming that all the component gases react with steam in the same proportion as in the natural gas and give only carbon monoxide and hydrogen:

$$\begin{aligned}
CH_4 &+ H_2O \longrightarrow CO + 3H_2\\
C_2H_6 &+ 2H_2O \longrightarrow 2CO + 5H_2\\
C_3H_8 &+ 3H_2O \longrightarrow 3CO + 7H_2\\
C_3H_6 &+ 3H_2O \longrightarrow 3CO + 6H_2\\
C_4H_{10} &+ 4H_2O \longrightarrow 4CO + 9H_2
\end{aligned}$$

One hundred volumes of original gas will give:

CO	H_2
87.7	263.1
15.4	38.5
8.4	19.6
1.2	2.4
1.6	3.6
114.3	327.2 volumes

because the natural gas composition is: 87.7% CH_4, 7.7% C_2H_6, 2.8% C_3H_8, 0.4% C_3H_6, 0.4% C_4H_{10}, and 1.0% N_2, or (327.2/114.3) = 2.863 volumes of H_2 for each volume of CO. For experiment 24, 2.863 × (6.5% CO_2 + 14.9 CO) = 61.3% H_2. However, as each volume of CO reacts with steam to give one volume of CO_2 and one of H_2, the calculated hydrogen percentage is 61.3 + 6.5 or 67.8, and the observed is 71.7, leaving 3.9% resulting from carbonization.

A similar calculation shows that each volume of natural gas gives 2.13 volumes of hydrogen when it carbonizes and, on a nitrogen-free basis, 2.15 volumes of hydrogen. This value, divided into the hydrogen percentage resulting from carbonization and multiplied by the ratio of the flow (measured at room temperature) of gas out of and into the reaction vessel, gives the percentage carbonization of the natural gas on an original volume basis. As for experiment 24, inflow is 0.145 and outflow is 0.572 cc. per second; therefore, carbonization is (3.9/2.15) × (0.572/0.145) or 7.16.

In Table II the column CO + CO_2 (corrected) is the percentage calculated to correct for undecomposed gas—that is, the percentage of carbon oxides in the gas on a hydrocarbon-free basis.

DISCUSSION OF RESULTS

To simulate industrial processes the experimental conditions were selected so that 80 to 99% of the natural gas was reacted per pass. In consecutive experiments under the same conditions, the first run had a smaller percentage carbonization than the second. The carbon deposited in the first test normally was not removed in the second. Between pairs of runs the carbon was removed by reaction with steam. Taylor and Neville (*5*) report that alkalies such as sodium or potassium carbonate are efficient catalysts for the carbon-steam reaction. There are alkali materials in the clay which could catalyze this reaction in the reaction cell as well as in the adjacent exit tubes where surface/volume ratio is greater. When a layer of carbon was deposited over the tube, the catalytic activity of the tube was decreased. Lower

Table II. Uncatalyzed Natural Gas-Steam Reaction

Run No.	Ratio, Steam Gas	Temp., ° C.	Contact Time, Sec.	CO_2, %	H_2, %	CO, %	Ratio, H_2/CO	Ratio, CO/CO_2	H_2 Calculated, %	Natural Gas Undecomposed, %	CO + CO_2 Cor., %	Carbonization, %
24	5	1225	3.4	6.5	71.7	14.9	4.8	2.3	67.8	21.1	23.0	7.2
25	5	1225	3.4	4.6	72.1	15.5	4.7	3.4	62.1	22.9	21.8	18.2
26	5	1298	3.5	6.7	72.3	14.8	4.9	2.2	68.3	8.7	22.9	7.1
27	5	1298	3.5	4.9	75.7	16.0	4.7	3.2	64.7	9.5	21.6	20.6
28	5	1312	0.29	4.6	75.1	13.0	5.8	2.8	55.0	23.6	19.0	31.1
29	5	1312	0.34	3.8	74.9	13.7	5.5	3.6	53.9	17.5	18.9	33.5
30	5	1417	3.3	5.9	73.5	16.2	4.6	2.7	69.2	2.47	22.9	8.7
31	5	1422	3.2	4.5	76.9	16.9	4.5	3.8	65.8	2.89	22.3	22.2
32	5	1400	0.34	3.4	77.2	16.6	4.7	4.9	60.7	6.13	20.6	21.7
33	5	1400	0.32	4.6	74.1	16.5	4.5	3.6	65.0	10.7	22.2	17.4
34	5	1509	3.1	6.9	74.7	15.5	4.8	2.3	71.0	1.66	23.0	7.5
35	5	1509	3.1	5.1	77.6	15.3	5.1	3.0	63.5	2.71	20.7	30.1
36	5	1506	0.21	4.2	74.9	19.4	3.9	4.6	71.8	3.24	23.9	6.6
37	5	1511	0.30	4.7	75.5	18.6	4.1	4.0	71.4	2.67	23.5	9.5
38	1.5	1509	3.6	2.4	78.2	17.9	4.4	7.6	60.5	1.38	20.6	30.8
39	1.5	1516	0.77	1.6	80.1	17.0	4.7	10.6	54.9	1.51	18.9	42.2
40	1.5	1413	3.8	2.5	78.6	17.1	4.6	6.8	58.6	2.84	20.0	37.2
41	1.5	1413	0.89	2.3	79.3	15.6	5.1	6.7	53.5	6.06	18.4	40.3
42	5	1402	0.36	5.0	74.4	18.0	4.1	3.6	70.8	8.18	23.7	7.6
43	5	1402	0.36	4.0	75.3	18.0	4.2	4.6	67.0	8.11	22.6	17.4
44[a]	5	1402	0.34	6.1	72.8	14.6	5.0	2.4	65.4	9.84	22.2	13.7
45[a]	5	1382	0.37	4.5	75.6	15.1	4.4	3.4	60.6	10.5	20.5	29.2
46[a]	1.5	1318	4.6	3.6	77.4	13.4	5.8	3.7	52.3	9.0	18.0	36.5
47[a]	1.5	1298	1.0	2.4	79.5	11.7	6.8	5.0	42.7	15.5	15.1	52.5
48[a]	1.5	1505	0.80	2.3	79.7	16.5	4.8	7.3	56.1	1.70	19.1	38.8
49[a]	1.5	1510	3.1	2.9	78.4	17.1	4.6	5.9	60.2	1.03	20.3	31.1
50[a]	1.5	1407	0.96	2.9	79.3	15.1	5.3	5.6	54.4	4.97	18.5	30.0
51[a]	1.5	1407	3.9	2.8	77.2	17.3	4.5	6.2	60.3	3.27	20.6	27.9
52[a]	1.5	1295	0.88	2.7	78.8	11.5	6.8	4.2	43.4	19.5	14.2	49.1
53[a]	1.5	1302	4.3	2.9	77.9	14.1	5.5	5.0	51.6	10.3	17.8	36.7

[a] Porcelain reaction vessel with small bore tube attached to each end of large bore.

carbonization percentages, under the same experimental conditions, were associated with a larger percentage of carbon dioxide plus carbon monoxide (corrected). Also that run of a pair which resulted in lower percentage carbonization had a higher percentage of carbon dioxide. Catalysis of the carbon monoxide-steam reaction in the cooler portion of the exit tubes, where carbon dioxide/monoxide ratio is higher at equilibrium, would result in greater carbon dioxide formation until the surfaces were deactivated by carbon deposits.

Experiments in which only contact time was varied produced smaller percentages of carbon dioxide at shorter contact times. This would be expected as equilibrium (corresponding to the lower temperatures in the exit tubes) for the water-gas shift reaction $CO + H_2O \rightarrow CO_2 + H_2$ would be approached at the longer contact times. In this equilibrium, higher carbon dioxide concentrations exist at lower temperatures.

For 5/1 and 1.5/1 steam/natural gas ratios, the ratio of carbon monoxide/dioxide, if no methane is present at equilibrium, has the following calculated values:

Temp., ° C.	Ratio, Steam/Gas	P_{CO}/P_{CO_2}
1227	5/1	2.41
1327	5/1	2.70
1527	5/1	3.23
1227	1.5/1	19
1327	1.5/1	20
1527	1.5/1	24

The ratio carbon monoxide/dioxide increases slowly with increasing temperature and rapidly with decreasing concentration of steam. The effect of excess hydrogen (due to reaction to carbon) in the equilibrium mixture has only a small effect on the ratio. For example, 10% excess hydrogen at 1527° C. increases the 5/1 steam/gas value of carbon monoxide/dioxide from 3.23 to 3.63. These calculated values, which assume pure methane as the fuel, are in error for the natural gas of the composition given previously. The calculated equilibria for these higher hydrocarbons show higher carbon monoxide concentrations than those calculated for methane.

The figures for CO/CO_2 in Table II show that the products obtained with 5/1 ratios were close to equilibrium, especially for runs such as 32 and 36 which yielded lower percentages of carbon dioxide.

For the 1.5/1 steam/gas ratio the product gases were all richer in carbon dioxide than equilibrium conditions would indicate; this is probably due to the water-gas shift in the exit tube. Small increases in carbon dioxide content for the 1.5/1 gas steam ratio resulted in large percentage changes in the CO/CO_2 ratio. For this reason the ratios of CO/CO_2 for the 1.5/1 runs appear to be much more in favor of carbon dioxide than for the 5/1 runs.

The percentage carbonization column in Table II shows little correlation with temperature or with time of contact. On the other hand, the second run of a pair almost invariably had a higher percentage of carbonization than the first, even though the values for the total decompositions of the natural gas had no such trend.

The explanation may be that an indeterminate amount of carbon is deposited on part of the surface which stops the catalytic activity of that portion of the surface. The carbonization of the first run of a pair is determined by the uncontrolled variable of time the apparatus runs before the exit gas is sampled. In any event, the second run of a pair would have a larger film of carbon deposited on the surface unless carbon stoppage of the gas passageway necessitated steaming the apparatus between runs.

The percentage of undecomposed gas, on an original volume basis, varied markedly with time of contact and temperature, but not with steam concentration. With increasing temperature, contact time had less effect on the percentage of gas decomposed, because over 95% of the gas was decomposed even at the shorter contact time. Thus at about 1500° C. the eight runs varied between 1 and 3.24% original gas undecomposed, with the shorter contact time run usually indicating a fraction of 1% less decomposition.

The results of this work show that design of pilot plants for the steam-natural gas reaction must allow for an indeterminate but appreciable amount of carbon deposition. Even at the highest temperature of these tests, 1500° C., some carbon deposition occurred.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Hawk, Golden, Storch, and Fieldner, Ind. Eng. Chem., 24, 23-7 (1932).
(2) Karzhavin, *Ibid.*, 28, 1042-4(1936).
(3) Karzhavin, *Chem. Eng. Congr. World Power Conf.*, *1936*, Paper PC 17.
(4) Strong, "Procedures in Experimental Physics", p. 28, New York, Prentiss-Hall, Inc., 1939.
(5) Taylor and Neville, *J. Am. Chem. Soc.*, 43, 2055 (1921).

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Clarification of Acid-Hydrolyzed Mash and Beer for the Production of 2,3-Butanediol from Corn

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The filtration and centrifugation characteristics of unfermented and fermented acid-hydrolyzed corn mashes used in the pilot plant production of 2,3-butanediol were determined with small scale laboratory apparatus. It was found that the clarification of these materials is greatly influenced by their hydrogen ion concentration and temperature. Optimum pH varies, depending on the type of mash. Thus, highest filtration rates were obtained at pH 5.0 with laboratory cooked unfermented mash (batch process); pH 5.0 and 6.2 with pilot plant cooked unfermented mash (continuous process); and pH 4.8 with pilot plant fermented beer. At constant pH, highest filtration rates were obtained at the highest temperature (210° F.). The clarification of these corn mashes by either filtration or centrifugation was further improved by the use of small amounts of bentonite (swelling type) added to the mash at pH 2.0 to 3.0 and high temperatures. It was discovered that unfermented acid-hydrolyzed corn mashes can be clarified readily by centrifugation when such mashes are treated with 1 to 2% (by volume) of various halogenated hydrocarbons at pH 6.0 to 7.0 and at any temperature below the steam distillation points of the latter.

AT PRESENT one of the principal components in the production of synthetic rubber is butadiene. The two main processes for the manufacture of this gas utilize, as a starting material, ethyl alcohol on the one hand and butane or butylene on the other. The latter two are petroleum refinery products which have also attained importance as starting materials for high octane gasoline. A third process, in the pilot plant stage, is intended to by-pass the alcohol production step and obtain butadiene by direct fermentation of grains or other fermentable materials to a butadiene intermediate, 2,3-butanediol. Once this intermediate has been separated from the fermented mash, it can be easily processed to butadiene.

A method which has been seriously considered for the separation of 2,3-butanediol from fermented grain mash (called glycol beer) utilizes liquid-liquid extraction with *n*-butanol as solvent. This process requires a well clarified beer before extraction can be effected. Very small amounts of undissolved solids in the beer feed cause excessive foaming in the extraction column and consequent loss of appreciable amounts of both solvent and solute. This paper is concerned with the elimination of these troublesome suspended solids in acid-hydrolyzed corn mashes.

Since the cooking and use of acid-hydrolyzed corn mash are still in the development stage, there is no reference to the clarification of this particular product in the literature. On the other hand, the clarification of its related products, distillery residues, has received much attention, especially since the repeal of prohibition. Unfortunately, most of the processes suggested are too costly when applied on an industrial scale and consequently find little, if any, application in the modern fermentation plants. Cooley (*1*) and Willkie and Prochaska (*5*) described separation methods in their discussions of modern by-product recovery systems; the usual method of separating suspended solids in distillery residues utilizes screens, presses, centrifuges, and filters, with little or no preliminary physical or chemical treatment of suspensions. Fulton (*2*) points out, however, that in certain cases bentonite treatment provides a simple and efficacious solution of the spent-mash clarification problem and, therefore, should not be overlooked. Consequently, the present investigation was concerned chiefly with laboratory filtration and centrifugation of various corn mashes.

PREPARATION OF CORN MASHES

The unfermented batch-cooked acid-hydrolyzed mash was prepared from a mixture of 2800 grams of ground corn (approximately 50% retained on No. 30 screen) in 7 liters of 0.33 *N* sulfuric acid solution. This was heated in a Pyrex carboy by direct steam injection to 307° F., held for 4 minutes, heated to 324° F., held another 4 minutes, and blown through a copper cooling coil into a sterilized glass container. The mash was diluted to 15.84 liters (38 gallons/bushel), which resulted in a sugar content totaling approximately 11.0% and suspended solids totaling 2.0 to 2.5%.

The unfermented continuous-cooked mash was prepared on a pilot plant scale by the continuous cooking process described by Unger and Grubb (*4*). The rates of flow of corn, water, and steam were adjusted to give a 40 to 44 gallon per bushel mash; the result was approximately 10.0% sugar content and 2.0% suspended solids.

The fermented continuous-cooked mash was prepared from the unfermented continuous-cooked mash described, by fermentation with *Aerobacter aerogenes* (Seagram 776). The resulting beer had a butylene glycol content of approximately 3.8% and total suspended solids of approximately 3.0%.

APPARATUS AND PROCEDURE

The apparatus used in filtration experiments consisted of a 4-inch Büchner funnel connected to a 250-ml. graduated cylinder maintained at 15.0 inches of mercury (vacuum) by means of an automatic regulator. In centrifugation experiments the apparatus consisted of a Clay-Adams Senior variable-speed 15.0-ml. test tube centrifuge (centrifugal force = 820 × gravity at 2000 revolutions per minute maximum speed) and a De Laval high speed centrifuge (centrifugal force = 30,000 × gravity at 18,000 r.p.m. maximum speed) employing 15.0-ml. conical centrifuge tubes graduated to the nearest 0.002 cc. at their elongated tips. Treatment of mash samples and temperature control were effected in a one-liter three-neck flask equipped with agitator, electric heating jacket, thermostat, and reflux condenser.

Mash samples were treated with concentrated sodium hydroxide or sulfuric acid solution, and pH measurements were made at 70 ± 2° F. From 300 to 500 ml. of this mash were

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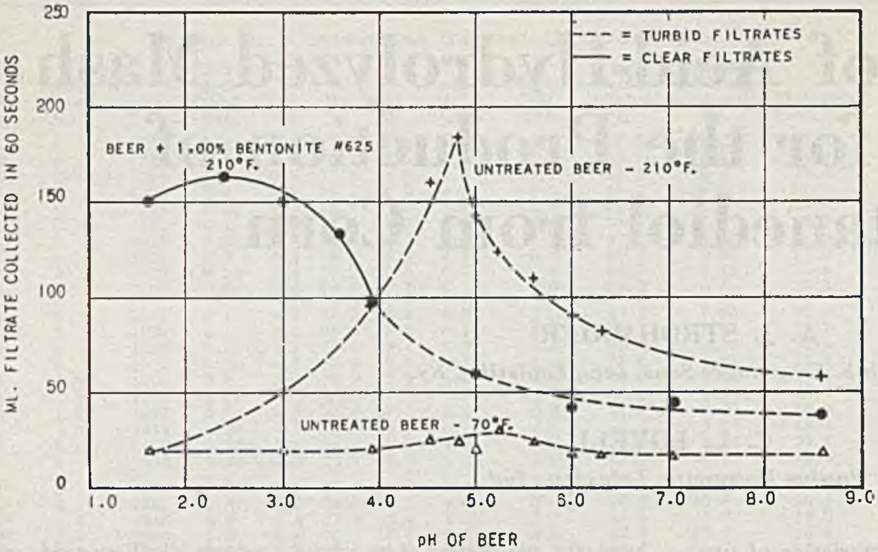

Figure 1. Effect of pH and Temperature on Filtration of Untreated and Bentonite-Treated Pilot Plant Beer

poured into the three-neck flask; the required amounts of powdered (Volclay bentonite) or liquid treating chemicals were added slowly with vigorous agitation.

In the filtration experiments the apparatus was brought to 15.0 inches (Hg) of vacuum. A new disk of dampened filter paper (Whatman No. 40, 9.0 cm. in diameter) was inserted in the Büchner funnel. Mash samples were poured over the filter paper, and the amount of filtrate was collected in 10-second intervals as noted by stopwatch.

In the centrifugation experiments 10-ml. mash samples were withdrawn from the three-neck flask and centrifuged at 2000 r.p.m. for periods of 10 to 80 seconds with a fresh sample for each centrifugation. The superjacent liquid was transferred to centrifuge tubes of the high speed machine and rotated at 18,000 r.p.m. for 2 minutes. Practically all suspended solids remaining from the first centrifugation were thus separated and measured.

RESULTS OF FILTRATION EXPERIMENTS

Unfermented Batch-Cooked Acid-Hydrolyzed Corn Mash. The most pronounced effects noted in filtration studies on acid hydrolyzed corn material were those of temperature and hydrogen ion concentration on filtration rates. Greatest rates of flow were obtained at 210° F. and pH 5.0. Also, the filtrates obtained in the pH range 3.1 to 7.0 were quite clear but attained increasing cloudiness as the pH diverged from these limits.

A peculiarity which may relate to the filtration characteristics of this mash was its variation in color with changes in pH. Klett-Summerson colorimeter readings indicated no color change until a pH of 5.0, the optimum filtration point, was reached. Beyond this point the color became progressively darker.

Unfermented Continuous-Cooked Acid-Hydrolyzed Corn Mash. Mash cooked by the continuous process also exhibited an optimum filtration point at a pH of 5.0. However, in contrast to that produced batchwise, an even better optimum point was obtained at pH 6.2. Greatest changes in color density occurred at pH 6.2 to 6.3.

In an effort to obtain greater clarity and higher rates of flow, the mashes were subjected to bentonite treatment as outlined in the work of Steiger (*3*) and Fulton (*2*). Excellent improvement in clarity and rates of flow resulted in the pH range 2.5 to 3.5. Above pH 4.0, however, clarification by this method became rather difficult.

Fermented Continuous-Cooked Acid-Hydrolyzed (Glycol) Beer. The changes in composition, etc., of acid-hydrolyzed corn mash during fermentation became apparent when an attempt was made to clarify the resulting product. Thus, although a definite optimum point was again indicated at pH 4.8 and 210° F., it proved impossible to obtain any but extremely turbid filtrates without resorting to chemical treatment. When bentonite was used, this fermented material became quite easy to clarify. The filtrates thus obtained proved to be crystal-clear and light amber in color. Highest rates of filtration were obtained between pH 1.6 to 3.2 but decreased sharply beyond this range (Figure 1).

DISCUSSION OF FILTRATION RESULTS

In explanation of the previous observations it should be pointed out that cereal grains contain considerable amounts of various proteins and, because of their amphoteric nature, exhibit some unusual electrochemical phenomena. Thus, in general, proteins are least soluble and most easily precipitable by heat at or near their isoelectric points. It is conceivable, therefore, that the maximum filtration rates secured near pH values of 5.0 and 6.2 may be due to the precipitation of certain troublesome proteins at their isoelectric points. On this basis it also seems reasonable to assume that the alkalies added to mash and beer for pH adjustment begin to form certain colored alkali-protein combinations at these isoelectric points; this would explain the sudden increases in color density at maximum filtration points. This is also borne out by the fact that ammonium sulfate or trichloroacetic acid (precipitants for proteins) will precipitate these dark colored compounds and leave light colored filtrates such as

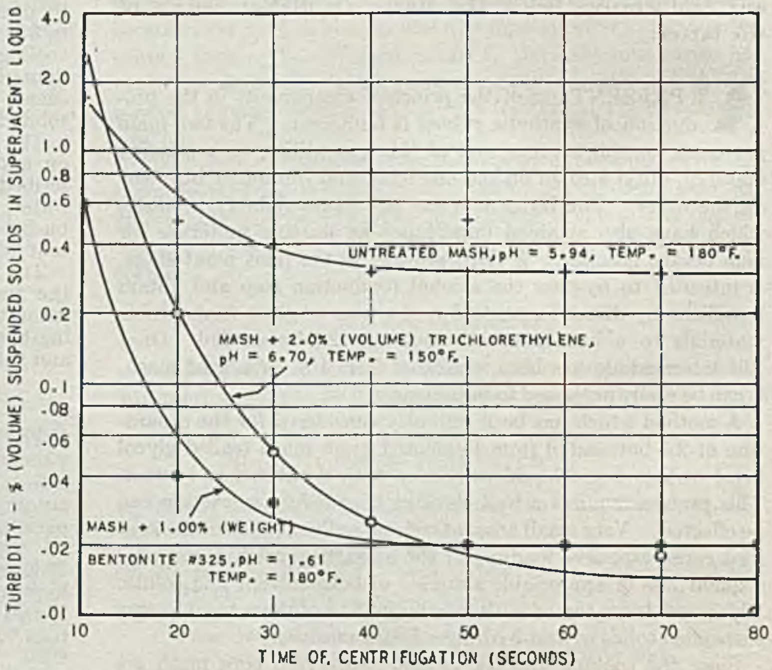

Figure 2. Time of Centrifugation vs. Turbidity of Treated and Untreated Pilot Plant Mash

Near optimum conditions of pH, temperature, and concentration those usually found in the pH range below optimum filtration points.

The high rates of filtration obtainable by the use of bentonite in mash or beer at low pH and the relative inefficiency of the same addition agent at any pH above 4.0 may well be attributed to the electronegative nature of the colloidally dispersed bentonite particles; the latter readily neutralize and agglomerate the electropositively charged proteins (at low pH) in the mash.

No effort was made to determine the identity of the proteins responsible for these phenomena except for an attempt at correlating the observed optimum filtration points with published data on isoelectric points. Unfortunately, published data on isoelectric points vary widely. Although zein and glutelin are strongly suspected to be the responsible proteins, it was impossible to arrive at any definite conclusions.

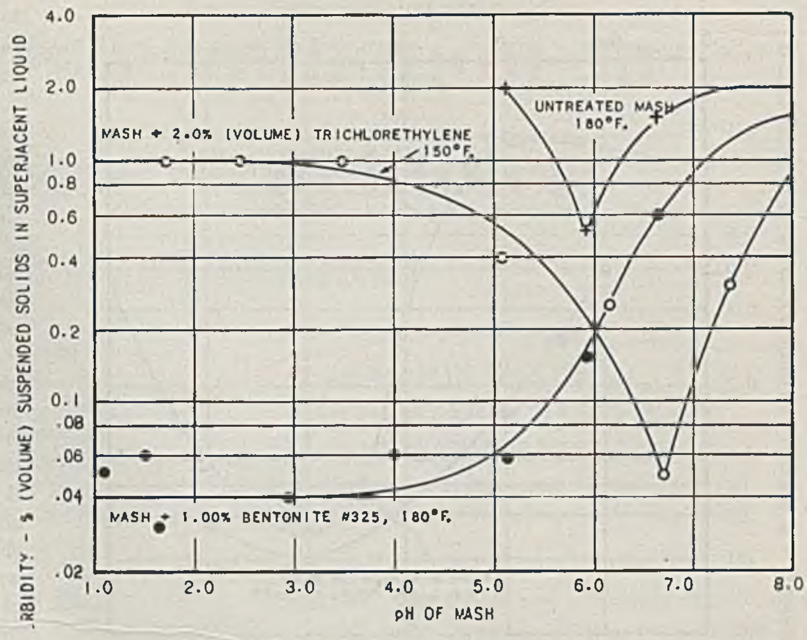

Figure 3. pH *vs.* Turbidity of Treated and Untreated Pilot Plant Mash (30 Seconds at 2000 R.P.M., 820 × Gravity)

RESULTS OF CENTRIFUGATION EXPERIMENTS

The use of bentonite as a mash clarification agent was further investigated by subjecting the suspensions to centrifugal force. In an effort to improve existing methods of treatment, various other chemicals (principally nitropropanes, polar ketones, trichloroethylene, Celite filter aid, and activated charcoal) were also tried as clarifying agents. Of these, only trichloroethylene and the related halogenated hydrocarbons were found to increase the rate and degree of clarification obtainable by centrifugation of this type of mash. Table I shows that this effect is especially noticeable with some of the chlorinated and brominated hydrocarbons of higher molecular weight. Thus, unfermented mash not treated with any clarifying agent could not be clarified below a suspended solids content of 0.2%, even after 80 seconds of centrifugation at 2000 r.p.m. The use of 2.0% (by volume) of hexachloropropylene, however, caused the deposition of all but 0.045% suspended solids in only 10 seconds under the same conditions.

Unfermented Continuous-Cooked Acid-Hydrolyzed Corn Mash. Figure 2 illustrates the effect of centrifugation time upon unfermented mash treated with bentonite and trichloroethylene at optimum pH, temperature, and concentration. Both of these are effective clarifying agents for unfermented acid hydrolyzed corn mash.

Figure 3 shows the effect of pH upon the clarification of treated unfermented mash. Bentonite-treated samples are most easily clarified in the pH range 1.5 to 5.0, whereas trichloroethylene-treated samples clarify best at or near their isoelectric point, pH 6.7.

The effect of temperature upon unfermented mash treated with bentonite and trichloroethylene is indicated in Figure 4. In both cases higher mash temperatures result in greater clarity. In the latter, however, this effect suddenly disappears at 150° F. and above because of the removal of trichloroethylene by steam distillation.

It is usually desirable to keep the amounts of treating agents at a minimum; Figure 5 illustrates the effect of their concentrations upon clarification. Optimum concentrations of bentonite and trichloroethylene are 0.8% by weight and 2.0% by volume, respectively.

Fermented Continuous-Cooked Acid-Hydrolyzed (Glycol) Beer. Similar centrifugation experiments were carried out on fermented beer. Contrary to expectations, trichloroethylene and all the other halogenated hydrocarbons which had been established as effective clarifying agents for unfermented mash proved to be ineffective in the clarification of fermented material.

Bentonite treatment resulted in excellent clarification, optimum conditions being pH 2.0 to 3.0, 210° F., and 0.4% (by weight) or more of bentonite.

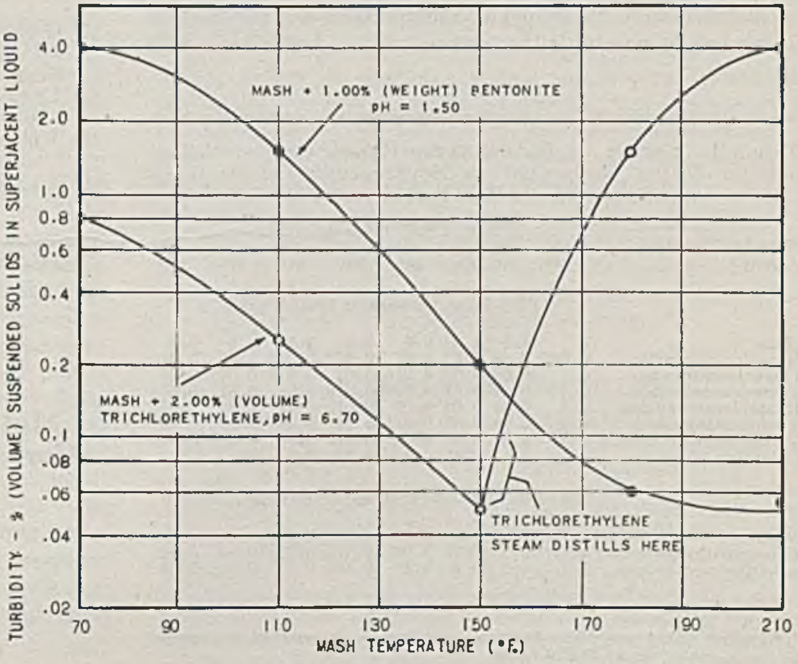

Figure 4. Temperature *vs.* Turbidity of Treated Pilot Plant Mash (30 Seconds at 2000 R.P.M., 820 × Gravity)

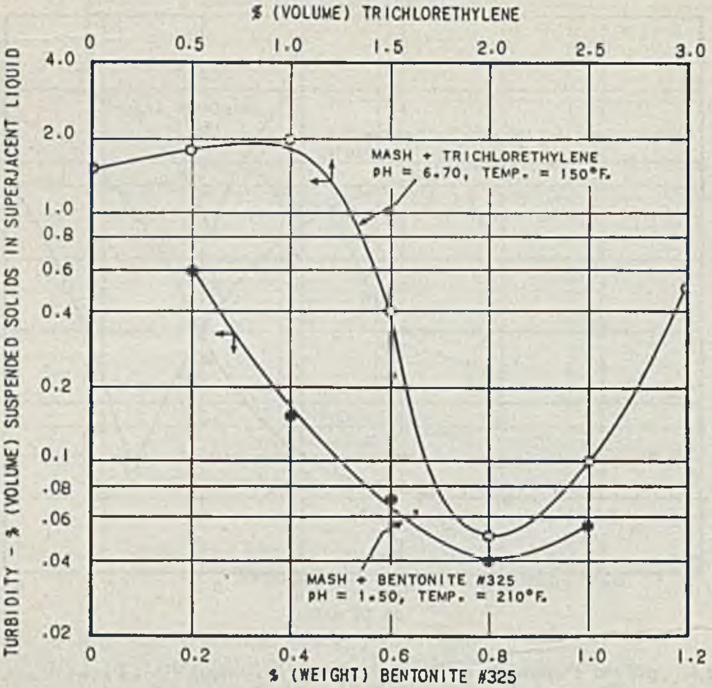

Figure 5. Effect of Concentration of Bentonite and Trichloroethylene on Clarification of Pilot Plant Mash

Near optimum conditions of pH and temperature; 30 seconds at 2000 r.p.m., 820 × gravity

DISCUSSION OF CENTRIFUGATION RESULTS

Probably the most important observation resulting from these centrifugation experiments is that concerning the effect of halogenated hydrocarbons on the rate and degree of clarification obtainable on unfermented acid-hydrolyzed corn mash. It is possible that this property will find application in other clarification problems as well. The use of halogenated hydrocarbons instead of the usual clarifying agents such as bentonite, etc., offers some definite advantages. This group of chemicals is immiscible with water and can, therefore, be easily recovered from the clarified products by flashing or steam distillation. Thus, the final products obtained are devoid of contamination and the treating agents can be recycled in the process. Although applicable only to the unfermented acid-hydrolyzed mash, centrifugation with halogenated hydrocarbons will simplify subsequent fermentation and glycol separation problems.

Table I. Effect of Halogenated Hydrocarbons on Suspended Solids Remaining in Superjacent Liquid after Centrifugation at 2000 R.P.M. and 150° F.[a]

Chemical Treating Agents[b]	Suspended Solids Remaining, %[c] 10 sec.	20 sec.	30 sec.	40 sec.	50 sec.	60 sec.	70 sec.	80 sec.
	Pilot Plant Propagator Mash[d], pH 5.76							
None	3	1.5	1.0	0.8	0.6	0.4	0.3	0.2
Hexachloropropylene	0.045	0.03	0.02	0.02	0.015	0.015	0.01	0.01
Polychloropropane	0.1	0.03	0.02	0.018	0.01	0.018	0.01	0.01
Tetrachloroethylene	0.1	0.04	0.03	0.025	0.018	0.02	0.01	0.015
Hexachlorobutadiene	0.1	0.04	0.02	0.02	0.015	0.02	0.02	0.02
Trichloroethylene	0.2	0.04	0.03	0.025	0.02	0.02	0.02	0.02
Carbon tetrachloride	0.25	0.07	0.04	0.03	0.02	0.02	0.018	0.015
Chlorobenzene	3	1	0.9	0.3	0.25	0.3	0.2	0.2
	Pilot Plant Acid-Hydrolyzed Corn Mash, pH 6.10							
None	7	5	..	4	...	3	...	2.5
Tribromoethylene	2	0.3	0.15	0.06	0.035	0.035	0.02	0.02
α,β-Dibromoethylene	2	0.6	0.4	0.3	0.12	0.08	0.06	0.04

[a] Initial temperature just prior to centrifugation.

[b] 2.0% of mash volume.

[c] Figures listed are percentages by volume as determined by special De Laval centrifuge at 18,000 r.p.m.

[d] An acid-hydrolyzed mash similar to that described except for its greater dilution (90 to 94 gallons per bushel instead of 40 to 44 gallons per bushel).

The minimum concentrations of treating agents found necessary for efficient clarification of these materials in the laboratory might be reduced still further by the use of industrial type equipment. Certain commercial centrifuges are designed to operate at higher-than-atmospheric temperatures and pressures. Such equipment would allow best exploitation of beneficial temperature effects and would no doubt result in notable economy of treating agents.

The experiments indicate that the effect of halogenated hydrocarbons on centrifugation of unfermented acid-hydrolyzed mash is not due to any coagulating action such as is noted in the use of bentonite. It is more likely that their effect is due to the combination of low surface tensions, excellent solvent action, and high specific gravities. Because of the first two characteristics these chemicals probably displace the water and corn oil on the surface and in the interstices of the solids. By virtue of the third characteristic this displacement results in an increase in apparent specific gravity of the mash particles, which allows extremely rapid settling when the particles are subjected to centrifugal action. Also, judging from the varying effectiveness of these chemicals upon fermented and unfermented mashes, this wetting and displacing action is dependent upon certain unknown characteristics of the suspended particles. It is hoped that similar experiments on more diversified clarification problems will ultimately explain these effects.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Paul Kolachov for his guidance in this project and to Joseph E. Seagram & Sons, Inc., through whose sponsorship this work was made possible.

LITERATURE CITED

(1) Cooley, L. C., Ind. Eng. Chem., 30, 615-21 (1938).
(2) Fulton, R. R., *Chem. & Met. Eng.*, 51, 184 (1944).
(3) Steiger, W., Brit. Patent 465,693 (May 13, 1937).
(4) Unger, E. D., and Grubb, H. W., Div. of Sugar Chem. and Tech., 107th Meeting of A.C.S., Cleveland, 1944.
(5) Willkie, H. F., and Prochaska, J. A., "Fundamentals of Distillery Practice", 1st ed., Joseph E. Seagram & Sons, Inc., 1943.

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Molecular Weight-Physical Property Correlation for Petroleum Fractions—Correction

An error has been called to our attention in this article which appeared in the April, 1946, issue of Industrial and Engineering Chemistry. In Table X, page 447, the figure 610 in the molecular weight column should read 620.

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Moisture Determination in Dehydrated Vegetables

VACUUM OVEN METHOD

The loss of weight that occurs when dehydrated potatoes, carrots, cabbage, and onions are heated in a vacuum oven has been studied as a function of time, temperature, fineness of grinding of the sample, and degree of evacuation in the oven. The loss due to thermal decomposition of the vegetables has been estimated, and the combined results have been used to establish conditions for the determination of moisture in the four vegetables.

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OF the numerous ways of determining moisture in dehydrated vegetables (*9*), the vacuum oven method is the most important because it is currently used as a reference for the calibration of other methods. Others described recently are the electrical methods (*7*), the distillation method (*4, 7*), and the Fischer volumetric method (*6*). The electrical methods are purely empirical and require calibration against a standard method. The distillation and the Fischer methods also require calibrations because usually no definite end point is reached in the determinations.

The vacuum oven method used at present by industrial laboratories is identical with that recommended by the Association of Official Agricultural Chemists for dried fruits (*1*). According to this method the material is ground in a food grinder and heated in a vacuum oven at 70° C. for 6 hours at a pressure not exceeding 100 mm. of mercury. It has already been pointed out (*8*) that these conditions for preparation of the sample and for drying are not sufficiently rigorous for dehydrated vegetables to ensure agreement among different testing laboratories. The present paper shows that the analytical results are not a good measure of moisture content. Results may be too low or too high. The result with carrots, for example, may represent only 60% of the water actually present in the sample (Table III). A change in procedure must be made for testing dehydrated vegetables, and this new procedure must be varied for different vegetables.

When an oven method is used for the determination of moisture, the loss in weight on heating is taken as a measure of the moisture content. With plant tissues loss in weight is a function of time of heating; only rarely does this loss reach a constant value. Loss in weight represents not only the water originally held but also other volatile materials, including volatile products of decomposition at elevated temperatures (*3*). It is impossible to tell from a single drying-rate curve when the mechanically held water is completely driven off and when further loss in weight may be ascribed to chemical changes in composition of the material. There is no sharp demarkation, and chemical changes probably occur at all stages of drying. The over-all loss in weight depends on many factors, such as method of preparation of sample, time of drying, degree of evacuation in the oven, and thermal stability of the material. The present paper reports a study of these factors as involved in determinations of moisture in dehydrated carrots, potatoes, onions, and cabbage. The major problem was to determine the time of drying required in order that loss in weight of sample would represent an accurate measure of moisture content.

The moisture content was arbitrarily defined in this work as the loss in weight, at equilibrium, when the ground material is dried in vacuo at room temperature over a desiccant that permits practically no water vapor pressure. It was assumed that, at room temperature and in the absence of air, decomposition and oxidation would be negligible. The experimental procedure established in accordance with this definition is referred to as the primary reference method. It was found, however, that a direct application of this definition was not practicable from a routine standpoint. Materials dried in vacuum desiccators over anhydrous magnesium perchlorate required many months to reach constant weight. A secondary reference method was therefore devised for a more rapid determination. This secondary method, referred to in this paper as the redrying procedure, was carried out as follows: A sample of the vegetable was dried in the oven for a long time (about 100 hours); at the end of this time it was assumed to be essentially dry. The sample was then permitted to absorb a known amount of water and the drying was repeated. The time required in the second drying to obtain a weight loss equivalent to the amount of added water was taken as the correct drying time of the material. Though several assumptions must be made to justify this procedure, the results obtained with it were found to agree reasonably well with those obtained by the primary reference method.

From the results obtained by the redrying procedure, definite conditions were set up for the routine moisture determination of each of the four vegetables. It is recognized that a standardized procedure does not take into account possible variations in drying characteristics of different specimens of the same vegetable. Variations may result from differences in composition or in previous treatment, such as blanching or drying. However, the present work indicates that major discrepancies have been eliminated; the analytical results were much more accurate and reproducible than those obtained by the vacuum oven method now in use by the dehydrated vegetable industry.

SAMPLING AND REPRODUCIBILITY

PREPARATION OF THE SAMPLE. Adequate preparation of a sample includes the problems of sampling and grinding. In dealing with these problems it is of primary importance to recognize that the dehydrated vegetable material is not homogeneous in moisture content when it issues from the drier. Not only do the various pieces differ but also a moisture gradient exists within a single piece, the outside portion being drier than the inside portion. When material is stored in a closed chamber, it becomes more homogeneous through diffusion of water among and within the pieces. The rate of diffusion is slow; the time required to attain moisture equalization decreases with increasing temperature and increasing moisture content, and increases with increasing size of the piece.

In order to obtain a representative sample of vegetable it was therefore necessary to grind and then mix the material well.

The size of the sample to be taken for grinding depends on considerations that are beyond the scope of this paper, but in this laboratory it was the practice to use not less than 100 grams, systematically sampled. The material was first ground coarsely in a Wiley mill (intermediate model) equipped with a U. S. 10-mesh sieve, and was passed through a quartering funnel. A 25-gram portion of the quartered material was then reground in the same mill to pass a U. S. 40-mesh sieve and was put away in a tightly stoppered container (bottles with screw cap and a rubber gasket), to be used later for the determination of moisture. The grinding was rapid, without excessive heating or exposure to air. The particles were limited in size by the sieve opening, and the holdup in the mill (residue in the grinding chamber) was very small. Finer grinding proved to be of no advantage. When a 60-mesh sieve was used, the grinding became objectionably long (with samples produced commercially at moisture content of 5 to 7%) and, as shown in Table III, the drying time was not shortened appreciably.

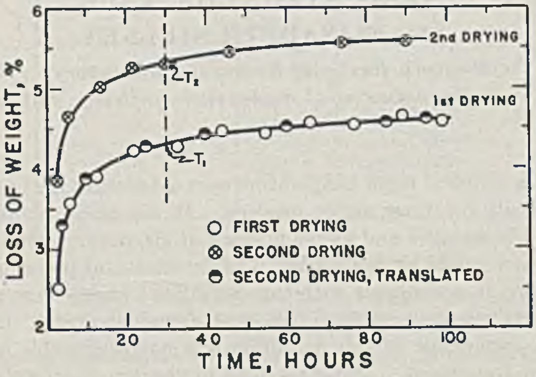

Figure 1. Drying and Redrying Curves for Carrots at 70° C.

In some laboratories it has been the practice to sieve the ground material and to select a certain sieved portion for moisture determination. It was demonstrated in this laboratory that this procedure is not applicable to freshly dehydrated vegetables because the moisture content of the sieved portion may differ appreciably from the average moisture content of the whole. In one test where freshly dehydrated diced carrots were ground in a Waring Blendor and sieved through a U. S. 30-mesh screen, it was found that the portion passing through the sieve had a moisture content of 6.4%, and that retained, 7.3%. Two to three weeks were found necessary for equalization of moisture in the dices at room temperature.

The grinding procedure described was applicable within a limited moisture range that varied with different vegetables. At low moisture contents (less than about 2%) errors arose from the absorption of water from the atmosphere during grinding and handling. At moisture contents higher than about 10% for potatoes and carrots, and 7% for cabbage and onions, the materials became rubbery in texture and were difficult to grind without clogging the mill.

In both cases it became necessary to add another step to the procedure. Prior to grinding, the very dry materials were allowed to absorb moisture from the air, whereas the wet materials were predried to a moisture level at which they could be ground safely and conveniently. Predrying is preferably done in a vacuum oven at 60° C. on coarsely ground material. The change in moisture content can be determined by weighing the unground or coarsely ground materials before and after their respective treatments, and an appropriate correction applied in the final moisture determination. This additional operation is, however, not required with most commercially dehydrated vegetables.

OVEN CONDITIONS. The ovens used were electrically heated, gravity convection type, similar to Model 510 of the Precision Scientific Company. The temperature of these ovens was usually read on a mercury thermometer inserted partially into the vacuum chamber. It is important to know the temperature distribution within the oven because a difference of 1° C. gives rise to a difference of approximately 0.1% in apparent moisture content. Temperature distribution was measured by means of thermocouples attached to various parts of the oven shelf. If the shelf was iron, a temperature gradient of about 2° C. existed along it (from front to rear of oven) when the oven was set at 70° C. (In other ovens in use at this laboratory, particularly those without an insulated door, the gradient was as much as 5° C.) The gradient was reduced to less than 0.5° C. when a $^{1}/_{8}$-inch copper shelf was substituted for the iron shelf. The reading of the mercury thermometer agreed with the temperature of the shelf only when the oven was at atmospheric pressure. The thermometer reading in vacuo was 3° to 4° C. lower, even though the temperature of the shelf remained essentially unchanged. The drop in the thermometer reading was attributable to insufficient heat transfer in the evacuated space. Control of the oven was therefore guided by thermometer readings when the oven was at atmospheric pressure.

The ovens were evacuated by means of mechanical oil pumps capable of reducing pressure in a vacuum-tight system to less than 1 micron. Pressure maintained in the oven may influence both rate and completeness of drying. It has been demonstrated, however, in drying experiments with particle of various sizes (*8*) that rate determination over most of the drying period gives rate of diffusion of water through the particles. Completeness of drying of such colloidal materials as are found in vegetable tissues must be considered from the following point of view: In drying, the moisture content of the material is lowered to a value that corresponds, at best, to the equilibrium moisture content for the particular set of conditions of temperature and humidity prevailing in the oven (*5*). It is important to note that, for some materials, the equilibrium moisture content may be appreciable even at very low humidities. Completeness of drying depends, therefore, not on the total pressure but on the partial pressure of the water vapor in the oven.

Pressure of water vapor in the oven can be kept low by efficient evacuation or by the passage of dry air through the oven, as suggested in the A.O.A.C. method (*1*). In the present experiments the total pressure maintained in the oven varied from 1 to 5 mm. of mercury. When the total pressure was raised to 50 mm. (by deliberately bleeding humid room air into the oven) the loss in weight at 70° C. for potatoes was found to be 0.4% lower, whereas for carrots the change was less than 0.1%. From this observation it was concluded that equilibrium moisture content of potatoes at the higher pressure (estimated relative humidity, approximately 0.5%) was sufficiently high to make the effect of the humidity change detectable; for carrots the change and probably the absolute value were not high enough to be detectable. Some supporting evidence for this interpretation is available from data on water vapor pressure (unpublished) for carrots and potatoes. From data at 35° C. it was estimated that at 0.5% relative humidity the moisture content of potatoes was about 0.7% and that of carrots about 0.1%. When the total pressure in the oven was 5 mm., the relative humidity was about 0.05%, and the equilibrium moisture content that corresponded to it (at 35° C.) was less than 0.1% for both potatoes and carrots. Rigorous proof of this point would require careful measurements of equilibrium moisture content at 70° C. and very low humidities.

The A.O.A.C. method requires that pressure in the oven be less than 100 mm. of mercury and that dry air be passed through the oven at a certain rate. The effectiveness of the latter practice is subject to certain limitations. In our experiments no effect on weight loss was found when dry air was passed; consequently the practice was discontinued. Under our conditions, with degree of evacuation limited by small leaks of air into the oven, the addition of dry air merely increased the total pressure but did not change the partial pressure of the water vapor in the oven. When a vacuum-tight oven is used, however, with a large capacity pumping system that is not capable of producing a very high vacuum, the use of dry air in sufficient quantity should have a beneficial effect; total pressure will remain nearly the same although the partial pressure of the water vapor will be lowered.

OTHER EXPERIMENTAL DETAILS. Samples to be dried varied in weight from 2 to 4 grams and were handled in small glass-stoppered weighing bottles, 20 mm. in diameter and 25 mm. high, with an outside ground cap of standard taper. The bottles were placed in the oven in a device that permitted all of them, at the end of the drying, to be closed simultaneously and quickly (*2*). Two empty bottles were included with each set of samples in the oven to serve as blanks. They were put through all the operations to check on reproducibility of weighing, on completeness of cooling to room temperature in the desiccators, and on other factors. Special precautions were taken to protect the samples from absorbing moisture from the air. At the end of the drying period the oven was brought to atmospheric pressure with air dried by passage through a calcium chloride tube. The air was introduced slowly for 20 to 30 minutes to ensure that it was adequately dried by the calcium chloride and also to keep the finely powdered samples from being blown out of the bottles. Another calcium chloride tube was maintained between the oven and the oil pump.

Determinations on a given sample were made in duplicate or triplicate; the results of analyses usually agreed within 0.03%

of the weight of the sample. This does not, however, represent the experimental error of the determination; the reproducibility for replicates which were not dried at the same time was only ±0.1%. The error arises principally from variations in the oven temperature and from inequalities of the temperature along the oven shelf. The experimental results are reported on dry basis and are given as averages of the replicates to the nearest 0.1%.

SECONDARY REFERENCE METHOD

A drying curve was first determined by measuring loss of weight of a sample in a vacuum oven at various time intervals. Drying was continued long enough (about 100 hours) to ensure that it was essentially complete. The sample was then allowed to absorb water from a humid atmosphere until it regained approximately its original amount of water. The exact weight of the added water was determined from the difference in weights of the dry and the remoistened sample. To ensure uniform distribution of moisture throughout the material, the remoistened sample was allowed to stand in a closed bottle for about 2 weeks. It was then dried again in the vacuum oven under the same conditions employed during the first drying. The time required to reduce the sample weight by an amount equal to that of added water (that is, the time to reach the dry weight obtained in the first drying) is called "redrying time". Thus, redrying time is not the time required to remove all the moisture but is the time when the sum of the moisture loss and the decomposition loss is equal to the amount of added water. Hence the redrying time is always shorter than the first drying period.

The moisture content of the original sample is taken to be the loss in weight in the first drying after a heating period equal to the redrying time, provided the original and remoistened samples show the same drying characteristics. Several assumptions are involved in this procedure. The first is that essentially all the water originally present has been removed at the end of the first drying run. The factors that support the plausibility of this assumption are the long drying period and the very low rate of loss of weight at the end of the drying—0.005% per hour or less. Since this loss in weight appears to be nearly constant in rate, it may be assumed that the loss is due principally to decomposition. Furthermore, it was found that the redrying time was unchanged when the first drying run was conducted for an additional 40 to 50 hours.

The second assumption is that weight loss increases with heating time in the same manner in both drying runs. This is capable of direct experimental verification by comparison of the weight loss-time curves for the two runs.

If the initial moisture content and the drying characteristics were the same in the first as in the second drying run, the results of the two runs could be represented by one drying curve. Since under the experimental conditions the initial moistures were not the same (because of practical difficulties in adjusting the moisture content to the same value), two different curves are obtained which can be tested for similarity by superposing one on another and showing that they are coincident. To superpose the two curves, it is necessary to shift one of them along both the time and the weight loss axes (equivalent to shift of origin). The shift along the time axis corresponds to the time necessary to dry the sample from the higher to the lower initial moisture level. The shift along the weight loss axis corresponds to the amount of water removed plus the weight loss due to accompanying decomposition. Since, in a general case, neither the amount of water nor the extent of decomposition is known, the comparison for similarity can be made only by graphical means (by trial), by manually superposing the two curves to determine whether the curve for lower initial moisture coincides with a portion of the curve for higher initial moisture.

The problem is, however, greatly simplified for all the experiments described in this paper. It was found that the shift along the time axis was entirely negligible (less than one hour) because of small differences in moisture content between the original and the remoistened sample and because of the rapid initial rate of drying. Therefore, it was sufficient to shift one curve along the weight loss axis to determine whether it would coincide with the other. This test for similarity can also be made numerically instead of graphically by calculating the difference in weight losses for the same heating times in the two drying runs. Constancy of the difference values shows that the drying characteristics are unchanged. If the two curves are not coincident, the results cannot be used for determination of drying time. In such cases, however, it was found that coincidence was obtained by drying at a lower temperature.

In order to calculate the original moisture content after the two curves are found to be similar, a third assumption must be made—namely, that a negligible amount of decomposition occurs in drying the sample from the higher to the lower initial moisture level. This assumption appeared to be justified under our experimental conditions, where the time involved was very short and the rate of decomposition at the temperature chosen for redrying was very low. The moisture content of the original sample was thus equal to the algebraic sum of the known moisture content of the remoistened sample and the shift along the weight loss axis (or difference value) found in testing for similarity of the two curves.

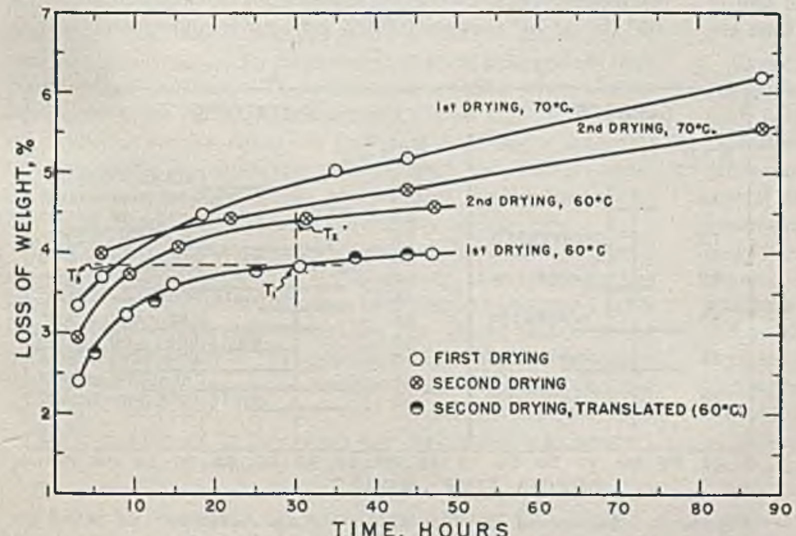

Figure 2. Drying and Redrying Curves for Cabbage at 60° and 70° C.

The 60° C. curves are similar; the 70° curves are not. Amount of water added prior to second drying at 60° C., 4.4%; redrying time (T_2), 30 hours; moisture content of original sample (T_1), 3.9%; drying time at 70° C. (T_3), 8 hours.

Table I shows typical experimental results for the drying and redrying of potatoes, carrots, cabbage, and onions. The data for carrots and cabbage are also illustrated graphically in Figures 1 and 2, respectively. Figure 1 shows that the second-drying curve is similar to the first-drying curve. When points from the second-drying curve are translated along the ordinate by a constant amount (1.0%), they fall very closely on the first-drying curve. (The translated points in Figures 1 and 2 are not the experimental ones but were taken at random from the smoothed curve for the second-drying run. This was done to avoid overlapping with the experimental points of the first-drying run.) The amount of water added to the sample prior to the second-drying run was 5.3%. The time required to remove this amount of water, as indicated by the vertical line at point T_2 on the second-drying curve, was 30 hours. At the corresponding time, T_1,

Table I. Results of Typical Redrying Experiments on Dehydrated Vegetables[a] Ground in a Wiley Mill through a 40-Mesh Sieve

Drying[b]	Loss in Weight at Various Times[c], % 3 hr.	6 hr.	16 hr.	30 hr.	40 hr.	50 hr.	80 hr.	100 hr.	Water Added after 1st Drying[d], %	Redrying Time, Hr.	Water in Original Sample, % (Dry Basis)
					Carrots, 70° C.						
1st	...	3.5	4.1	4.3	4.4	4.5	4.6	4.6			4.3
2nd	...	4.6	5.1	5.3	5.4	5.5	5.6	5.6	5.3	30	
Diff.	...	−1.1	−1.0	−1.0	−1.0	−1.0	−1.0	−1.0			
					Low-Sugar Potatoes, 70° C.						
1st	...	7.3	7.9	8.2	8.3	8.4	8.4	8.4			8.4
2nd	...	6.4	6.9	7.2	7.3	7.4	7.4	7.4	7.4	50	
Diff.	...	0.9	1.0	1.0	1.0	1.0	1.0	1.0			
					High-Sugar Potatoes, 70° C.						
1st	...	8.1	8.9	9.4	9.6	9.7	9.9	10.0			9.5
2nd	...	6.0	6.6	7.0	7.2	7.3	7.5	7.6	7.1	35	
Diff.	...	2.1	2.3	2.4	2.4	2 4	2.4	2.4			
					Cabbage, 70° C.						
1st	3.3	3.7	4.4	4.9	5.1	5.4	6.0	..			...
2nd	...	4.0	4.3	4.6	4.7	4.9	5.4	..	4.2	..	
Diff.	...	−0.3	0.1	0.3	0.4	0.5	0.6	..			
					Cabbage, 60° C.						
1st	2.4	2.9	3.6	3.9	4.0	4.0	...	..			3.9
2nd	2.9	3.4	4.1	4.4	4.5	4.6	...	..	4.4	30	
Diff.	−0.5	−0.5	−0.5	−0.5	−0.5	−0.6	...	..			
					Onions, 70° C.						
1st	5.8	6.0	6.4	6.7	6.9	7.0	7.5	..			...
2nd	...	5.8	6.0	6.2	6.3	6.4	6.7	..	6.0	..	
Diff.	...	0.2	0.4	0.5	0.[illegible]	0.6	0.8	..			
					Onions, 60° C.						
1st	5.1	5.6	6.0	6.0	6.1	6.1	...	..			6.0
2nd	4.6	5.0	5.4	5.5	5.6	5.6	...	..	5.5	30	
Diff.	0.5	0.6	0.6	0.5	0.5	0.5	...	..			

[a] Imperator carrots, White Rose potatoes, Flat Dutch cabbage, and yellow sweet Spanish onions.

[b] 1st and 2nd represent, respectively, the weight losses in the first and second drying runs. Diff. represents differences between weight losses in the two runs. The amount of water added to the sample prior to the second drying run is shown in the third column from the right.

[c] In order to group conveniently in one table the results for all four vegetables, the data were taken from smoothed drying curves. The actual experimental values did not deviate from the curves by more than 0.1%.

[d] Amount of added water and loss in weight are calculated on dry basis.

on the first-drying curve, the weight loss was 4.3%. This is then taken to be the moisture content of the original sample before the first drying. From this result and the loss of weight at the end of 100 hours, 4.6% (Table I), we may estimate the loss of weight due to decomposition. The over-all or cumulative loss at 100 hours is 4.6 − 4.3 = 0.3%. The average rate of loss is 0.3/100 = 0.003% per hour, which is very small and thus accounts at least partially for the reproducibility of the drying. It must be understood, however, that the rate of loss may be relatively greater at the beginning of the drying when the material is moist than at the end when it is dry.

Similar conclusions on the similarity of the drying curves may be drawn from the data for carrots in Table I. The constancy of the difference values is a measure of their similarity. The difference values are constant within the experimental error, ±0.1%. The table also shows the quantity of added water in the remoistened sample and the time for redrying. This time, together with data for the first drying, was used to obtain the original moisture content of the sample, as shown in the last column of Table I.

The results obtained on two samples of potatoes of identical variety and origin, but of different sugar content, are also shown in Table I. One sample contained 26.2% of total sugars, and the other 2.4% (dry basis). The high sugar concentration was developed during 8-week storage of the raw potatoes (prior to dehydration) at 32° F. Both materials showed reproducible drying characteristics as indicated by the difference values of Table I. The low-sugar potatoes required a redrying time of 50 hours, whereas the high-sugar ones required 35 hours. The difference may be explained by the greater amount of decomposition suffered by the high-sugar material. The loss in weight that results from decomposition compensates for the incomplete loss of water and shortens the drying time. The amount of decomposition in the low-sugar potatoes is, in fact, unmeasurable. A constant weight is apparently reached in the two dryings after 50 hours. The high-sugar potatoes do not attain a constant weight, even after 100 hours of drying; the average rate of decomposition, estimated in the same manner as for carrots, is 0.005% per hour. The decomposition was evidenced by marked browning of the high-sugar potatoes during drying. The color of the low-sugar potatoes remained virtually unchanged.

The drying characteristics of cabbage are very similar to those of onions but differ markedly from those of carrots and potatoes. The drying and redrying curves at 70° C. are not similar. The differences in Table I show a progressive increase from −0.3 to +0.6 for cabbage (Figure 2) and from 0.2 to 0.8% for onions. It was concluded, therefore, that the drying should be conducted at a lower temperature. The results at 60° C. show the desired similarity, and the redrying time for both vegetables was found to be 30 hours. From the value of the moisture content determined at 60° C. and the drying data at 70° C., it was possible to determine the drying time at 70° C. The time was 8 hours for cabbage (point T_3 in Figure 2) and 6 hours for onions. In this case the drying times are of the same order of magnitude as 6-hour time currently used in the industry. The estimated rates of decomposition are 0.002% per hour for cabbage and onions at 60° C.; at 70° they are 0.019% per hour for onions and 0.026%.

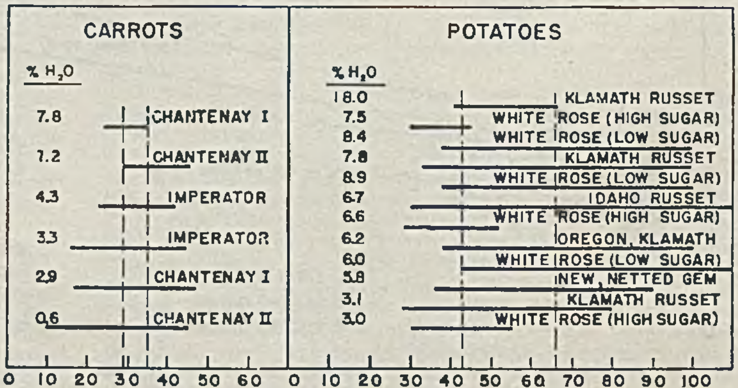

Figure 3. Range of Drying Time for an Accuracy of ±0.1% in Moisture Content

White Rose potatoes, high-sugar and low-sugar, contained, respectively, 26.2 and 2.4% total sugar (on dry basis). Sugar content of other potato samples was less than 5%. Chantenay I and II represent same variety of carrots from two different sources.

per hour for cabbage. Thus the average decomposition rate appears to be about ten times greater at 70° than at 60° C.

There is considerable latitude in the choice of drying time when definite limits are set for accuracy of determination. Thus, for an accuracy of ±0.1%, the limits for the particular samples listed in Table I are as follows: Carrots, 23 to 42 hours; low-sugar potatoes, 38 to more than 100 hours; high-sugar potatoes, 30 to 45 hours; cabbage, 60° C., 22 to 40 hours; cabbage, 70° C., 7 to 9 hours; onions, 60° C., 15 to 45 hours; onions, 70° C., 5 to 8 hours. The latitude for onions and cabbage at 70° C. is small, 2 to 3 hours, because the drying time falls on a relatively steep portion of the drying curve, whereas in all other cases the nearly horizontal portion is involved.

COMPARISON OF PRIMARY AND SECONDARY REFERENCE METHODS

The following experiments were planned to determine the suitability of the redrying procedure as a secondary reference method. Samples of various vegetables (ground to pass a 40-mesh sieve) were dried at room temperature in evacuated desiccators containing Anhydrone (anhydrous magnesium perchlorate). Phosphorus pentoxide, used in earlier experiments, was found unsatisfactory because the commercially available chemical contained a volatile impurity (probably lower oxides of phosphorus) that sublimed in the highly evacuated desiccators and was deposited on the sample bottles and on the walls of the desiccator. It was shown conclusively that the deposit was not caused by a mechanical spray of finely powdered phosphorus pentoxide.

Carrots and potatoes were dried with Anhydrone for a period of 11 months; cabbage and onions, 9 months. All the materials reached equilibrium (constant weight) as judged by the fact that during the last few months of drying the changes in weights of samples were both positive and negative within the experimental error, ±0.02%. The actual time necessary to remove all but the last 0.1% of the weight was about 6 months for carrots and high-sugar potatoes, and 3 months for low-sugar potatoes, cabbage, and onions.

Duplicate samples of these vegetables were run through the redrying procedure at elevated temperatures. Comparison of the results by the two methods is shown in Table II for three samples of carrots, three of potatoes, and one each of cabbage and onions. All the materials listed in Table I were included. The agreement of the two sets of results was within 0.2% or better, which is considered satisfactory and serves to confirm the suitability of the redrying procedure as a secondary reference standard. It has been mentioned that high-sugar potatoes and carrots, which are normally rich in sugar, dry more slowly at room temperature than do low-sugar potatoes. The relation is reversed when the redrying times (at 70° C.) are compared (Table II). This reversal probably results from the fact that high-sugar materials undergo greater decomposition at 70° C. than do low-sugar materials. The decomposition loss compensates for the incomplete loss of water and thus shortens the relative drying time.

With White Rose (low-sugar) potatoes the weight loss over magnesium perchlorate was 0.2% greater than that in the vacuum oven, even after 100 hours of drying in the latter (Table II). This difference may have been due to the fact that the relative humidity over the magnesium perchlorate was very much lower than that in the vacuum oven. It is also possible that the vapor pressure of water over the calcium chloride, used to dry the inlet air to the oven, was high enough to account for the lower result obtained in oven drying.

The vapor pressure of calcium chloride (technical, anhydrous) was found to be 0.3 mm. of mercury at 35° C. This pressure would produce a relative humidity of 0.1% in the oven at 70° C., which may correspond to an equilibrium moisture content of 0.1 or 0.2%, as previously explained in the section on "Oven Conditions".

SUITABLE CONDITIONS FOR VACUUM OVEN METHOD

In order to establish drying conditions suitable for routine analysis of large numbers of different samples, it was desirable to know how the drying time varied with variety, moisture content, and fineness of grinding of the vegetable, and also how the drying time was affected by a change in temperature of the oven.

Effect of Moisture Content and Variety on Drying Time. Figure 3 shows the results obtained with various materials of different moisture levels, ground to pass a 40-mesh sieve and dried at 70° C. The horizontal line for a given sample indicates the range of drying time within which the moisture content did not deviate by more than ±0.1% from the value found by the redrying procedure. The vertical lines include the range common to all samples studied except the high-sugar potatoes. Thus it is seen that for two varieties of carrots at moisture levels of 0.6 to 7.8%, the range was from 29 to 35 hours. For five varieties of potatoes containing 3 to 18% water, the range was from 43 to 67 hours. The three samples of White Rose (high-sugar) potatoes (Table II) behaved more like carrots and fell in a lower drying range of 30 to 45 hours. However, this material was not representative of the commercial variety of potato; if it were included with the others, it would merely narrow the range to the limits of 43 to 45 hours.

Table II. Comparison of Drying Experiments at Elevated Temperatures in Vacuum Oven Drying at Room Temperature in Evacuated Desiccators over Anhydrone[a]

	Drying Conditions		Apparent Moisture Content, % (Dry Basis)	
	Hours	° C.	Vacuum oven drying[b]	Drying over Anhydrone[c]
Carrots				
Chantenay I	30	70	7.8	7.7
Imperator[d]	30	70	4.3	4.1
Chantenay	35	70	7.2	7.0
Potatoes				
White Rose[d]				
Low-sugar	50	70	8.4	8.6
High-sugar	35	70	9.5	9.5
Klamath Russet[e]	45	70	7.8	8.0
Cabbage[d], Flat Dutch	30	60	3.9	3.8
Onions[d], yellow sweet Spanish	30	60	6.0	6.1

[a] Prior to drying, all materials were ground in a Wiley mill to pass a 40-mesh sieve.

[b] Conditions determined by redrying.

[c] At room temperature. Carrots and potatoes were dried 11 months, cabbage and onions 9 months.

[d] Materials same as described in Table I.

[e] Sugar content was less than 5% (dry basis).

Effect of Fineness of Grinding on Drying Time. The variation of drying time with fineness of grinding for one sample each of potatoes and carrots is indicated in Table III. The moisture content of both materials, determined by the redrying procedure on 40-mesh grind, was 7.2%. It is apparent that the drying time decreased with increasing fineness of grinding. The minimum drying time changed from 80 to 35 hours for potatoes and from 65 to 25 hours for carrots as fineness of grinding was changed from 10 to 60 mesh. It is interesting to note that there was little or no change in drying time from 40 to 60 mesh.

Similar experiments on cabbage have shown no change in drying time with change in fineness of grinding. This observation agrees with that of Lee and Moyer (7). These authors postulated that all leafy vegetables would show behavior similar to cabbage, while all root vegetables would resemble carrots and potatoes.

The last column in Table III illustrates the magnitude of error involved when the result with 6-hour drying (currently used in the industry) is taken as a measure of the moisture content. The difference between the determined value (7.2%) and the 6-hour value is very large and represents errors varying from 11 to 37% of the total water present. Even larger errors might be found if

Table III. Variation of Drying Time[a] with Fineness of Grinding[b]

	Apparent Moisture Content after 6-Hr. Drying, % (Dry Basis)	Difference[c], %
Chantenay carrots, 7.2% moisture		
10-mesh, 65–90 hr.	4.5	2.7
20-mesh, 44–64 hr.	5.4	1.8
40-mesh, 25–40 hr.	6.0	1.2
60-mesh, 25–40 hr.	6.3	0.9
Klamath Russet potatoes, 7.2% moisture		
10-mesh, 80–130 hr.	5.3	1.9
20-mesh, 57–130 hr.	5.8	1.4
40-mesh, 40–85 hr.	6.1	1.1
60-mesh, 35–85 hr.	6.4	0.8

[a] Range of drying time that permitted a deviation in moisture content of ±0.1%.

[b] Ground so that all material passed wire mesh indicated (intermediate Wiley mill).

[c] Difference between moisture content found by redrying procedure (7.2%) and apparent percentage after 6 hours.

the analyses were made on sieved portions of unequilibrated samples—that is, freshly dehydrated material.

Variation of Drying Time with Temperature. It is apparent that the drying times established from these results would be objectionably long for commercial routine determinations. The time may be shortened by raising the temperature, but it must be remembered that increase of temperature also increases rate of decomposition; precision of the determination may suffer thereby, particularly if the drying time is shifted from the nearly horizontal portion of the drying curve to the steep portion.

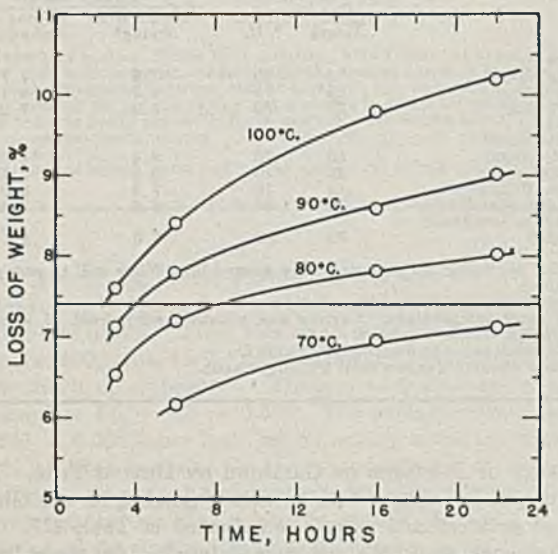

Figure 4. Drying Curves for Carrots at Various Temperatures

Moisture content was determined by redrying procedure at 70° C. and is indicated by horizontal line crossing the ordinate at 7.4%.

It has already been shown in the discussion of Table I that the drying time for cabbage and onions was shortened from 30 hours at 60° C. to about 7 hours at 70° C. Similar information was obtained on carrots and potatoes from drying curves at various temperatures; these data are illustrated for carrots in Figure 4. The horizontal line in this figure indicates the moisture content of the material as determined from measurements at 70° C. The intersection of this line with the curves shows the drying time at different temperatures. The results for carrots and potatoes are listed in Table IV.

The drying time, as given, allowed for ±0.1% deviation from the value determined at 70° C. The latitude in drying time became progressively smaller as the temperature was increased. The drying time was less than 3 hours for carrots at 100° C. and also for potatoes at temperatures higher than 110° C. Under those conditions the reproducibility of measurements became poor, and no attempt was made to establish the actual values of the drying times.

The data for different drying temperatures can be used to estimate the error made in a determination when the oven temperature deviates from the desired value by 1° C. The error differed for different temperatures, but in order of magnitude it amounted to about 0.1% per 1° C. for the four vegetables investigated.

SUMMARY AND CONCLUSIONS

A study was made of several factors that affect the determination of moisture in dehydrated vegetables by the vacuum oven method. Evidence was presented in Table III and in a previous article (*8*) to show that the present industrial vacuum oven method is not satisfactory from the standpoint of either precision or accuracy. It was concluded that the oven method can be made to yield accurate results only if it is calibrated against another reference method. The primary reference method adopted for calibration consisted of drying to constant weight in vacuo over anhydrous magnesium perchlorate. Since this method was inconveniently slow, an equivalent secondary reference method (based on a redrying procedure) was also established and was used to determine the conditions for drying of potatoes, carrots, cabbage, and onions. The conditions are summarized as follows:

A carefully obtained sample of the material, not less than 100 grams in weight, was ground coarsely in a Wiley mill (intermediate model) equipped with a U. S. 10-mesh sieve. The ground material was passed through a quartering funnel, and a 25-gram portion was reground in the same mill with a 40-mesh sieve. Subsamples of the reground material weighing 2 to 5 grams were placed in weighing bottles with tightly fitting ground-glass covers and used for the determination of moisture. If the material was so moist that it clogged the mill, or so dry and hygroscopic that an appreciable error resulted from the adsorption of water from the atmospheres, either predrying or premoistening had to be carried out prior to grinding.

The drying was accomplished in a vacuum oven maintained at a pressure of 5 mm. of mercury or less. The temperature setting of the oven refers to the temperature of the oven shelf, which should be copper to minimize temperature gradients. The drying times for a permissible error in the determination of ±0.1% were as follows: carrots at 70° C., 29 to 35 hours; potatoes at 70° C., 43 to 67 hours; cabbage at 60° C., 22 to 40 hours; onions at 60° C., 15 to 45 hours. Data are also given for shorter drying times at higher temperatures.

In choosing a convenient schedule for a large number of samples, it may become desirable to dry potatoes and carrots in the same oven at the same time. Choosing 40 hours at 70° as the drying time for both vegetables would result in very small sacrifice in accuracy. The additional error (above 0.1%) would amount to only a few hundredths per cent (Figure 3) for some samples and would be zero for others.

Table IV. Drying Time at Various Temperatures for Potatoes and Carrots[a] Ground to Pass a 40-Mesh Sieve

Temperature, ° C.	Time Range, Hr.[b]	
	Carrots	Potatoes
70	29 to 45	35 to 100
80	7 to 10	18 to 25[c]
90	3.5 to 4.5	8 to 12
100	<3	5.5 to 9
110	<3	<3

[a] Chantenay carrots, 7.4% H_2O; Klamath Russet potatoes, 7.3% H_2O.

[b] The range of time allows for a deviation of ±0.1% in moisture content.

[c] Not determined experimentally; value given was obtained by interpolation of results at other temperatures.

The required drying time varies with different kinds of vegetables. For routine or control work where the limits of error could probably be extended to ±0.2%, however, it may be possible to assign the same drying time to a whole group of vegetables. For example, beets, sweet potatoes, and other vegetables of similar texture may fall in the same class with carrots and potatoes (40 hours at 70° C.), and leafy vegetables may fall in the same class with cabbage and onions (30 hours at 60° C.). Measurements on other vegetables are now in progress to obtain this information.

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LITERATURE CITED

(1) Assoc. of Official Agr. Chem., Methods of Analysis, 5th ed., p. 336 (1940).
(2) Chastain, S. M., Ind. Eng. Chem., Anal. Ed., 16, 579 (1944).
(3) Clifford, P. A., *J. Assoc. Official Agr. Chem.*, 17, 215 (1934).
(4) Curl, A. L., *Canner*, 98, 22 (1944).
(5) Gortner, R. A., "Outlines of Biochemistry", p. 231, New York, John Wiley & Sons, 1938.
(6) Johnson, C. M., Ind. Eng. Chem., Anal. Ed., 17, 312 (1945).
(7) Lee, F. A., and Moyer, J. C., *Food Ind.*, 15, 64 (1943).
(8) Makower, B., and Myers, S., *Proc. Inst. Food Tech.*, 1943, p. 156.
(9) U. S. Dept. of Agr., *Misc. Pub.* 540 (June, 1944).

SOYBEAN PROTEIN PRODUCTION

Effects of Temperature and Water-Flake Ratio

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The pilot plant production of soybean protein was studied with respect to the effect of temperature and of water-flake ratio on the dispersibility of the protein and on consequent economic balance. The effect of temperature is relatively small but the effect of the water-flake ratio, when translated into terms of plant capacity, is of primary importance economically. When the price of protein is 20 cents per pound, the proper water-flake ratio for maximum profit is about 11 to 1 with slight dependence on the price of meal; but when the price is 10 cents per pound, the water-flake ratio is about 20 to 1 with increased meal price influence. In large scale production such a shift in proportions is economically important.

A DETAILED study of pilot plant production of soybean proteins, with the purpose of ascertaining limits for factors affecting the economy of the process, led to investigation of the effects of temperature and water-flake ratio as the first step. The initiation of this study was indicated in the first paper of the series (*2*) which described a pilot plant, steps in the protein-recovery process, the effect of pH on the process, and the superiority of alcohol-extracted flakes as a raw material.

The plan of the present work was to investigate in the pilot plant the dispersibility of soybean protein from commercial soybean flakes having a high water solubility, at temperatures of 30, 45, 60, and 75° C., and at water-flake ratios of 5 to 1, 7.5 to 1, 10 to 1, 20 to 1, and 30 to 1. As a standard, a laboratory study was made of the dispersibility of soybean protein from ground flakes which had had no heat treatment; that is, the oil was extracted in the laboratory with cold hexane, and the residual solvent was removed by air drying. To eliminate effects of particle size and stirring and, thereby, to make an exact comparison of pilot plant and laboratory materials, a sample of the commercial flakes used in the pilot plant was ground and the protein was extracted under the same conditions as those employed in the laboratory studies.

Distilled water was utilized in protein extractions both in the laboratory and in the pilot plant to avoid the effect of ions in natural water which vary in concentration from one locality to another. The commercial flakes contained 7.98% nitrogen at

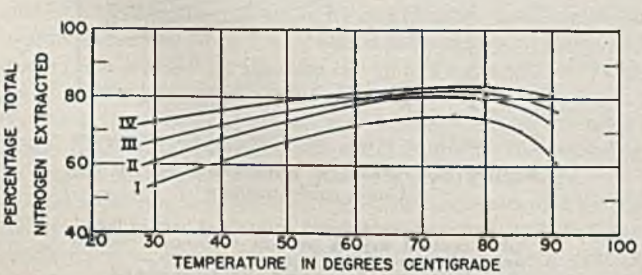

Figure 1. Effect of Temperature on Extraction of Nitrogen with Water from Laboratory Samples of Soybean Meal

I. Water meal ratio, 5 to 1
II. Water meal ratio, 10 to 1
III. Water meal ratio, 20 to 1
IV. Water meal ratio, 30 to 1
Each point is the average of two determinations.

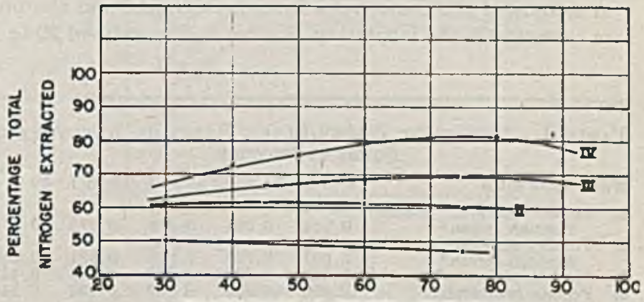

Figure 2. Effect of Temperature on Nitrogen Extraction from Soybean Flakes in Pilot Plant and Laboratory

I. Pilot plant extraction at water-flake ratio of 10-1
II. Pilot plant extraction at water-flake ratio of 20-1
III. Pilot plant flakes ground and extracted in laboratory at water-flake ratio of 20-1
IV. Identical to curve III of Figure 1

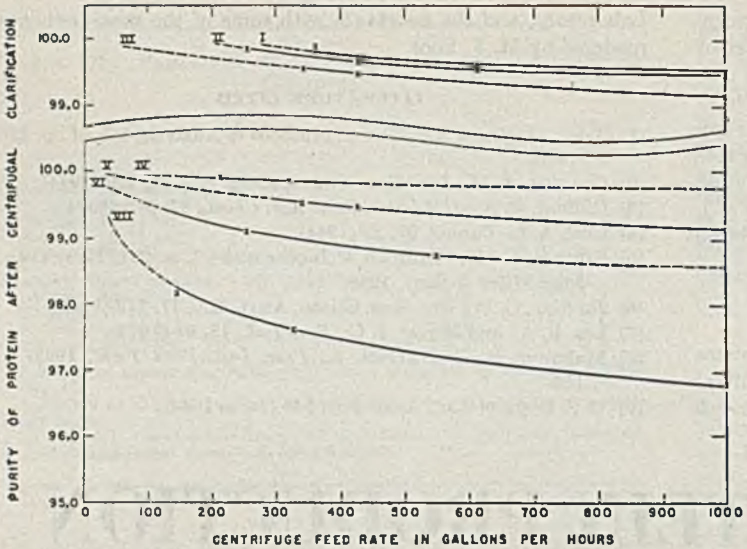

Figure 3. Effect of Rate of Centrifugation on Purity of Protein

I. Extraction ratio 20 to 1, 60° C.
II. Extraction ratio 20 to 1, 45° C.
III. Extraction ratio 20 to 1, 30° C.
IV. Extraction ratio 30 to 1, 30° C.
V. Extraction ratio 20 to 1, 30° C.
VI. Extraction ratio 10 to 1, 30° C.
VII. Extraction ratio 7.5 to 1, 30° C.

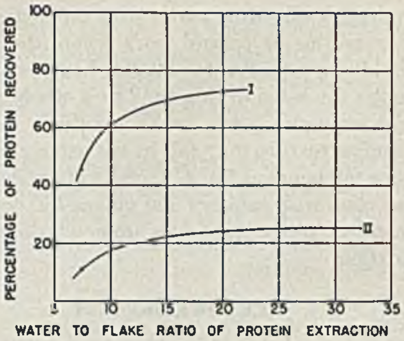

Figure 4. Protein Recovered from Dispersions at Various Water-Flake Ratios

I. Percentage of dispersed protein recovered
II. Percentage of original raw material recovered as protein

8.86% moisture, and the laboratory material contained 7.75% nitrogen at 8.73% moisture; both contained about 1% oil. For the laboratory experiments the materials were ground to pass a 100-mesh screen.

EFFECT OF TEMPERATURE

Figure 1 shows curves representing the solubility of soybean protein in finely ground laboratory samples at various temperatures and at several water-flake ratios. The procedures used in determining the solubility of soybean protein have been described in earlier publications (*5*, *6*) and should be consulted for details. In all of the curves there is a maximum somewhere between 70° and 75° C. which indicates a definite advantage for the use of elevated temperatures. The increase in percentage of protein dispersed is about one eighth of the percentage dispersed at 30° C. for the 30 to 1 water-flake ratio, whereas for the 5 to 1 ratio increase is about one third more at 75° than at 30° C.

When this temperature effect was studied with unground flakes, on the pilot-plant scale the nearly flat curves I and II of Figure 2 were obtained. The absence of an increase in solubility with an increase in temperature would seem to indicate changed solubility characteristics due either to (*a*) slight heat treatment received by the commercial flakes, (*b*) difference in particle size between the flakes and the finely ground laboratory material, or (*c*) the operation of both influences.

A sample of the commercial flakes was ground and the protein extracted in the laboratory at a water-flake ratio of 20 to 1. The resulting yield appears as curve III of Figure 2; the corresponding laboratory sample is represented by curve IV. The intermediate position of curve III indicates that particle size is relatively unimportant in diffusion of the dispersed protein. It is more probable that the decrease in solubility of the protein is caused by denaturation during processing and by aging (*1*, *3*, *5*). The maximum shown in curve IV represents an increase in solubility of one fourth over that at 30° C., whereas the increase of curve III is only one tenth.

It would be expected that an increase in temperature would improve centrifugal clarification as a consequence of the accompanying decrease in viscosity. The small change is shown in the upper portion of Figure 3 for the clarification of a dispersion extracted at a water-flake ratio of 20 to 1.

Protein precipitated from the hot solution resulting from processing at elevated temperatures settled about ten times as fast

Table I. Effect of Water-Flake Ratio on Recovery of Soybean Protein

Water-flake ratio	5 to 1	7.5 to 1	10 to 1	20 to 1	30 to 1
1. Total dissolved solids through screen[a]	0.044	0.294	0.428	0.475	0.510
2. Total suspended solids through screen[a]	0.007	0.067	0.074	0.061	0.046
3. Mash over screen[a]	0.949	0.639	0.497	0.463	0.443
4. Protein recovered[a]	0.023	0.112	0.169	0.244	0.246
5. Dissolved solids remaining as whey[a]	0.021	0.182	0.259	0.231	0.264
6. Original dispersion through screen, %	7.4	53.5	77.2	82.7	82.9
7. Purity of protein with no clarification, %	76	62	70	79	79

[a] Values reported as pounds per pound of original raw material. All runs made with distilled water at 30° C. on 80-mesh screen.

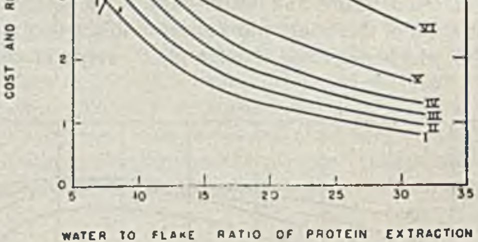

Figure 5. Effect of Extraction Ratio on Costs and Income

Cost curves are calculated on basis of cost of flakes plus cost of drying protein and mash minus returns from mash:
I. Cost when flakes cost 1 cent per pound
II. Cost when flakes cost 1.5 cents per pound
III. Cost when flakes cost 2 cents per pound
IV. Cost when flakes cost 2.5 cents per pound
Income curves represent returns from protein:
V. Income when protein sells for 10 cents per pound
VI. Income when protein sells for 15 cents per pound
VII. Income when protein sells for 20 cents per pound

as protein resulting from cold extraction and precipitation. Whether occluded impurities can be removed by washing such a fast-selling and therefore compact precipitate is the subject of another investigation. Information from that investigation should also lead to a decision regarding the desirability of heating the dispersion just before precipitation rather than heating the entire extraction mass.

As might be expected from the settling rate, protein precipitated from hot solutions also filters readily at a much lower concentration of slurry than does cold precipitated protein. A wet-curd filtration rate of 5 pounds per square foot of filter area per hour is attained at a slurry concentration of about 2% solids for this protein; the previously reported (*2*) slurry concentration for the same rate of filtration is 9% for protein from hexane-extracted material and 5% for protein from alcohol-extracted flakes. This case of filtration for the hot precipitated protein is not a measure of the rate of filtration in terms of dry protein, since wet curd in this case contains only 10 to 15% solids; our previously reported results (*2*), on the other hand, showed a solids content of 35 to 40% for protein from hexane-extracted flakes and of 30 to 35% for protein from alcohol-extracted flakes. This variation in the nature and consistency of the precipitate is being studied further.

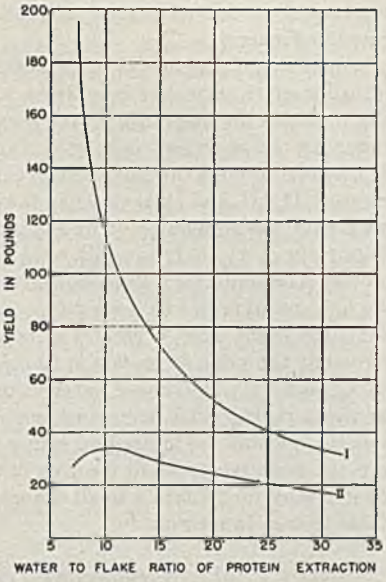

Figure 6. Effect of Extraction Ratio on Yield of Mash and Protein for a Given Capacity

I. Mash (undispersed residue) recovered
II. Protein recovered

EFFECT OF WATER-FLAKE RATIO

The effect of water-flake ratio on the dispersibility of soybean protein under nearly ideal conditions is presented in Figure 1, where it is apparent that at 30° C. an increase of about 6% occurs for each step of the series of ratios. At 70° C. the first step is 6% but thereafter the increase diminishes to 1.5% for each step. The dispersibilities under pilot plant conditions for water-flake ratios of 10 to 1 and 20 to 1 are shown in Figure 2. The 5 to 1 flake slurry proved to be too thick for satisfactory handling in our equipment. The 20 to 1 water-flake ratio extracted about 10% more protein at 30° C. than did the 10 to 1 ratio and was nearly as efficient at this temperature as the laboratory extraction.

The percentage of dispersed protein recovered at the several water-flake ratios is shown in curve I of Figure 4; the percentage of original flakes recovered as protein is given in curve II.

The difference between dispersed and recovered acid-precipitable protein is accounted for by the dispersion retained by the mash on a separator which, in our pilot plant, is a gyrating screen. Other methods of separation might move the curve up or down, but probably the shape would not be changed materially.

The quantity of protein recovered per pound of original flakes is given in line 4 of Table I. These values multiplied by 100 give the results in percentages or in pounds per 100 pounds of flakes. The quantity recovered per pound of flakes increases with increasing water-flake ratio and becomes nearly constant at higher ratios. Related information on dissolved solids in whey, recovered mash, and suspended solids also appears in Table I.

The recovery of protein is a function of the equipment and method used in the process. The values given for our process could obviously be improved by: (*a*) a press which would reduce the water (as dispersion) clinging to the mash from 88 to 70-75%, (*b*) a spray or water wash following the first separation of dispersion which permits nearly complete recovery of dispersion, or (*c*) a continuous countercurrent extraction.

The removal of suspended solids listed in line 2 of Table I is shown at various rates of centrifugation in the lower portion of Figure 3. Clarification is excellent in all cases.

ECONOMIC CONSIDERATIONS

In the extraction part of the process for producing protein from soybean flakes, it was found that the rate of production in a given size tank was dependent upon the solvent-flake ratio used. For a tank of given capacity, the solvent-flake ratio giving the highest yield is not the one giving the highest rate of production.

The present investigation shows that, to carry out the protein extraction operation in the most profitable manner, a compromise must be reached between high protein yield and rate of production. Other factors which enter into the relationship between solvent-flake ratio and profitable production are cost of the meal, selling price of protein, and selling price of residue. In the design of a new plant, other cost factors, such as water, labor, electricity, etc., will vary with the location and the installation, and must be included in the final calculations. In the following calculation these factors are considered constant; they do not seem to enter significantly into a study of the economic balance of water-flake ratio. Although the following example refers to an extraction tank with a capacity of 2000 pounds, the results serve to illustrate a general principle which holds for a tank of any size.

The yield in pounds of protein and pounds of dry mash for an extraction tank of 2000-pound capacity at various water-flake ratios is shown in Figure 5. The maximum quantity of protein is produced at a ratio of 11 to 1 in spite of the fact that the yield

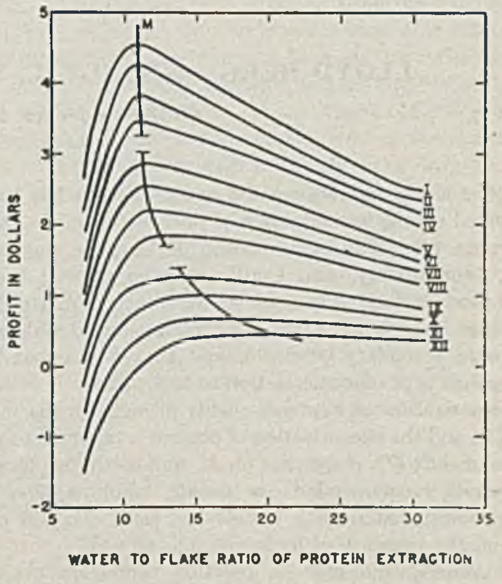

Figure 7. Interrelation of Profit Indices, Water-Flake Ratio, Cost of Flakes, and Selling Price of Protein

Curve No. for Following Price of Flakes, per Lb.				Price of Protein, per Lb.
$0.01	$0.015	$0.02	$0.025	
I	II	III	IV	$0.20
V	VI	VII	VIII.	0.15
IX	X	XI	XII	0.10

of protein per pound of flakes increases with increasing dilution (line 4, Table I). This condition arises because increasing dilution decreases the quantity of flakes that can be processed in a given capacity.

If it is assumed that the dried mash corresponds in value to the original flakes, despite its greater value for industrial uses (*2*, *4*), the cost of the raw proteinaceous material may be computed for a 2000-pound charge as the difference between total cost of original flakes and recovered value of dry mash. Since the quantities of mash and protein vary considerably with the ratio of water to flakes, a drying cost for these materials may be included in the cost index; our calculations included a cost of one cent per pound for both.

Cost indices in dollars for production of protein at various water-flake ratios are shown in curves I, II, III, and IV of Figure 5; they refer to a 2000-pound tank charged to capacity when the cost of flakes is 1, 1.5, 2, and 2.5 cents per pound, respectively. These figures include drying cost for the quantities of mash and protein produced at several ratios. Gross incomes in dollars derived from sale of protein produced in the described charge at various ratios are shown in curves V, VI, and VII (Figure 5) when the selling prices of soybean protein are 10, 15, and 20 cents per pound, respectively. The index of profit accruing from an extraction is obviously measured by the spread between the cost curves and the gross income curves.

The point on Figure 5 where cost curve IV intersects income curve V indicates a zero profit index. This point is of interest since it lies near the point of maximum protein production for a given extraction tank capacity. Maximum separation between these curves and, therefore, an index of maximum profit, lies near a 20 to 1 water-flake ratio. Such behavior in the economy of extraction is caused by variation in participation of flakes, mash, and protein at several water-flake ratios. This is indicated in Figure 6.

A method of plotting data to obtain the proper water-flake ratio for given economic conditions is illustrated by Figure 7; this indicates the separation of the curves shown in Figure 5 and, therefore, the profit indices in dollars at the various ratios. Line *M* is drawn through the maximum in each curve. It is clear from curves I, II, III, and IV that, when the price of protein is 20 cents per pound, the production of protein is most profitable at a water-flake ratio of 11 to 1; at this ratio the maximum quantity of protein is obtained for a given capacity of extraction tank. When the price of protein is 15 cents per pound (curves V, VI, VII, and VIII) the profit index is greater at ratios slightly above 11 to 1; and when the price of protein is 10 cents per pound (curves IX, X, XI, and XII), the proper water-flake ratio for maximum profit increases rapidly with increasing cost of flakes. In the latter case the maxima are located on rather flat curves and are therefore not sensitive to small changes in the ratio, whereas at the highest price for protein a small change in ratio makes an appreciable change in returns.

LITERATURE CITED

(1) Beckel, A. C., Bull, W. C., and Hopper, T. H., Ind. Eng. Chem., 34, 973 (1942).
(2) Belter, P. A., Beckel, A. C., and Smith, A. K., *Ibid.*, 36, 799 (1944).
(3) Jones, D. B., and Gersdorff, C. E. F., *J. Am. Chem. Soc.*, 60, 723 (1938).
(4) McKinney, L. L., Deanin, Rudolph, Babcock, Glen, and Smith, A. K., Ind. Eng. Chem., 35, 905 (1943).
(5) Smith, A. K., and Circle, S. J., *Ibid.*, 30, 1414 (1938).
(6) Smith, A. K., Circle, S. J., and Brother, G. H., *J. Am. Chem. Soc.*, 60, 1316 (1938).

Octane Rating Improvement of Olefinic Gasolines by Isomerization

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ONLY a comparatively small amount of work has been reported on the isomerization of pure olefins in the gasoline boiling range (*4*). The isomerization of 1-hexene was studied by Hay, Montgomery, and Coull (*6*), who showed that the resulting product tended toward the equilibrium mixture, that single-branch isomers were primary products and double-branch isomers were secondary products, and that double-bond shift was the easiest type of isomerization to accomplish.

The isomerization of heptenes yields principally the methylhexenes (*1*), and the isomerization of octenes is reported to yield a double-bond shift (*7*), isooctenes (*5*, *8*), and methylheptenes (*9*). The catalysts recommended are usually alumina, thoria, or kieselguhr impregnated with phosphoric acid. Hay *et al.* (*6*) recommend the presence of hydrogen ions as well.

In an isomerization process, reaction conditions are maintained which tend toward the establishment of thermodynamic equilibrium. This equilibrium is definite for every set of conditions, and at any equilibrium a finite amount of each isomer exists. As the number of carbon atoms in the hydrocarbon increases, the number of isomers is increased. For example, there are six isomeric pentenes, whereas the hexenes number seventeen possible and known isomers. When a large number of isomers are possible, it is unusual for any one isomer to comprise the major portion of the equilibrium mixture under any set of conditions.

The octane ratings of the isomers vary considerably with structure, the straight chain compounds having the lowest value and the highly branched chain, the highest. The shift of the double bond toward the middle of the olefin molecule usually gives an isomer having a higher octane rating. Table I shows the octane ratings, Motor Method Clear, for some of the olefins of the gasoline boiling range. This list represents only a small fraction of the total number of isomers; the data on the remaining olefins are lacking.

Since data on thermodynamics, octane number, and octane number blending are not sufficiently complete to enable a precise calculation of equilibrium values, only a rough estimate can be made for the octane number of the equilibrium mixture of the C_6, C_7, C_8, and C_9 olefins. There is no reason to suppose that any one isomer would predominate at equilibrium conditions at temperatures from 100-600° C.; therefore Table I indicates an octane rating of 80 as a fair approximation. Thus, since most charge stocks are not 100% olefinic, and since complete equilib-

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The olefins in an olefinic gasoline can be isomerized with a minimum of such side reactions as cracking, hydroforming, treating, aromatization, and cyclization. Optimum results are obtained at 375-425° C. reaction temperature and 0.3-1.3 volume per volume catalyst per hour space velocity. The process is characterized by liquid yields in excess of 95%, usually 97-99%. The most suitable catalyst is alumina, maintained at the proper degree of activation by impregnation with anhydrous hydrogen chloride. The life of this catalyst appears to be long if the burn-off is carefully controlled so that the catalyst is thoroughly cleaned but never sintered. Octane number improvement averages approximately four units when a charge stock such as debutanized stabilized distillate is subjected to isomerization. Thermally cracked distillates are the best charge stocks because of their high olefinic content and relatively low octane number.

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rium is not attained, an actual value somewhat below 80 might be expected from an olefin isomerization process.

EQUIPMENT AND PROCEDURE

The equipment used in this work is shown diagrammatically in Figure 1. Olefinic feed stock was charged from a 5-gallon bottle equipped with a siphon which was connected to a 2-liter graduated separatory funnel. The charge bottle was weighed before and after each run, the level of liquid in the separatory funnel being kept the same. Two pumps were used during the course of the investigation. The first one used was a slurry pump equipped with a neoprene tube. A needle valve was installed in the line to maintain a back pressure of about 5 pounds per square inch gage on the pump in order to eliminate pulsation of flow. Subsequently this pump was replaced by a small stainless steel bellows pump (*2*).

The reactor was made of a piece of 2.5-inch Pyrex tubing and had a capacity of about 1600 ml. It was equipped with four thermowells which extended to about the center of the tube. The reactor was surrounded by an iron furnace heated by two 1000-watt electric heaters, one for the preheater section and one for the reactor section. Usually 800 ml. of catalyst were packed between two layers of half-inch Berl saddles. The reactor was equipped with several adapters so that more than one liquid (or gas) could be introduced simultaneously. An electrically heated vessel, 10 inches high and 4 inches in diameter, was attached to the bottom of the reactor; the vessel was filled with clay and/or bauxite for cleaning and dehalogenating the treated gasoline. The product was condensed first by cold water and then by a dry ice-trichloroethylene mixture and collected in a tared flask.

Pump rates were established to give the desired space velocity, and the temperature was controlled so that the reactor averaged about the desired temperature. The highest temperature recorded was usually 25-30° C. above the reported average temperature.

Uncondensable gas was measured by a wet test gas meter before being passed out of the exit line.

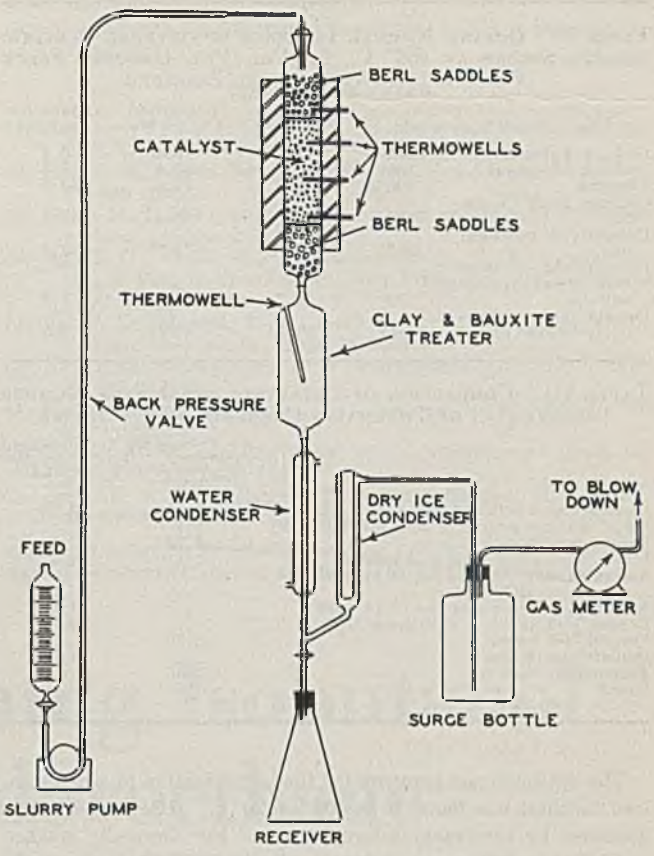

Figure 1. Diagram of Equipment

CHARGE STOCKS AND CONDITIONS

An important consideration was the selection of a charge stock. The principal aim of this work was the isomerization of olefins with a minimum of side reactions such as aromatization, cracking, cyclization, treating, and hydroforming to improve the antiknock octane rating. Therefore a good charge stock to use was one with a high olefin content, especially one containing olefins of the nonbranched type boiling in the gasoline range. This requirement was best fulfilled by a thermally cracked distillate. A catalytically cracked gasoline does not respond so well to the process because it has already been isomerized to some extent.

Thermodynamic considerations indicated an upper limit to the octane number obtainable by olefin isomerization. Then, the lower the octane number of the original charge, the greater the possibility for improvement by means of this isomerization. Table II shows the improvement obtained by olefin isomerization with a number of different charge stocks, using as catalyst alumina impregnated with anhydrous hydrogen chloride. The hexene and heptene mixtures were prepared by dehydrating *n*-hexanol and 2-heptanol over bauxite at 400° C. and 0.75 vol./vol. cat./hr. The *n*-octene was obtained from the Connecticut Hard Rubber Company. In the extreme case of 1-octene the greatest improvement was obtained because the difference between the original octane number, 36.8, and the equilibrium value, approximately 80, was greatest. On the other hand charge stocks already possessing a high octane number, such as the codimer or the polyform distillate, showed relatively little improvement because the olefin content already has an octane number approximately that of the equilibrium value. Of the commercially important stocks, thermally cracked stabilized distillate is benefited most by this process. This would be expected since it contains a high percentage of olefins with a relatively low octane number. Since there was little difference in octane number improvement in the range of space velocities investigated (0.18-1.6 vol./vol. cat./hr.), 0.5 vol./vol. cat./hr. was arbitrarily chosen (Table II).

Table I. Octane Numbers of Some Olefins of the Gasoline Boiling Range (*3*)

Olefin	Octane No., Motor Method Clear
2-Hexene	78
2-Methyl-2-pentene	78
3-Methyl-2-pentene	79
3,3-Dimethyl-1-butene	94
2-Methyl-1-hexene	75
2-Methyl-2-hexene	84
2,3,3-Trimethyl-1-butene	89
1-Octene	35
2-Octene	57
3-Octene	68
4-Octene	74
3-Methyl-1-heptene	66
6-Methyl-1-heptene	63
2-Methyl-2-heptene	71
3-Methyl-2-heptene	74
6-Methyl-2-heptene	66
2,3-Dimethyl-1-hexene	84
2,4,4-Trimethyl-1-pentene	86
2,4,4-Trimethyl-2-pentene	89
3,4,4-Trimethyl-2-pentene	86
3-Methyl-1-octene	84
2-Methyl-2-octene	84

Table II. Octane Number Increase of Several Olefinic Charge Stocks at 400° C., 0.5 Vol./Vol. Cat./Hr. Space Velocity, and Atmospheric Pressure

Charge Stock	Olefin, %	Original Octane No.	Isomerized Octane No.	Octane No. Increase
1-, 2-, & 3-Hexene	100	79.1	79.4	0.3
1-, 2-, & 3-Heptene	100	73.4	80.0	6.6
1-Octene	100	36.8	75.0	38.2
Codimer from C_4 olefins	100	83.0	83.4	0.4
Debutanized polyform dist.	28-31	72-73	74-75	2.0
Debutanized, thermally cracked, coke-still dist.	32	70.3	72.0	1.7
Debutanized, thermally cracked dist.	38-43	66-68	69-72	3-5

Table III. Comparison of Catalysts for Octane Number Improvement of Thermally Cracked Charge Stocks

Catalyst	Av. Octane No. Improvement	
	1-6 vol./vol. cat.	6-12 vol./vol. cat.
$^1/_8$-in. alumina pellets + anhydrous HCl	3.56	3.63
$^1/_8$-in. alumina pellets + aqueous HCl (1 *N*)	3.7	....
$^1/_8$-in. alumina pellets	3.78	2.6
U.O.P. solid phosphoric acid pellets	3.1	2.3
Activated alumina granules (8-14 mesh) + anhydrous HCl	....	2.6
Activated alumina granules (8-14 mesh)	....	1.9
Porocel (4-8 mesh) + anhydrous HCl	....	2.37
Porocel (4-8 mesh)	2.7	....
Bauxite (14-18 mesh)	....	1.35
Alumina on silica gel	−3.56	....
Isocel	−5.4	....

The optimum temperature for the isomerization of a debutanized distillate was found to be 400° ± 20° C. The upper limit is governed by the cracking temperature. For thermally cracked distillates in this range of space velocity, 400° C. is about the limit at which no appreciable cracking will occur. Liquid yields in the range 97-99% were always obtained at these conditions. Below 350° C. the octane rating increase falls off. This is in agreement with the work of Hay *et al.* (*6*) which showed that chain branching decreased as temperature decreased.

CATALYSTS

Table III compares catalysts with respect to improvement in Motor Method Clear octane number of thermally cracked debutanized distillate; the conditions employed were 400° C. reactor temperature and 0.5 vol./vol. cat./hr. space velocity. This table shows two values in some cases because the increase of the octane number decreased as the total volume of charge per volume of catalyst increased. Satisfactory catalysts were solid phosphoric acid (Universal Oil Products Company) and alumina pellets, either untreated or impregnated with aqueous or anhydrous hydrogen chloride. In general, alumina impregnated with anhydrous hydrogen chloride appeared to be the best.

The catalysts capable of improving octane number to some extent were activated alumina granules (8-14 mesh), both with and without anhydrous hydrogen chloride impregnation, and Porocel (4-8 mesh), with and without hydrogen chloride. Catalysts which had little or no effect, or were even detrimental to the octane rating with respect to the charge stocks investigated, were Super Filtrol, bauxite, Isocel, and alumina on silica gel.

The activation of alumina catalyst by means of anhydrous hydrogen chloride is novel and was carried out in the following manner: 800 ml. of catalyst were placed in the reactor and dried at approximately 250° C. The dried catalyst was permitted to cool to room temperature; anhydrous hydrogen chloride was then passed over it for 2 hours, after which time the temperature was gradually raised to reaction temperature (400° C.). The time required for this rise in temperature was 1 hour, making a total of 3 hours for reactivation. The hydrogen chloride was shut off, and the catalyst was purged with dry nitrogen gas for 10 to 15 minutes in order that all excess hydrogen chloride be swept out. The amount of anhydrous hydrogen chloride absorbed on the catalyst at proper activation was determined as follows: 800 ml. of the catalyst were permitted to cool to room temperature and were then titrated with 0.5098 *N* potassium hydroxide; 256.3 ml. were required, which corresponded to 4.04 volumes of hydrogen chloride absorbed per volume of catalyst. The above procedure was repeated using 400 ml. of catalysts; titration of the catalyst required 127.6 ml. of 0.5098 *N* potassium hydroxide solution which corresponded to 4.025 volumes of hydrogen chloride absorbed per volume of catalyst—that is, 0.7 weight % hydrogen chloride. The untreated catalyst showed no acidity.

The alumina impregnated with aqueous hydrogen chloride was prepared by allowing 1000 ml. of $^1/_8$-inch activated alumina pellets to soak in eight successive 600-ml. portions of 1 *N* hydrochloric acid for about 12 hours per portion. After removal of the last portion of hydrochloric acid, the pellets were dried for 16 hours at 130° C.

Table IV shows the relation of octane rating to the volume of charge per volume of catalyst. The charge was thermally cracked distillate isomerized at 400° C., with 0.5 vol./vol. cat./hr. and atmospheric pressure. The values shown represent intervals of approximately 2 vol./vol. cat. The highest octane rating occurred at 2 vol./vol. cat. with a slight decrease in each value as this ratio increased. Alumina impregnated with aqueous hydrogen chloride (run 84) gave the highest octane rating at the start but became deactivated at the end of 20 vol./vol. cat.; regeneration with air (run 85) failed to bring it back to its original activation. Alumina impregnated with anhydrous hydrogen chloride showed almost as good an increase in octane number, and regeneration with air plus reactivation with anhydrous hydrogen chloride restored it to its original activation. As isomerization proceeds, a film of carbon is deposited on the catalyst which must be burned off periodically. This is accomplished by passing a controlled low rate of air over the catalyst, maintaining the temperature at 550° C. or under so that the catalyst is not sintered. The life of a catalyst properly regenerated by this prescribed method appeared to be very long. One batch of alumina catalyst was used for 262 vol. charge/vol. cat. with an air burn-off and reactivation with anhydrous hydrogen chloride for every 9 to 15 vol./vol. cat. throughput. Average octane number improvement was 3.3 for the Motor Method Clear rating, 3.7 for Motor + 1 cc. of tetraethyllead and 3.1 for Motor + 3 cc. tetraethyllead.

When the catalyst was reactivated with anhydrous hydrogen chloride, the isomerized distillate had a chlorine content averaging 0.05%. The adverse effect of chlorine in the distillate, particularly in relation to lead susceptibility, was shown when the product gave octane rating increases averaging 2.7, 0.8, and 1.6 units for Motor Method Clear, Motor + 1 cc. of tetraethyllead, and Motor + 3 cc. of tetraethyllead, respectively. To remedy

Table IV. Effect of Throughput on Octane Number

Run No.	82	84	85	87	88
Catalyst	U. O. P. solid phosphoric acid	Alumina + aqueous HCl	Catalyst from 84 regenerated with air	Alumina + anhydrous HCl	Catalyst from 87 regenerated with anhydrous HCl
Octane No. of charge	67.8	67.8	67.8	67.8	67.8
Octane No. of product					
1	72.1	73.1	70.0	72.4	72.0
2	72.0	71.8	70.5	71.1	71.8
3	71.4	72.4	70.1	71.1	70.9
4	70.8	72.1	69.8	71.3	70.2
5	70.4	71.9	69.8	70.6	70.3
6	70.4	71.5	69.9	70.6	70.0
7	70.2	71.5	69.9	70.3	69.9
8	70.3	70.9	70.0	70.4	69.9
9	70.1	70.9	69.3	69.9	69.9
10	69.5	70.7	69.3	69.9	70.0
11	69.2	70.0	69.6	70.2	....
Composite	70.4	71.0	69.8	70.9	70.5

this difficulty, a clay and bauxite treatment at 250° C. was instituted for the purpose of degumming, decolorizing, and dechlorinating the product. Bauxite (12-16 mesh) and clay (18 mesh) were used and replaced at the start of each cycle. When thermally cracked distillates were subjected to this clay and bauxite treatment alone, a slight octane rating increase (0.5-1.2) was obtained, probably due principally to the removal of gums.

The sulfur content of the commercial distillates investigated was 0.04-0.06%. No appreciable change in sulfur content was noted in any of the charge stocks, and it is unlikely therefore that any octane-rating change could be attributed to sulfur.

Proof that isomerization of the olefins takes place with only a small amount of side reactions such as cracking, hydroforming, aromatization, or cyclization, and that octane number improvement is due almost exclusively to isomerization, is best shown by the isomerization of pure 1-octene. The improvement in octane rating was 38.2 and 22.4 units for Motor Method Clear and Motor + 3 cc. of tetraethyllead, respectively. A molecular weight determination by the freezing point method, using benzene as the solvent, gave a value of 111 for the isomerized product (octene = 112). The isomerized product was subsequently hydrogenated (100% excess hydrogen) to facilitate analysis; the results showed that the product was 1.7% lighter than C_8, 3.8% dimethylhexanes, 36.0% methylheptanes, 47.6% *n*-octane, and 10.9% residue.

LITERATURE CITED

(1) Arbuzov, Y. A., and Zelinskiĭ, N. D., *Compt. rend. acad. sci. U.R.S.S.*, 30, 717-21 (1942).

(2) Corson, B. B., and Cerveny, W. J., Ind. Eng. Chem., Anal. Ed., 14, 899 (1942).

(3) Doss, M. P., "Physical Constants of the Principal Hydrocarbons", Texas Co., 1943.

(4) Egloff, G., Hulla, G., and Komarewsky, V. I., "Isomerization of Pure Hydrocarbons", New York, Reinhold Publishing Corp., 1942.

(5) Egloff, G., Morrell, J. C., Thomas, C. L., and Bloch, H. S., *J. Am. Chem. Soc.*, 61, 3571-80 (1939).

(6) Hay, R. G., Montgomery, C. W., and Coull, J., Ind. Eng. Chem., 37, 535-9 (1945).

(7) Hugel, G., and Szayna, A., *Ann. combustibles liquides*, 1, 781-836 (1926).

(8) Petrov, A. D., and Cheltsova, M. A., *Compt. rend. acad. sci. U.R.S.S.*, 15, 79-84 (1937).

(9) Zelinskiĭ, N. D., Arbuzov, Y. A., and Batuev, M. I., *Ibid.*, 46, 150-3 (1945).

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Systems Containing Isobutanol and Tetrachloroethane

LIQUID-VAPOR AND LIQUID-LIQUID EQUILIBRIA

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Liquid-vapor equilibrium data at one atmosphere for the binary system isobutanol—1,1,2,2-tetrachloroethane are presented. Solubility data at 25° C. are given for the following ternary systems: isobutanol-tetrachloroethane-water, isobutanol-acetone-water, tetrachloroethane-acetone-water, isobutanol-ether-water, isobutanol-sodium chloride-water, and isobutanol-sodium hydroxide-water. The quaternary system isobutanol-tetrachloroethane-acetone-water was investigated to determine the solubility region within the tetrahedron representing the system.

THE azeotropic dehydration of solutions containing thermolabile compounds, followed by extraction with suitable solvents, presented the problem of separating isobutanol, tetrachloroethane, acetone, and ether from the resulting mixtures. The problem required that hitherto unpublished equilibrium data be determined experimentally. The extent and precision of these data, which are the subject of this paper, were governed by the use for which they were intended.

LIQUID-VAPOR BINARY SYSTEM

The pure components isobutanol and tetrachloroethane were prepared separately by fractionation in a Stedman column; the isobutanol was distilled to give a fraction boiling at 107° C. at atmospheric pressure, and the tetrachloroethane at 146° C. The specific gravity of a mixture of the two components was determined by using calibrated equipment and weighing a pipetted volume. The data for the variation of specific gravity with composition at 25° C. are given in Table I and plotted in Figure 1.

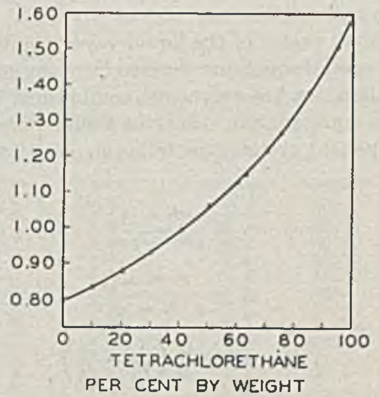

Figure 1. Specific Gravity at 25° C. for Isobutanol—1,1,2,2-Tetrachloroethane System

Table I. Specific Gravity of Isobutanol—1,1,2,2-Tetrachloroethane System at 25° C.

Tetrachloroethane, % by Wt.	Sp. Gr., Actual	Sp. Gr., Calcd.	Tetrachloroethane, % by Wt.	Sp. Gr., Actual	Sp. Gr., Calcd.
0.00	0.796	...	60.40	1.129	1.139
10.15	0.834	0.838	63.55	1.149	1.156
20.26	0.879	0.886	70.40	1.217	1.226
30.40	0.930	0.938	75.15	1.266	1.273
40.50	0.991	0.996	85.06	1.379	1.379
50.45	1.060	1.064	95.05	1.510	1.513
			100.00	1.588	...

Table II. Liquid-Vapor Equilibrium of Isobutanol—1,1,2,2-Tetrachloroethane System at One Atmosphere

Isobutanol in Liquid, Mole %	Isobutanol in Vapor, Mole %	Isobutanol in Liquid, Mole %	Isobutanol in Vapor, Mole %
4.0	20.9	36.5	69.0
7.2	27.0	50.4	78.5
7.0	39.4	71.0	85.5
14.5	48.0	86.0	92.5
23.0	61.1	96.4	98.8

The actual values are in agreement with the calculated values if the volumes of the two components are assumed to be additive (*3*).

The liquid-vapor equilibrium relation was determined in the Othmer apparatus (*1*). The compositions of liquid and distillate were determined by specific gravity after equilibrium had been established. This method of analysis was reliable because of the large difference in the specific gravities of the two components. The experimental values for the liquid-vapor equilibrium relation are given in Table II.

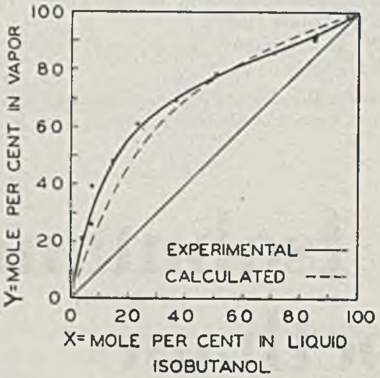

Figure 2. Liquid-Vapor Equilibrium Data for Isobutanol—1,1,2,2-Tetrachloroethane System at One Atmosphere

The theoretical values of the liquid-vapor equilibrium can be calculated by special equations, derived from the general thermodynamic relation for heterogeneous equilibrium known as the Gibbs-Duhem equation (*5*). For the liquid-vapor equilibrium in a two-component system, the following equations can be derived:

$$x_1 = \frac{e^{m_2} - 1}{e^{m_2} - e^{m_1}}$$

$$y_1 = \frac{e^{-m_2} - 1}{e^{-m_2} - e^{-m_1}}$$

where

$$m_1 = \frac{L_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)$$

$$m_2 = \frac{L_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)$$

x_1 = mole fraction of component *A* in liquid phase
y_1 = mole fraction of component *A* in vapor phase
L_1 = latent heat of vaporization of component *A* at T_1, cal./gram-mole
L_2 = latent heat of vaporization of component *B* at T_2, cal./gram-mole
T_1 = boiling point of component *A* at 1 atm., ° K.
T_2 = boiling point of component *B* at 1 atm., ° K.

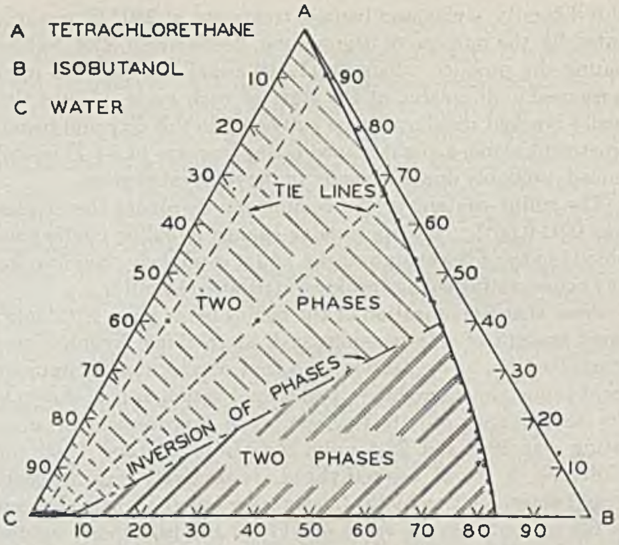

Figure 3. Ternary Diagram for Isobutanol—1,1,2,2-Tetrachloroethane—Water System in Per Cent by Weight at 25° C.

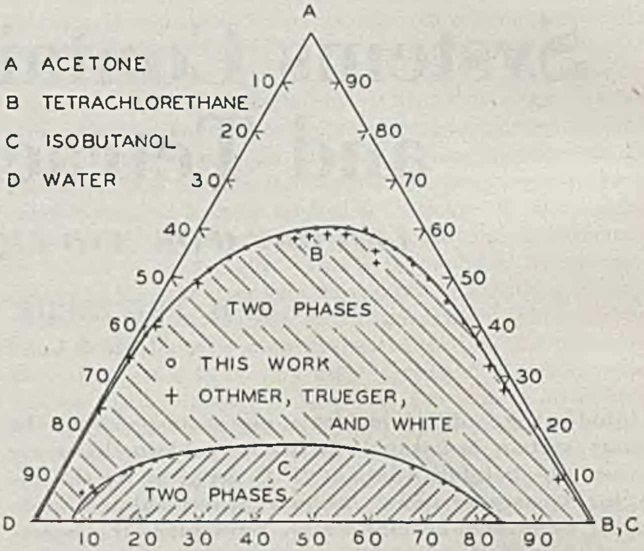

Figure 4. Ternary Diagrams for Isobutanol-Acetone-Water System and 1,1,2,2-Tetrachloroethane—Acetone—Water in Per Cent by Weight at 25° C.

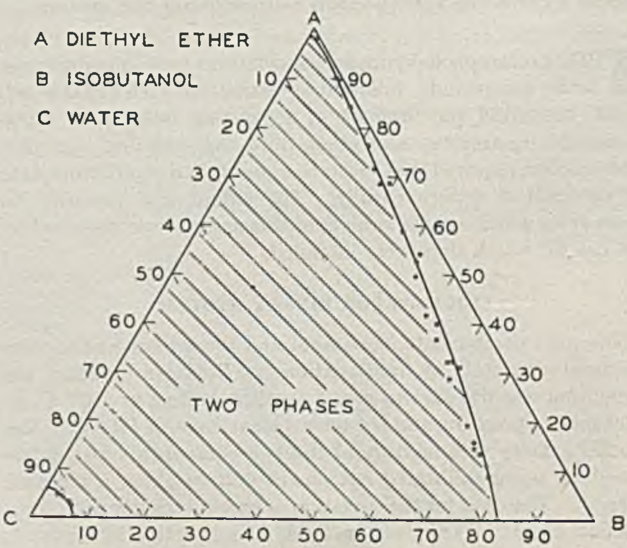

Figure 5. Ternary Diagram for Isobutanol-Ethyl Ether-Water System in Per Cent by Weight at 25°C.

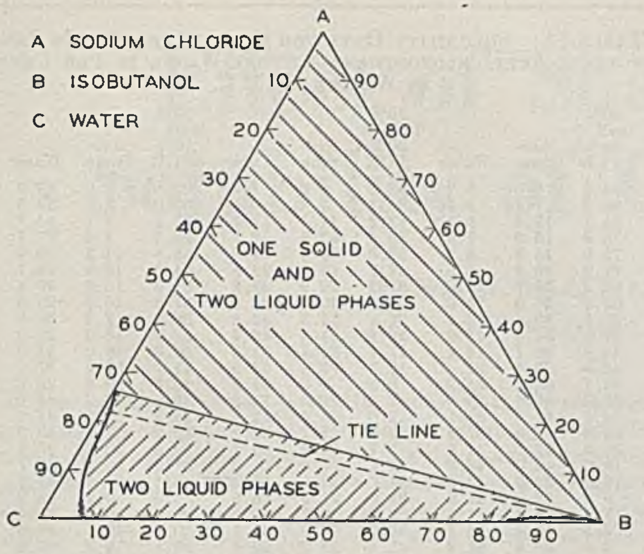

Figure 6. Ternary Diagram for Isobutanol-Sodium Chloride-Water System in Per Cent by Weight at 25° C.

T = boiling point of mixture, ° K.
R = gas constant, 1.987 cal./gram-mole/° C.
e = base of natural logarithms, 2.718

The experimental data, plotted with the theoretical values in Figure 2, show that an azeotrope is not formed by any mixture of isobutanol and tetrachloroethane at atmospheric pressure.

CONDENSED TERNARY SYSTEMS

The ternary diagrams for various combinations of the solvents isobutanol, tetrachloroethane, acetone, and ether with water were determined at 25° C. The boundary of the two-layer region was determined by the cloud point method. The tie lines were determined by preparing a mixture of known over-all composition, shaking it thoroughly to establish equilibrium, and allowing the two layers to separate. The amount of water in the solvent layer was determined by the Karl Fischer method (*4*). The tie line was drawn by projecting a line through the point which represented the over-all composition and the experimentally determined composition of one of the layers.

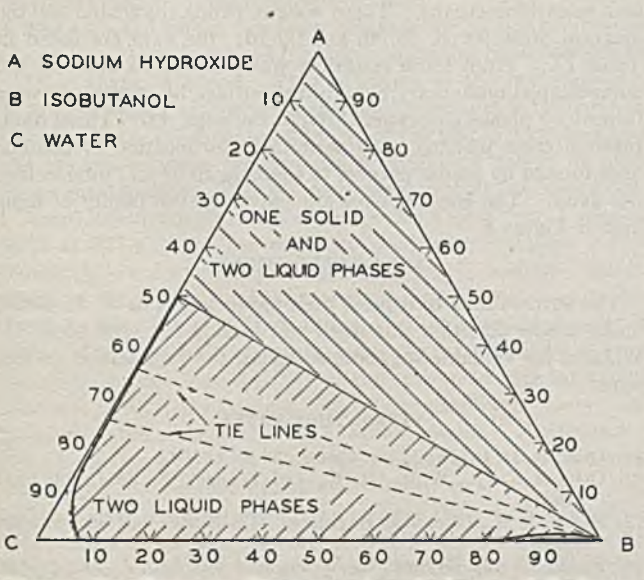

Figure 7. Ternary Diagram for Isobutanol-Sodium Hydroxide-Water System in Per Cent by Weight at 25° C.

Table III. Solubility Data for Isobutanol—1,1,2,2-Tetrachloroethane—Water System in Per Cent by Weight at 25° C.

Isobutanol	Tetrachloroethane	Water	Isobutanol	Tetrachloroethane	Water
0.0	99.9	0.1	59.5	32.6	7.9
0.0	0.3	99.7	62.1	28.5	9.4
19.6	79.4	1.0	63.1	27.8	9.1
27.0	70.7	2.3	68.0	21.8	10.2
30.1	67.3	2.6	71.2	17.4	11.4
30.3	66.9	2.8	73.8	13.6	12.6
35.9	60.7	3.4	74.6	11.0	14.4
42.8	52.8	4.4	76.0	10.6	13.4
45.4	48.7	5.9	78.3	7.3	14.4
49.9	44.2	5.9	79.9	5.0	15.1
50.4	44.0	5.6	83.6	0.0	16.4
54.2	39.0	6.8	7.6	0.0	92.4

Tie Lines

Initial Compn.			Solvent Layer		
Isobutanol	TCE	Water	Isobutanol	TCE	Water
21.0	40.0	39.0	31.0	66.5	2.5
5.0	40.0	55.0	9.0	90.5	0.5

Table IV. Solubility Data for Isobutanol-Acetone-Water System in Per Cent by Weight at 25° C.

Isobutanol	Acetone	Water	Isobutanol	Acetone	Water
73.5	6.0	20.5	18.0	13.4	68.6
69.2	8.4	22.4	15.7	12.7	71.6
62.1	11.6	26.3	13.9	11.9	74.2
52.9	14.5	32.6	12.4	11.1	76.5
41.7	15.9	42.4	11.4	10.3	78.3
34.9	15.8	49.3	10.0	8.8	81.2
35.0	15.7	49.3	8.4	6.2	85.4
29.7	15.4	54.9	7.4	7.0	85.6
26.3	14.9	58.8	6.0	6.0	88.0
21.3	14.1	64.6			

The data for the system isobutanol-tetrachloroethane-water are given in Table III and plotted in Figure 3. In this system the one-phase region is relatively small because neither component is completely miscible with water. The lowest broken line in Figure 3 shows the region in which inversion of the two layers occurs as a result of a change in the specific gravity of the solvent layer relative to the specific gravity of the water layer. The point at which the broken line intersects the boundary for the solvent layer is approximately 39% tetrachloroethane and 54%

Table V. Solubility Data for 1,1,2,2-Tetrachloroethane—Acetone—Water System in Per Cent by Weight at 25° C.

Tetrachloroethane	Acetone	Water	Tetrachloroethane	Acetone	Water
61.3	36.8	1.9	20.9	60.1	19.0
56.1	41.4	2.5	20.8	60.1	19.1
51.1	45.7	3.2	18.2	59.4	22.4
45.7	50.0	4.3	18.1	59.1	22.8
41.3	53.3	5.4	15.2	58.0	26.8
40.7	53.7	5.6	10.5	55.9	33.6
37.0	56.0	7.0	8.3	54.3	37.4
34.6	57.3	8.1	6.1	51.7	42.2
31.9	58.7	9.4	4.8	49.4	45.8
29.8	59.5	10.7	2.1	41.3	56.6
26.4	60.3	13.3	1.5	37.5	61.0
24.2	60.5	15.3	0.8	29.8	69.4

Table VI. Solubility Data for Isobutanol-Ethyl Ether-Water System in Per Cent by Weight at 25° C.

Isobutanol	Ether	Water	Isobutanol	Ether	Water
0.0	6.0	94.0	43.2	49.8	7.0
0.0	98.7	1.3	49.4	41.9	8.7
1.5	98.4	0.1	52.0	40.0	8.0
2.1	4.4	93.5	53.5	36.8	9.7
3.2	4.2	92.6	57.8	32.2	10.0
5.6	3.2	91.2	58.6	32.3	9.1
6.0	2.6	91.4	59.9	28.8	11.3
9.2	90.0	0.8	60.2	31.1	8.7
14.7	84.2	1.1	67.8	19.5	12.7
21.8	76.7	1.5	67.9	19.2	12.9
25.0	71.8	3.2	70.5	15.8	13.7
27.5	68.7	3.8	71.7	14.5	13.8
29.4	68.7	1.9	73.0	13.4	13.6
36.3	58.9	4.8	75.4	11.0	13.6
41.9	54.3	3.8	76.9	9.0	14.1
42.0	52.9	5.1			

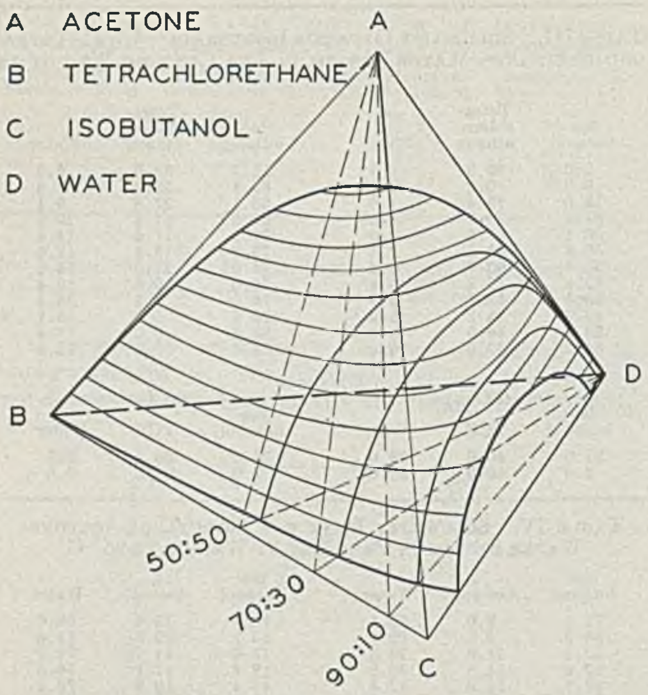

Figure 8. Quaternary Diagram for Isobutanol-Tetrachloroethane-Acetone-Water System in Per Cent by Weight at 25° C.

isobutanol. The data for the systems isobutanol-acetone-water and tetrachloroethane-acetone-water are given in Tables IV and V; the diagrams are shown in Figure 4. Figure 4 also presents data for the latter system obtained by Othmer, White, and Trueger (*2*). The data for the system isobutanol-ether-water are given in Table VI and the ternary diagram is plotted in Figure 5.

Solubility data for the systems isobutanol-sodium chloride-water and isobutanol-sodium hydroxide-water at 25° C. are presented in Tables VII and VIII, and the ternary diagrams are plotted in Figures 6 and 7. The tie lines were determined by the procedure previously described; compositions of the resulting layers were analyzed by either specific gravity or, in the case of sodium hydroxide, by titration.

Table VII. Solubility Data for Isobutanol-Sodium Chloride-Water System in Per Cent by Weight at 25° C.

Isobutanol	NaCl	Water	Isobutanol	NaCl	Water
0.0	26.0	74.0	5.6	3.3	91.1
0.8	25.6	73.6	5.9	2.7	91.4
0.8	24.2	75.0	5.9	2.6	91.5
1.0	22.5	76.5	5.9	2.4	91.7
1.1	21.3	77.6	6.1	2.2	91.7
1.3	19.6	79.1	6.3	1.9	91.8
1.6	16.8	81.6	6.5	1.5	92.0
2.1	14.6	83.3	6.6	1.5	91.9
2.6	11.8	85.6	85.1	0.2	14.7
			88.0	0.3	11.7

Tie Lines

Water Layer			Solvent Layer		
Isobutanol	NaCl	Water	Isobutanol	NaCl	Water
1.2	22.0	76.8	96.5	0.4	3.1

Table VIII. Solubility Data for Isobutanol-Sodium Hydroxide-Water System in Per Cent by Weight at 25° C.

Isobutanol	NaOH	Water	Isobutanol	NaOH	Water
0.0	50.0	50.0	3.5	5.8	90.7
0.1	32.1	67.8	4.5	3.9	91.6
0.4	21.7	77.9	5.2	2.8	92.0
0.9	14.5	84.6	6.2	1.3	92.5
3.1	6.7	90.2	93.0	1.1	5.9

Tie Lines

Water Layer			Solvent Layer		
Isobutanol	NaOH	Water	Isobutanol	NaOH	Water
0.1	35.0	64.9	99.5	0.3	0.2
0.4	24.8	74.8	99.5	0.3	0.2

Table IX. Solubility Data for Quaternary System Isobutanol-Tetrachloroethane-Acetone-Water in Per Cent by Weight at 25° C.

50% IsoB + 50% TCE	Acetone	Water	70% IsoB + 30% TCE	Acetone	Water	90% IsoB + 10% TCE	Acetone	Water
94.8	0.0	5.2	92.3	0:0	7.7	86.8	0.0	13.2
86.3	7.8	5.9	85.7	4.9	9.4	82.0	3.2	14.8
81.1	12.2	6.7	77.2	11.1	11.7	77.2	7.1	15.7
76.8	15.8	7.4	58.4	22.9	18.7	73.9	8.4	17.7
75.0	16.8	8.2	53.3	25.4	21.3	68.8	11.5	19.4
71.0	20.2	8.8	44.7	28.4	26.9	64.0	13.9	22.1
66.3	23.7	10.0	37.3	29.9	32.8	61.5	15.0	23.5
62.5	26.5	11.0	31.6	30.4	38.0	57.3	16.7	26.0
56.5	30.4	13.1	26.4	31.3	42.3	56.0	17.2	26.8
51.4	33.4	15.2	22.8	31.5	45.7	52.7	18.3	29.0
44.9	36.7	18.4	17.1	31.7	51.2	50.0	19.0	31.0
40.2	38.4	21.4	13.3	33.5	53.2	41.7	20.4	37.9
35.1	39.7	25.2	0.8	0.0	99.2	40.7	20.5	38.8
30.0	40.5	29.5	1.5	20.3	78.2	40.8	20.3	38.9
24.5	41.4	34.1	2.0	25.6	72.4	38.3	20.5	41.2
20.8	41.8	37.4	2.6	28.2	69.2	36.2	20.5	43.3
15.8	42.7	41.5	3.7	31.2	65.1	34.5	20.2	45.3
16.0	42.0	42.0	5.7	33.3	61.0	31.9	20.4	47.7
12.3	42.5	45.2	14.7	33.1	52.2	28.5	20.3	51.2
9.8	42.3	47.9	22.0	31.2	46.8	25.9	20.2	53.9
7.0	41.4	51.6	28.3	31.5	40.2	23.5	20.1	56.4
5.5	40.4	54.1	33.9	30.0	36.1	20.0	20.1	59.9
3.9	38.8	57.3	41.4	29.2	29.4	20.1	19.3	60.6
1.4	33.7	64.9				17.5	19.9	62.6
0.9	25.9	73.2				15.4	20.1	64.5
0.5	0.0	99.5				13.8	20.3	65.9
						10.4	20.7	68.9
						9.7	20.9	69.4
						2.7	0.0	97.3
						2.9	1.4	95.7
						3.1	6.9	90.0
						3.4	8.8	87.8
						3.5	12.4	84.1
						3.8	14.1	82.1
						4.0	16.0	80.0
						4.5	17.9	77.6
						5.0	19.8	75.2
						5.6	20.8	73.6
						6.6	21.4	72.0
						14.7	21.0	64.2

CONDENSED QUATERNARY SYSTEM

The quaternary system isobutanol-tetrachloroethane-acetone-water is shown in Figure 8 by an equilateral tetrahedron *ABCD*. The ternary systems represented on the faces of this tetrahedron were described in the previous section. To obtain the limiting mutual solubilities of the quaternary system, measurements were made by the cloud point method at three ratios of isobutanol and tetrachloroethane. These weight ratios, indicated on the diagram, were 50:50, 70:30, and 90:10; the data are listed in Table IX. From these results it was possible to describe the dome-shaped quaternary equilibrium surface by means of traces formed by planes generated through the edge *AD*. These data, through cross plotting, also permitted the location of contour lines formed by planes parallel to the base *BCD* and intersecting the dome. The contour lines are shown by the family of light lines in Figure 8.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Othmer, D. F., Ind. Eng. Chem., 35, 614 (1943).
(2) Othmer, D. F., White, R. E., and Trueger, E., *Ibid.*, 33, 1240 (1941).
(3) Perry, J. H., Chemical Engineers' Handbook, 2nd ed., p. 1354 (1941).
(4) Smith, D. M., Bryant, W. M. D., and Mitchell, J., Jr., *J. Am. Chem. Soc.*, 61, 2407 (1939).
(5) Van Rysselberghe, P., *J. Phys. Chem.*, 38, 1161 (1934).

Effect of Soaps on Mutual Solubility of Organic Liquids

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Whereas solubilization is the incorporation of insoluble material in or upon colloidal micelles, blending is an effect caused by similar forces without necessarily forming colloidal particles. The examples presented show the great effect of soap in making organic liquids such as glycols miscible with hydrocarbon solvents such as carbon tetrachloride and the hydrocarbons themselves. The soap becomes highly soluble in the mixture even if it is only slightly soluble in one or both of the solvents separately. Blending is illustrated with diagrams and data for soaps with propylene glycol and benzene. Methyl alcohol and cyclohexane show similar behavior. Of the soaps, potassium and sodium stearate are most effective, since they are even more powerful blenders than sodium oleate. Twelve per cent sodium oleate suffices to make benzene and propylene glycol miscible in all proportions at room temperature.

SOAPS strongly enhance the mutual solubility of liquids. A few examples of this effect, mainly involving phenolic compounds, have been the subject of investigation (*1, 9, 12, 13*). In all of the systems studied, however, water was one of the liquids employed as solvents, and, because of the colloidal behavior of soap in aqueous solution, the results are difficult of interpretation. The data presented in the present paper are based chiefly on a study of the mutual solubility of the pure organic solvents, benzene and propylene glycol. This system offers advantages for accurate study. The upper critical solution temperature, T_c, is not very high (near 80° C.), and the refractive indices of the two liquids are fairly widely separated. Moreover, one of the authors showed (*5, 7*) that any such glycol-hydrocarbon solvent mixture forms a powerful solvent for soap.

The accepted theory has been (*10*) that the mutual solubilities of two liquids are increased if a third substance, highly soluble in each of them, is added. This is known as the influence of a mutual solvent. If, however, the third substance is insoluble in either or both, the mutual solubility of the pair is decreased and the critical solution temperature is gradually raised or even made unattainable. This is sometimes referred to as salting out.

Soaps are strikingly insoluble in benzene (less than 1 part in 1000 at 20° C.) and are not very soluble in propylene glycol (about 1% sodium stearate and about 12% sodium oleate). Data on the system benzene-propylene glycol are of interest because its behavior is contrary to the commonly accepted point of view. The experimental results show that the addition of soap increases the mutual solubility of the system to such an extent that the two liquids become completely miscible at room temperature in the presence of 14% of sodium oleate. The solutions thus formed are optically clear and nonfoaming, and they pass unchanged through an ultrafilter. Stearic acid and oleic acid produce even more pronounced blending than sodium stearate and sodium oleate, respectively, probably because the effects described here are supplemented by the Timmermans effect; for example, the critical solution temperature of a 40-60 benzene-propylene glycol mixture becomes 53.8° and 43.3° C., with the addition of 5% sodium stearate and stearic acid, respectively.

The materials used were the best quality of pure anhydrous chemicals available and were further purified. Most of the measurements were made by mixing the ingredients in various proportions by weight, heating the system in a sealed tube until it was homogeneous, and recooling until the solubility was just exceeded. Overshooting does not occur when a second liquid phase is being formed, and the point of complete solution was readily noted. Some of the measurements were derived by direct analysis of one or both of the mutually saturated layers. Equilibrium could be attained merely by blending, and a clear solution obtained without heating the systems above the point of complete solution.

The results are presented in Tables I, II, and III and Figures 1 and 2. When only two components are present, they are given in per cent by weight. Added soap is expressed as per cent by weight of the total system, even though the ratios of benzene and glycol, given in parts by weight, add up to 100.

MUTUAL SOLUBILITY

The data in Table I, presented graphically in Figure 1, show that upon the addition of soap the mutual solubility is greatly increased and the critical solution temperature, T_c, is progressively lowered, until the benzene and propylene glycol become

Table I. Effect of Addition of Sodium Oleate on Mutual Solubility of Propylene Glycol and Benzene, Showing Minimum Temperature at Which Each System Becomes a Single Homogeneous Phase

Solvent Compn., Glycol:Benzene	Temp., ° C.
No Added Soap	
1.01:98.99	28.0
2.02:97.98	56.0
3.00:97.00	63.9
3.97:96.03	67.4
4.97:95.03	68.8
9.98:90.02	75.0
17.6:82.4	78.0
20.2:79.8	78.7
25.3:74.7	79.8
30.4:69.6	79.6
40.3:59.7	79.7
50.5:49.5	78.2
60.5:39.5	73.7
67.2:32.8	66.8
68.2:31.8	64.2
69.8:30.2	63.3
80.1:19.9	35.6
82.7:17.3	20.0[a]
1% Sodium Oleate	
10:90	71.3
25:75	78.5
40:60	78.4
50:50	77.3
65:35	67.8
77.8:22.2	42.0
3% Sodium Oleate	
9.96:90.04	58.5
17.2:82.8	63.7
23.8:76.2	68.3
39.2:60.8	73.0
57.1:42.9	67.9
71.1:28.9	50.2
5% Sodium Oleate	
10.4:89.6	28.8
19.8:80.2	52.9
39.5:60.5	64.8
48.7:51.3	64.8
58.5:41.5	59.3
69.8:30.2	43.4
7.5% Sodium Oleate	
23.9:76.1	42.3
39.4:60.4	54.2
48.4:51.6	53.7
68.6:31.4	32.0
10% Sodium Oleate	
29.2:70.8	36.7
38.8:61.2	42.6
44.3:55.7	43.6
49.0:51.0	42.5
58.4:41.6	35.5
70.5:29.5	13.1
15% Sodium Oleate	
29.2:70.8	9.0
39.2:60.8	14.7
44.4:55.6	14.7
48.7:51.3	13.6
61.5:38.5	8.4

[a] Data obtained by cloud point method.

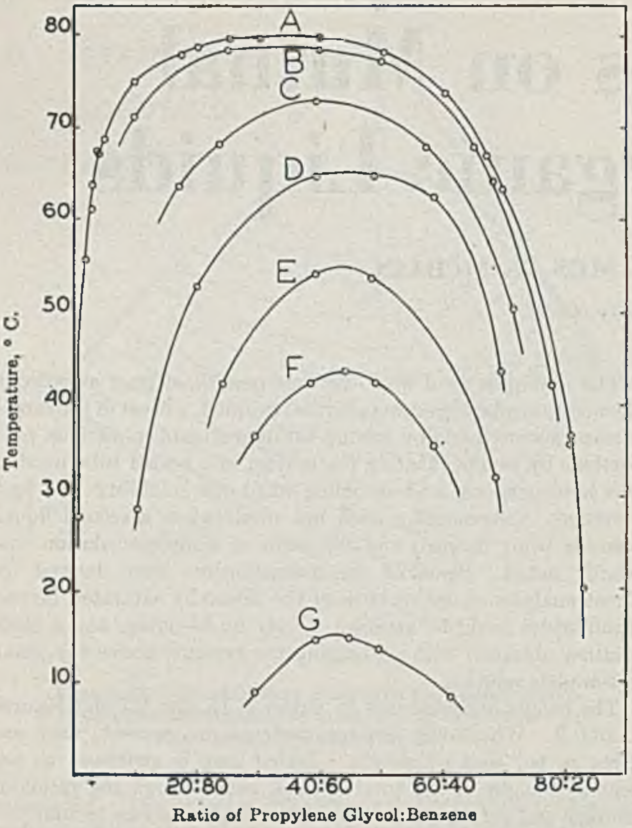

Figure 1. Effect of Added Sodium Oleate in Increasing Mutual Solubility and in Lowering Critical Solution Temperature of Propylene Glycol-Benzene System

Sodium oleate is given as per cent by weight of total system: *A*, no soap; *B*, 1%; *C*, 3%; *D*, 5%; *E*, 7.5%; *F*, 10%; *G*, 15%.

Table II. Effect of Addition of Various Soaps on Mutual Solubility of Propylene Glycol and Benzene, Showing Minimum Temperature at Which Each System Becomes a Single Homogeneous Phase

Solvent Compn., Glycol:Benzene	Temp., ° C.	Ratio, Propylene Glycol:Benzene	Temp., ° C.
—5% Sodium Stearate—		—10% Sodium Palmitate—	
29.5:70.5	55.0	25.3:74.7	39.5
37.4:62.6	58.9	29.7:70.3	35.0
49.4:50.6	59.1	39.5:60.5	39.5
58.8:41.2	54.4	49.5:50.5	38.4
		59.8:40.2	29.5
—10% Sodium Stearate—		—5% Potassium Palmitate—	
25.0:75.0	42.7		
27.9:72.1	40.0	20.1:79.9	46.7
40.4:59.6	34.5	29.3:70.7	57.9
50.0:50.0	33.4	37.3:62.7	61.9
58.9:41.1	25.5	59.0:41.0	57.0
—15% Sodium Stearate—		—5% Sodium Myristate—	
29.4:70.6	59.5	24.2:75.8	57.2
39.4:60.6	48.5	38.6:61.4	62.0
49.2:50.8	47.5	48.1:51.9	64.5
59.8:40.2	40.5	57.4:42.6	60.7
—5% Sodium Palmitate—		—5% Sodium Laurate—	
25.0:75.0	54.4	24.5:75.5	62.7
39.2:60.8	62.3	37.9:62.1	68.0
47.9:52.1	61.2	48.4:51.6	68.0
57.9:42.1	56.9	56.9:43.1	64.1

completely miscible at ordinary temperatures. Moreover, the range of immiscibility below T_c becomes strikingly narrower. The curves show a drift in T_c toward the glycol-rich side; this is similar to the drift of the viscosity minimum in mixtures of cosolvents (*6*, *8*) toward the better solvent as the concentration of solute is increased.

Table II and Figure 2 show the increase in mutual solubility of benzene and propylene glycol with a series of sodium and potassium soaps. Effectiveness of the soap increases rapidly with increase in the number of carbon atoms; stearate with 18 carbons is almost twice as effective as laurate with 12 carbons, the intermediate members being evenly spaced between. The solubility of soap in glycols, however, is in the reverse order. There is no appreciable difference in blending power between potassium and sodium palmitate. The blending power of a soap is not parallel to its solubility in pure ethylene glycol or in a mixture of equal parts of ethylene glycol and *n*-butyl alcohol. The oleate is much more soluble in either glycol or benzene than is the stearate with the same 18-carbon chain. The former, however, has less blending power than the latter; in this respect the oleate is approximately equal to the myristate which has only 14 carbon atoms.

The more concentrated system of stearates in Figure 2 differs from that of oleates shown in Figure 1, where increasing oleate exhibits a steadily increasing blending power. When the stearate is increased from 10 to 15%, its blending power is decreased. Even sodium oleate shows this effect at much higher concentrations, where the system becomes semiliquid. In other words, at any given temperature (Figure 3), a minimum concentration of soap is necessary to make the insoluble pair completely miscible; but as the concentration of soap is increased, it reaches a saturation limit. This results in an unusual type of three-component system in which each component is almost insoluble in each of the other two but exhibits a region of miscibility extending like a tongue across the three-component diagrams.

The limited solubility of the soap is reflected in the curves of Figure 2 for higher concentrations of palmitate and stearate. The portions of the curves drawn in full have the usual significance of the boundaries of a completely homogeneous liquid; the dotted extensions of these curves on the left hand or benzene side of the diagram show that in this region the excess of solid soap has separated out.

Sodium stearate is a more powerful blending agent than sodium oleate. Table III presents the results for the mutual solubility of benzene and propylene glycol in the presence of sodium oleate or sodium stearate; the values given are minimum temperatures of complete miscibility, T_c, as they are progressively lowered by addition of soap. Also, at each value of T_c there is calculated the additional number of gram moles of benzene and propylene glycol brought together, as compared with the amounts present in the two separate, mutually saturated layers containing no soap at that temperature. For example, the first line of Table III shows that, after the addition of 5% sodium oleate, the maximum of the solubility curve lies at about 56% benzene and 44% propylene glycol (considering the total solvent as 100%), and also that the critical solution temperature has been lowered from 80° to 65.3° C. At 65.3° in the absence of soap, the solubility is 32% benzene in 68% propylene glycol, and 3.5% propylene glycol in 96.5% benzene. Hence the soap has increased the solubility of benzene by 24% and that of the glycol by 40.5%. These additional amounts brought

Table III. Effect of Soaps on Critical Solution Temperature, T_c, of Propylene Glycol and Benzene

Soap	% Added	T_c, ° C.	Composition at T_c, Moles/Mole of Soap: Glycol	Composition at T_c, Moles/Mole of Soap: Benzene	Additional Moles Blended per Mole Soap: Glycol	Additional Moles Blended per Mole Soap: Benzene
Sodium oleate	5.0	65.3	33.5	41.5	31.8	26.1
	7.5	55.0	21.7	26.9	21.0	19.3
	10.0	43.6	15.8	19.6	15.6	15.3
	15.0	15.3	9.64	12.7	9.5	11.2
Sodium stearate	5.0	59.9	33.7	41.7	32.6	29.3
	10.0	35.5	16.3	19.4	16.0	15.3

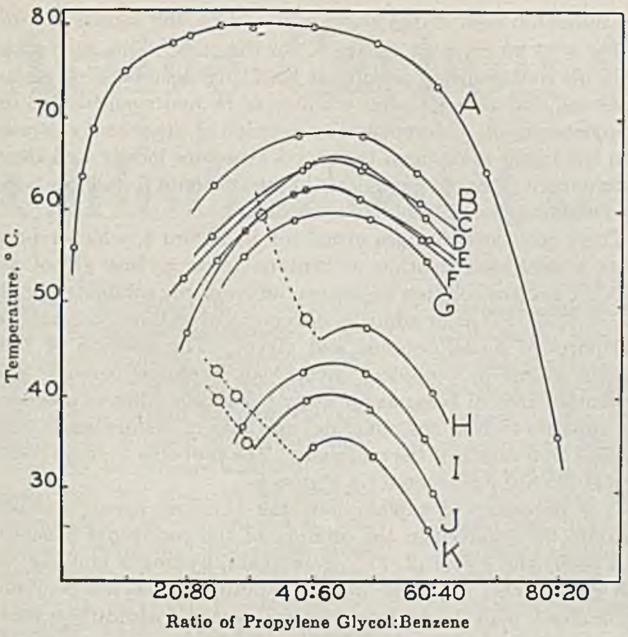

Figure 2. Effect of Added Sodium and Potassium Soaps in Increasing Mutual Solubility and in Lowering Critical Solution Temperature of Propylene Glycol-Benzene System

The curves bound single liquid phases, but the dashed lines are boundaries where excess solid soap has separated. Added soap is per cent by weight of the total system, as follows: *A*, no soap; *B*, 5% sodium laurate; *C*, 5% sodium myristate; *D*, 5% sodium oleate; *E*, 5% potassium palmitate; *F*, 5% sodium palmitate; *G*, 5% sodium stearate; *H*, 15% sodium stearate; *I*, 10% sodium oleate; *J*, 10% sodium palmitate; *K*, 10% sodium stearate.

into solution equal 30 moles of benzene and 18 moles of propylene glycol per molecule of sodium oleate present.

Figure 3, drawn from the data of Table IV, illustrates the type of equilibria existing in the three-component system. Data for the upper curve were obtained in either of two ways; by directly measuring the solubility of sodium oleate in known mixtures of the two solvents (represented by crosses), or by preparing solutions of two solvents (at a definite ratio) containing soap concentrations that decreased by intervals of 1% (represented by circles). In the latter method the data in Figure 3 correspond to the compositions at which the solutions just failed to remain clear. The lower curve was obtained by noting the cloud point on addition of benzene to known compositions (represented by circles). The tie lines were obtained by analytical methods. Each symbol on a tie line represents the composition of a prepared mixture, the ends of which, shown by the corresponding symbols, represent the observed compositions of the two liquid layers into which this mixture separates.

Figure 3 refers to 20° C. only. The lower part of the figure represents the two liquid layers as they were progressively blended upon addition of soap, much as chloroform and water are blended upon addition of acetic acid. Then appears the region of clear homogeneous liquid containing all three components; the upper boundary results from the limited solubility of soap in either of the pure solvents or in their mixtures. A minimum concentration of soap is necessary for a homogeneous solution; in other words, at room temperature a 15% sodium oleate solution can be prepared with a glycol concentration anywhere between 25 and 95%, but a 5% oleate solution requires more than about 75% glycol, except at elevated temperatures.

TABLE IV SOLUBILITY OF SODIUM OLEATE IN BENZENE-PROPYLENE GLYCOL MIXTURE AT 20° C.

Solvent Compn., Benzene:Glycol	Soly., G./100 G. of Soln.	Solvent Compn., Benzene:Glycol	Soly., G./100 G. of Soln.
100: 0	< 0.1	60: 40	20.85
90:10	8.05	40: 60	22.97
80:20	12.53	20: 80	23.97
70:30	16.48	0:100	10.82

It is an interesting corollary of the data of Figure 3 that when impure materials are used, blending may be much more pronounced. If, for example, two materials appear mutually insoluble, and one contains a blending agent as impurity, it might be impossible to prepare a dilute solution of the latter in the second liquid, whereas a concentrated solution could be prepared because sufficient blending agent is present. Such behavior is frequently observed (*4, 11*) with many lyophilic solutes such as synthetic and natural resins, cellulose derivatives, proteins, etc., and is generally explained as a result of colloidal effects. A similar situation may exist in the manufacture of lubricating grease (*3*) where a minimum amount of water is found necessary to dissolve calcium soaps in the mineral oil.

DISCUSSION

The data presented here show the mutual blending of two partially immiscible liquids by the addition of soap as a blending agent. The soap itself is insoluble in one of the liquids and soluble only to a limited extent in the other; yet when it is added in sufficient amount, it makes the liquids completely miscible. The essential mechanism of this effect may be derived from a consideration of van der Waals forces, of polar and dipole forces, and of hydrogen bonding; these forces result in bringing together like molecules and like parts of molecules.

These same forces are responsible for the formation of association colloids and for the solubilization of otherwise insoluble materials by means of such colloidal particles. It has been definitely shown that in aqueous solutions the molecules of colloidal electrolytes associate end to end in pairs and side by side in

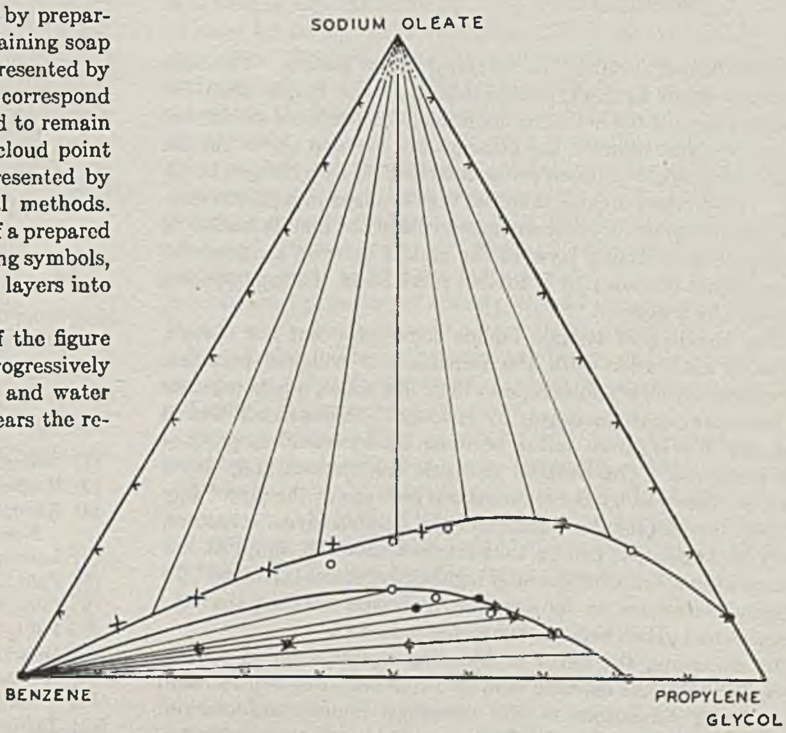

Figure 3. Limited Range of Clear Solutions of Benzene and Propylene Glycol Obtained by Blending with the Proper Proportions of Sodium Oleate at 20° C.

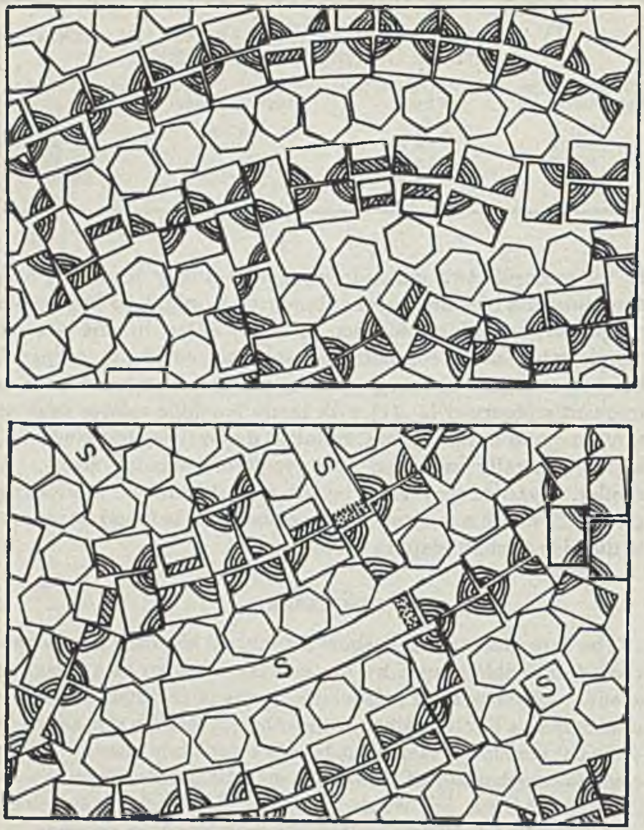

Figure 4. Diagram of a Cross Section of a Saturated Solution of Benzene in Propylene Glycol (*above*) and the Completely Miscible Solution Resulting from Addition of Sodium Stearate as Blending Agent (*below*)

The benzene molecules are represented as hexagons, 5.7 × 5.7 × 4.5 Å. and the propylene glycol as rods, 6 × 4.5 × 4.5 Å. The shaded portions show average position of polar groups, and the sodium stearate as somewhat flexible rods, 26 × 4.5 × 4.5 Å., marked *S*. The dotted areas indicate polar ends.

parallel layers, forming the so-called x-ray leaflets. The long spacings given by x-ray diffraction are even longer than the double length of the detergent molecule, because there are further layers of water between the polar groups exposed on the double leaflet of detergent. Such water must be held by hydrogen bonding. Then when organic material is solubilized in aqueous solution of detergent, it is incorporated within the double leaflets of detergent as a further layer in the middle between the nonpolar ends This is shown by a further increase in the long spacing revealed by x-rays.

The blending of organic liquids sometimes, but not always, involves association with the formation of colloidal particles. Propylene glycol is a polar liquid which, like water, is held together at lower temperatures largely by hydrogen bonding in addition to van der Waals forces acting between the hydrocarbon parts of the molecules. The benzene molecule can contact and, therefore, be dissolved by the hydrocarbon portions of the glycol only if there is room for the benzene in the bonded glycol structure. Very little benzene can be thus inserted into the liquid at low temperatures, but at sufficiently high temperatures (above 80° C.) thermal vibration so loosens the hydrogen bonding that the benzene and glycol become completely miscible.

In discussing the effect of blending agents such as sodium stearate, as in the extreme case of Table III, it is well to recall the actual dimensions of the molecules under consideration: benzene, 4.5 × 5.7 × 5.7 Å.; propylene glycol, cross section 4.5 × 4.5 Å., 6 Å. long; sodium stearate, cross section 20.5 square Å., 26 Å. long. If calculated as a rod 4.5 square Å., the minimum area of the stearate would be 468 square Å., together with an extra 41 square Å. for the ends. One such soap molecule could contact directly at least seventeen benzene molecules and still have its polar end free to be hydrogen-bonded to propylene glycol. Moreover, the insertion of the coated stearate into the liquid must open the glycol structure locally and thus expose more glycol to benzene; this can account for all the benzene and propylene glycol that is blended.

These considerations are visualized in Figure 4, which represents a saturated solution of benzene in propylene glycol at 65.3° C. and the solution at the maximum of the solubility curve (T_c = 65.3° C.) after addition of 5 parts of sodium stearate to 100 parts of mixed benzene and glycol. The position of the oxygen atoms of propylene glycol can fluctuate beween two extremes; that of being as far away from each other as possible (at opposite ends of the molecule) and that of being almost side by side on one side of the molecule. The probable average position is the one represented by Figure 4.

It is necessary to explain how the blending agent, sodium stearate, is dissolved in the mixture of the cosolvents benzene and propylene glycol (*5*, *7*). Here again, hydrogen bonding to the glycol holds the polar head in solution, while the benzene molecules bridge the hydrocarbon tail to the hydrocarbon part of the propylene glycol molecule. Such an arrangement of continual fluctuation and exchange of molecules and positions, although it is merely an average dynamic state, must be much more stable for a long heavy molecule such as stearate than for a lower homolog of the series such as acetate or even laurate.

The forces here adduced are the same as those which produce colloidal micelles of soap in aqueous solution. The micelles consist of layers of molecules packed side by side and end to end; there are layers of water between polar ends of the soap molecule and layers of any solubilized hydrocarbon, etc., between the nonpolar ends. This structure in aqueous solution has been established (*2*) by Hess *et al.* and Thiessen *et al.* in Germany, and by Harkins *et al.* and investigators at the Shell Development Company and Stanford University in this country.

In developing our theory of soap solubility we observed that other compounds in addition to the glycols possess the power to solvate the polar part of soap. Some of these compounds are phenol, cresol, terpineol, cholesterol, and methyl alcohol. Methyl alcohol possesses some interesting features. It has limited solubility with hydrocarbons like hexane and cyclohexane, and the effect of soap is to lower T_c according to our theory in contrast to the generally accepted point of view. T_c is lowered considerably so as to make methyl alcohol miscible with cyclohexane at room temperature on addition of a sufficient soap concentration (for example, 11.7% sodium oleate). In fact, all glycol-hydrocarbon solvent systems of limited miscibility show this behavior with soap to a greater or lesser extent. Systems in which the effect is very prominent are ethylene glycol with chloroform, and propylene glycol with carbon tetrachloride.

LITERATURE CITED

(1) Bailey, *J. Chem. Soc.*, 123, 2579 (1923).
(2) Hughes, Sawyer, and Vinograd, *J. Chem. Phys.*, 13, 131 (1945).
(3) Klemgard, "Lubricating Greases", pp. 91-2 and Chap. V, New York, Reinhold Pub. Corp., 1937.
(4) Larson and Greenberg, *J. Am. Chem. Soc.*, 55, 2798 (1933).
(5) Palit, *J. Indian Chem. Soc.*, 19, 271 (1942).
(6) *Ibid.*, 19, 435 (1942).
(7) Palit, *Oil & Soap*, 23, 72 (1946).
(8) Quarles, Ind. Eng. Chem., 35, 1033 (1943).
(9) Smith, *J. Phys. Chem.*, 36, 1401, 1672, 2455 (1932).
(10) Timmermans, *Z. physik. Chem.*, 58, 129 (1907).
(11) Tschirch and Stock, "Die Harze", Band I, pp. 111, 147, Berlin, Gebrüder Borntraeger, 1932.
(12) Weichherz, *Kolloid-Z.*, 49, 159 (1929).
(13) Woodman, *J. Soc. Chem. Ind.*, 52, 185 (1933).

Active Carbon from Chlorinated Coal

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Bituminous coal of various sizes was chlorinated at several temperatures. In the apparatus used (a 36-inch length of $^{3}/_{4}$-inch nickel pipe) 6-20 mesh coal could be chlorinated to a 100% gain in weight in 24 hours. Small amounts of chlorinated hydrocarbons were produced, but the principal product was an activated carbon. After chlorination the coal was powdery in texture and smelled strongly of hydrogen chloride. This material was pelleted with a small amount of hydrolyzed starch as binder. The pellets were baked in the absence of air for 1 hour at 500° C. After baking, the hardened pellets were crushed and sieved to 8-20 mesh size and were steam-activated at 800° C. for 3 hours. As produced, the activated carbon had an apparent density of about 0.5 gram per cc., an accelerated chloropicrin life of 67 minutes, heat of wetting of 12 calories per cc., and a chlorine content of about 0.12%.

THE chlorination of aliphatic compounds has received much attention in this laboratory, and this work has been extended to include aromatic compounds and coal. The purpose of the investigation was to prepare valuable products from the reaction of chlorine with coal. At the outset it was a moot point whether these products would be chlorinated hydrocarbons or active carbon or, possibly, both. The investigation culminated in the development of means for preparing an excellent gas-adsorptive carbon; the indications are that this process may yield small amounts of valuable chlorinated compounds as by-products. Carbon tetrachloride and hexachlorobenzene were identified in the exit tube from the chlorinator but were not determined quantitatively.

Only a small amount of work has been done on the chlorination of coal with the aim of preparing valuable products from it. Most of the literature on this subject deals with the value of halogens as an analytical tool for the study of coal. Attempts have been made to produce an active carbon from coal without chlorine (*2, 3*) and with chlorine (*1, 2A, 5, 6, 7, 8, 10, 11*). These processes do not describe the properties of the carbon in terms of modern tests or else produce a carbon of doubtful value. There have been only a few attempts to obtain chlorinated products from coal. Of these the most significant is that of Weiler (*9*). He treated coal with chlorine and antimony pentachloride for 6 days at 200° C., then 4 more days at 400° C. The volatile products obtained were carbon tetrachloride, hexachloroethane, hexachlorobenzene, and other unidentified, highly chlorinated hydrocarbon derivatives. Even under this drastic treatment the volatile products accounted for only 5% of the carbon originally present in the coal.

MATERIALS AND APPARATUS

Coals. Four 100-pound samples were obtained from a local coal company. The description of these samples were: (1) Sewell seam coal from White Oak Coal Company, McDonald, W. Va.; (2) Island Creek Pocahontas Coal from Island Creek Coal Company, Holden, W. Va.; (3) anthracite from Avoca Coal Company, Getz, Pa.; (4) Indiana coal from Walter Bledsoe Company, Terre Haute, Ind. The analyses of these coals follow:

Coal No.	1	2	3	4
Moisture, %	0.5	0.8	1.4	7.0
Volatile matter, %	24.4	37.0	5.9	34.0
Fixed carbon, %	72.7	54.7	83.6	52.7
Ash, %	2.4	7.5	9.1	6.3
Sulfur, %	0.3	1.0	0.8	2.2
Calorific value, cal./gram	8700	6300	7390	6500

At first, attempts were made to prepare chlorinated compounds by heating coal with chlorine in a sealed nickel pipe, but the amounts of chlorinated carbon compounds obtained at the pressure which the pipe would stand were negligible. After this phase of the work was explored to some extent, it was decided to attempt to prepare activated carbon.

Chlorinator. As Figure 1 shows, the chlorinator consists of a vertical nickel tube, *A*, which passes through a salt bath, *B*. The bath is heated by resistance wires around the outside, *C*, and is well insulated. Nickel tube *A* is connected to an iron, water-cooled condenser, *D*, which, in turn, is connected to a one-liter suction flask. The flask leads to a flowmeter which connects to a waste vent. The salt bath contains a thermocouple well, *E*, to facilitate temperature measurements.

Steam Activator. Material to be activated was placed in a stainless steel (18-8) chamber (Figure 2), which was in the form of a rectangular parallelopiped, 2 × 2 × 8 inches. This chamber connects at both ends to stainless tubing which rests in iron tees, *H*, used as bearings. One of the tee supports, *J*, is held in place by an iron plate (not shown) held with three bolts and wing nuts. The wing nuts are easily removed, the plate is lifted, and support *J* slid out. The chamber separates at the indicated point, and the larger portion can be readily removed for charging or emptying. One of the two open tubes has a stainless steel thermocouple well through it, *K*, and through the other there is a steam inlet tube, *L*. Both of these tubes are fitted with welded collars to prevent coal granules from falling out during rotation while activation is going on. The activation chamber is heated by wires wound around the furnace walls, *N*, and is kept from moving longitudinally by spacers, *O*, and transite insulators, *P*. During a run the furnace is heated by an electrically controlled Adjust-A-Volt. The activation chamber proper is rotated during use by motor *Q*, the speed of which is reduced by two 48:1 reducers in series (only one is shown).

Pellet Press. This apparatus was a hand-operated coal pelleting press described in Cenco Catalogue J. 1941, No. 23770.

Accelerated Chloropicrin Tester and Heat of Wetting Apparatus. Details of this apparatus are given as a chloropicrin (PS) test on charcoal, in Part II of Chemical Warfare Service Pamphlet 2 (Canister and Absorbent Test Methods).

CHLORINATION

A typical run was made on 4-20 mesh (National Bureau of Standards) coal. This size was used because it gained as much weight during chlorination as the more finely ground material and was not so difficult to remove from the chlorinator.

A small nickel tube with a perforated plate on top was placed, plate side up, in the bottom of the chlorinator. This plate

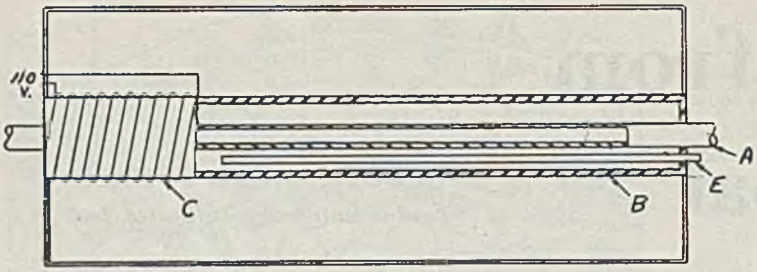

Figure 1. Inside View of Chlorinator

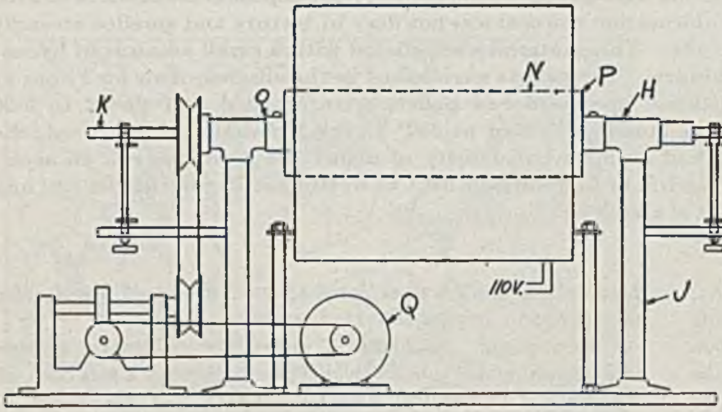

Figure 2. Steam Activator

came just above the chlorine inlet. The bottom cap was screwed tight. A 4-inch tin funnel was placed on the top of the chlorinator, and 100 grams of 4-20 mesh coal were poured in slowly. The top cap was then screwed on firmly. The heating elements were plugged in, and the chlorine was turned on. A record was kept of time, temperature, and chlorine flow (Table IV). After a predetermined time, the heat and chlorine were turned off, and the apparatus was allowed to cool. Early runs indicated that 6-8 hours were needed for the apparatus to cool to a safe handling temperature. To speed the cooling process to about 2 hours, a loop of $^1/_4$-inch o.d. copper tubing was placed in the salt bath, and distilled water was permitted to flow through this tubing to dissipate the heat.

When the chlorinated coal had cooled to about 75° C., the caps and then the coal were removed. In general, the chlorinated product appears much less likely to form a hard cake under conditions of either slow rate of heating or high rate of chlorine flow. A set of data for a typical run is given in Table I.

The product as it came out of the chlorinator was in the form of a fine powder. This powder was made into pellets with a small amount of hydrolyzed starch solution as binder. The pellets were put into a container with a snugly fitting lid, and the container was placed in a muffle furnace, heated to 500° C., and held at that temperature for one hour. This treatment produced pellets which could not be broken by hand. The pellets were crushed in a mortar and sieved to the desired size (6-20 N.B.S.) for steam activation.

Table I. Chlorination Data for Carbon 2-6

Material, Grams		Conditions Time, hr.	 Temp., ° C.	 Cl flow, l./min.
Charge to chlorinator (4-20 mesh)	101	0	25	0.5
Chlorinated coal removed	188	1	130	0.5
Gain in weight (86%)	87	2	160	0.5
Amount pelleted	178	2.3	200	0.5
Lowdex-B (binder soln.)	12	3.0	230	0.5
Pellets (10 g. lost)	180	6.2	220	0.5 (reduced to 0.2)
		21	225	0.2
Pellets after heating to 500° C. for 1 hr.	128	25	225	0.2
Pellets crushed and sieved (6-20 N.B.S. sieve)	79	45	230	0.2

STEAM ACTIVATION

The material was placed in the activation chamber, which was fixed in position. The chamber was rotated by an electric motor through two 48:1 speed reducers in series at a rate of about 1 revolution in 3 minutes. In its first design the chamber was rotated forty-eight times as fast, and losses of carbon through the ends, past collars *N*, were high; when another reducer was added, these losses became negligible. After the chamber was put into position, the heating element was turned on and a water boiler heating coil connected. Steam was generated in a 1-liter Büchner flask heated by a 6-inch electric hot plate. The side arm of the flask was attached with a short piece of rubber tubing to steam inlet tube *L*. After the temperature rose to 400° C., the motor was turned on and rotation was started. When the temperature was about 750° C., the current to the heating element was decreased until it would maintain the furnace at 800° C. Usually about 3 hours were necessary to heat the furnace from room temperature to 800° C. and about as long to cool it to a temperature at which the chamber could be removed.

Table II gives a representative set of data for a steam activation run of one hour.

Table II. Steam Activation of Carbon 2-6 to 2-6-1

Materials		Heating Schedule Time, hr.	 Temp., ° C.	 Time, hr.	 Temp., ° C.
Charge	79 g.	0	25	1.5	810
Removed	41 g.	0.5	330	1.75	815
Water used	150 cc.	0.85	575	2.00	795
		1.25	740	2.3	800
		1.35	788	2.4	800 (heat off)
		1.4	800		

Yield of Activated Carbon. For all coals tested, the gain in weight on chlorination and the loss in weight on baking and activation were of the same order of magnitude. A sample calculation is given for carbon 2-6-1:

100 g. coal
178 g. chlorinated coal
126 g. baked pellets
79 g. granules

188 g. chlorinated coal
126 g. baked pellets
79 g. 6-20 N.B.S. granules
41 g. 6-20 N.B.S. activated carbon

The fines of baked chlorinated coal may be pelleted using the same binder as for the chlorinated coal, and thus all the chlorinated coal eventually can be converted to activated carbon.

$$\text{Conversion:}\quad 100\text{ g. coal} = 41 \times \frac{188}{178} = 42.5\text{ g. activated carbon}$$

$$\text{Yield:}\quad 100\text{ g. coal} = 41 \times \frac{188}{178} \times \frac{128}{79} = 70.0\text{ g. activated carbon}$$

Table III. Chlorination Data

Sample No.	Form Chlorinated	Temp., ° C.	Time, Hr.	Grams of Coal Charged	Grams of Chlorinated Coal Removed
1-1	4-20 mesh	Room	48	80	110
1-2	4-20 mesh	225	21.5	102	180
1-2c	4-20 mesh	225	24	90	170
1-3	$^1/_2$-in. pellets	290	28.5	84	165
1-4	$^1/_2$-in. pellets	390	24	76	98
1-4b	4-20 mesh	380	24	90	143
1-5	4-20 mesh	380	49	94	138
1-5b	4-20 mesh	365	24	95	156
2-1	4-20 mesh	225	47	101	188
2-2	$^1/_2$-in. pellets	220	24	72	136
2-2a	4-20 mesh	225	24	100	176
2-2b	<20 mesh	225	24	100	175
2-2d	4-20 mesh	225	24	100	175
2-2e	4-20 mesh	225	24	100	172
2-2f	4-20 mesh	220	24	100	176
2-2g.	4-20 mesh	225	24	100	169
2-2h	4-20 mesh		24	100	156
2-2i	4-20 mesh	225	24	100	180
2-2i	4-20 mesh			90	159
2-2k	4-20 mesh	225	24	100	170
2-21	4-20 mesh	225	24	95	171
2-2m	4-20 mesh	220	24	90	185
2-p	4-20 mesh	225	24	90	176
2-2q	4-20 mesh	225	24	90	201
2-3	4-20 mesh	275	22	91	120
2-4	$^1/_2$-in. pellets	380	15.5	51	66 ± 5
2-5	$^1/_2$-in. pellets	450	19.5	67	77
2-6	4-20 mesh	225	47	101	188
2-9	$^1/_2$-in. pellets	410	18.5	50	80
2-10c	4-20 mesh	225	24	100	157
3-4	4-20 mesh	385	54	100	143

CARBON TESTING

The efficiency of an adsorbent in a gas mask canister depends primarily on two factors: What is the maximum amount of gas the carbon can retain before vapors begin to escape through the column? How firmly is the gas held? The subject is discussed by Fieldner, Oberfell, Teague, and Lawrence (*4*). The accelerated chloropicrin test consists in passing air containing 7000 p.p.m. of chloropicrin through a tube of activated carbon, 1.41 cm. in diameter and 10 cm. long, at a rate of 1.00 liter per sq. cm. per minute. The time for which the carbon extracts 99.9% of the chloropicrin from the air stream is a measure of the quantity of vapor it can hold before reaching the break point. The tenacity with which the carbon holds vapors was formerly determined by the retentivity test but is now measured by the heat of wetting. In this test the rise in temperature when 2 or 3 grams of carbon are added to 20 ml. benzene is noted. From these data the heating of wetting is computed in terms of calories per milliliter of charcoal.

DISCUSSION OF RESULTS

The sample number in Tables III, IV, and V refers to coal used—temperature of chlorination (approximately one hundredth of actual figure)—time of steam activation (hours). A duplicate run is indicated by a small letter after the second number. For example, sample 2-2 (Table III) refers to Island Creek coal chlorinated at 225° C. for 24 hours; sample 2-2i-3 (Table IV) refers to Island Creek coal chlorinated at 225° C. for 24 hours and steam activated for 3 hours at 800° C. The exact treatment of a sample should be checked in the table before any conclusion is drawn.

Some of the coals of Table III were chlorinated as finely ground pellets and some as 4-20 mesh material. In Table V the rate of air flow on some of the tests was 0.6 and on others was 1.00 liter per sq. cm. per minute. The latter figure is used in Chemical Warfare Service specifications.

Table IV. Steam Activation Data at 800° C.

Sample No.	Mesh Size	Time, Hr.	Water Used, Cc.	Charge, Grams	Product, Grams
1-1-3	6-20	3.0	...	48.5	[b]
1-2b-3	6-20	3.0	200	82.5	27
1-2c-3	6-20	3.0	200	101	43
1-2-3	5-10	3.0	250	41	18
1-2-1	5-10	1.0	150	35	15
1-3-1	5-10	1.0	...	69	[b]
1-4-1	5-10	0.5	...	...	[b]
1-4b-1	6-12	1.0	...	52	23
1-5-3	6-20	3.0	150	66	39
1-5b-3	6-20	3.0	250	53	27
2-1-1	5-10	1.0	150	25	16.2
2-1-2	5-10	2.0	450	28	17
2-2-1	5-10	0.75	215	45	[b]
2-2a-1	5-10	1.0	...	73	40
2-2bd-1	5- 0	1.0	...	103	57
2-2eb-1	5-10	1.0	...	102	54
2-2f-1	6-12	1.0	150	52	33
2-2g-1	6-12	1.0	250	50	25
2-2h-1	6-20	1.0	...	50	30
2-2i-3	6-20	3.0	175	69	43
2-2jk-3	6-20	3.0	...	160	78
2-21-3	6-20	3.0	...	...	...
2-2m-3	6-20	3.0	...	63	26
2-2p-3	6-20	3.0	50	93	37
2-2q-3	6-20	3.0	150	108	44
2-3-1	5-10	1.0	120	46.5	31.5
2-4-1	5-10	1.0	...	....	[b]
2-5-1	5-10	1.0	...	28	19
2-6-1	6-20	1.0	150	79	41
2-10c-1	$^3/_{16}$ in.[a]	1.0	120	50.5	19[c]
2-10b-1	$^3/_{16}$ in.[a]	1.0	125	22	8
2-9-1	5-10	2.0	450	28	17
3-4-1	5-10	1.0	125	65	39[d]

[a] Pellet size in inches.
[b] Large losses during activation due to faulty retainer.
[c] These pellets were not baked prior to steam activation.
[d] Steam activation done in two batches.

Chlorination. Both the literature and the general impression gained by the laboratory work indicate that the coal will gain much weight if it is chlorinated at low temperatures (below 100° C.). The drawback to such a procedure is that the time required for fairly complete chlorination is 72 hours or more. Assuming, then, that the gain in weight of coal is a measure of the degree of chlorination and that 24 hours is a convenient period for a single chlorination, the minimum temperature at which chlorination is fairly complete in 24 hours must be found. The data of Figure 3*A* show that Sewell coal, chlorinated at 275° C., yields a less highly chlorinated coal than at 225° C. Figure 4 gives further evidence of the desirability of chlorinating at a temperature at which the chlorine uptake is at a maximum. This plot shows that chlorination of 225° C. yields a carbon which is more active (under the same treatment) than those chlorinated at higher temperatures.

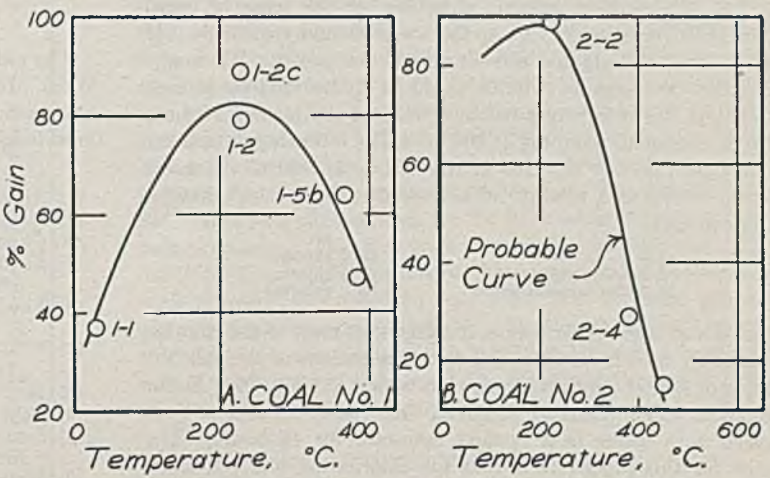

Figure 3. Per Cent Gain in Weight of Coals 1 and 2 after Chlorination

Table V. Accelerated Chloropicrin Tests

Sample No.	Sample Wt., Grams	Gain in Wt., Grams	Time, Min.:Sec.	Air Flow, L./Sq. Cm./Min.	Apparent Density
1-1-3	7.990	2.646	36:53	1.00	0.51
1-2b-3	7.375	4.404	58:15	1.00	0.47
1-2c-3	7.775	4.517	59:10	1.00	0.50
1-2-1	7.155	2.976	65:00	0.6	0.46
1-2-3	7.518	3.240	70:00	0.6	0.48
1-3-1	....	...	65:00	0.6	
1-4-1	9.075	1.518	36:00	0.6	0.58
1-5-3	7.796	2.501	33:20	1.00	0.49
1-5a-3	8.329	2.297	27:00	1.00	0.53
1-5b-3	7.355	3.118	40:04	1.00	0.47
1-5b-3	7.210	2.723	37:00	1.00	0.46
2-1-1	7.592	1.507	32:40	0.6	0.485
2-1-2	7.198	1.883	42:30	0.6	0.46
2-2-1	7.538	3.727	65:00	0.6	0.48
2-2-1	8.321	3.135	70:00	0.6	0.53
2-2a-1	7.818	1.305	28:30	0.6	0.50
2-2a-1	8.036	1.368	30:00	0.6	0.51
2-2bd-1	7.717	2.550	57:00	0.6	0.50
2-2ed-1	7.610	2.863	64:00	0.6	0.485
2-2jk-3	8.195	3.617	46:35	1.00	0.52
2-2jk-3	7.753	3.304	43:35	1.00	0.50
2-2m-3	7.338	3.382	43:30	1.00	0.46
2-2p-3	6.992	3.889	52:08	1.00	0.45
2-2q-3	7.441	3.200	43:30	1.00	0.47
2-3-1	7.527	0.738	16:30	0.6	0.48
2-4-1	6.153	2.030	44:00	0.6	0.39
2-5-1	7.510	1.371	30:00	0.6	0.48
2-9-1	9.048	3.395	75:30	0.6	0.58
2-10c-1	8.047	1.038	23:00	0.6	
3-4-1	7.787	2.531	54:00	0.6	0.50
C-1	7.673	1.885	37:06	1.00	0.50
C-1	7.632	2.604	34:25	1.00	0.49
C-2	7.156	2.808	37:23	1.00	0.46
M-3	7.219	2.773	36:46	1.00	0.46
M-4	7.274	3.552	46:00	1.00	0.46
Comp.-1	7.474	2.826	37:11	1.00	0.48
Comp.-1	7.661	2.966	40:30	1.00	0.49
Comp.-1-2	6.943	3.506	45:40	1.00	0.445
Comp.-1-2	7.133	3.691	38:35	1.00	0.445

Steam Activation. The temperature of activation was 800° C. because for the same percentage oxidation of charcoal, the lower the temperature at which activation occurs, the more active is the carbon. It is not convenient to use temperatures below 800° C. because the activation is too slow. Three hours at 800° C. was found to produce a carbon of good activity.

REDUCTION OF CHLORINE CONTENT

Specifications require the chlorine content of carbon for gas masks to be below 0.35%. To study the union of chlorine with carbon, the following experiment was performed: In each of two fat-extraction flasks (250 ml.) were placed 5 grams of finely ground mixture M-3 (described later). To one, 50 ml. of water were added, and to the other 50 ml. of Tetralin (technical). The flasks were placed on a heater, and the solvent was permitted to reflux for 42 hours.

The chlorine may be present in the carbon as (*a*) inorganic chloride, (*b*) complex organic chlorides, or (*c*) some of each. If the chlorine is present as *a*, the water should remove it. If present as *b*, the organic solvent should remove it. We might argue that the organic chloride could be hydrolyzed by boiling water, but this is hardly possible in view of the history of these carbons—namely, steaming at 800° C. The following data seem to indicate that the chlorine in the carbon is held as inorganic chloride. M-3 is a mixture of activated carbons which have a similar history:

M-3	0.69% chlorine
M-3, water-extracted	0.25% chlorine
M-3, Tetralin-extracted	0.55% chlorine

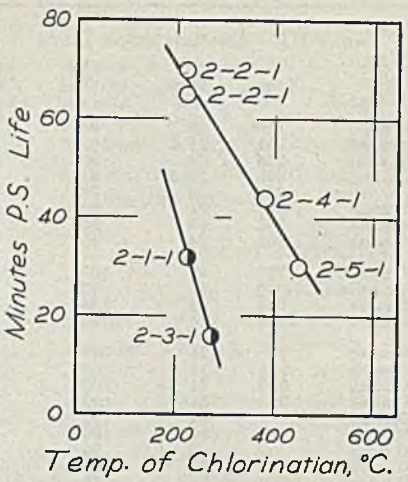

Figure 4. Coals Steamed for One Hour

○ Chlorinated as pellets
◑ Chlorinated as 4–20 mesh

In view of these experiments, it seems that most of the chlorine is probably held in combination with the cations of the ash. A sample of Island Creek coal was chlorinated at about 225° C. for 24 hours. The material removed from the chlorinator was washed with water in a Soxhlet extractor for 48 hours. The reason for this procedure is that the chlorinated coal contained some adsorbed hydrogen chloride which dissolved in the water to form dilute hydrochloric acid solution, a good solvent for many inorganic materials. The chlorinated coal from two runs was combined, extracted with water as just described, and labeled 2-2jk. This material was pelleted, baked at 500° C., crushed, and sieved to 8-20 mesh. It was then steam-activated at 800° C. for 3 hours and labeled 2-2jk-3:

Accelerated chloropicrin test	46:35
Density (apparent)	0.52
Chlorine, %	0.11, 0.15 (av., 0.13)

While the process used in preparing 2-2jk-3 yields a good activated carbon and is economical, it has the disadvantage that it requires apparatus which can withstand dilute hydrochloric acid.

ACTIVE CARBON FROM LOW-ASH COAL

In view of the evidence that chlorine is present in activated carbon primarily as inorganic chloride, it was decided to try to prepare a good grade carbon from coal No. 1 (Sewell). This material was chosen because of its low ash content (2.4% as compared to about 7% for Island Creek coal). The Sewell coal was chlorinated (40-20 mesh) at 225° C. for 24 hours pelleted, baked, crushed, and steam-activated for 3 hours at 800° C. Tests were run on this carbon (1-2c-3) in our laboratory and also by W. C. Pierce at Northwestern University:

	Our Test	Pierce Test	C.W.S. Specifications
P.S. life, min.:sec.	59:10	69:00	40:00
Chlorine, %	0.12	0.11	0.35 (max.)
Heat of wetting, cal./cc./min.	12	Not reptd.	8.5

ACKNOWLEDGMENT

The aid of W. E. Fish and J. Hession in building apparatus, W. L. McCabe in giving advice on the most recent tests for active carbon, and W. C. Pierce in testing samples is hereby acknowledged.

LITERATURE CITED

(1) Anonymous, *J. Soc. Chem. Ind.*, 55, 223 (1936).
(2) Barker, M. E., U. S. Patent 1,933,579 (1933).
(2A) Chaney, N. K., *Ibid.*, 1,499,908 (1924).
(3) Fieldner, A. C., and Hall, R. E., U. S. Bur. Mines, *Tech. Paper* 479 (1930).
(4) Fieldner, A. C., Oberfell, G. G., Teague, M. C., and Lawrence, J. N., J. Ind. Eng. Chem., 11, 519 (1919).
(5) McCulloch, A., and Hargraves, R. E., *J. Inst. Fuel*, 12, 382 (1939).
(6) McCulloch, A., and Eccles, A., Brit. Patent 355,019 (1930).
(7) Ochi, S., *J. Fuel Soc. Japan*, 9, 246 (1930).
(8) Soare, A. G., and Georgescu, R., *Bul. Chim. Soc. Romåne Chim.*, 37, 79 (1934).
(9) Weiler, J. F., *Fuel*, 14, 190 (1935).
(10) Williams, A. E., *Colliery Eng.*, 10, 347-8 (1933).
(11) Williams, A. E., *Engineer*, 154, 203 (1935).

Inhibition of Myrcene Polymerization during Storage

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MYRCENE, 2-methyl-6-methylene-2,7-octadiene, isolated from the leaves of *Myrcia acris* (oil of bay) by Power and Kleber (*6*), has been found to occur in a number of other essential oils (*8*). No large scale source of supply, however, was readily available until Goldblatt and Palkin (*3*) discovered that myrcene can be obtained in good yield by simple thermal isomerization of β-pinene from oil of turpentine. The increase in supply thus afforded leads to the necessity of considering the problems of storage, in anticipation of the utilization of myrcene. A study made of the deterioration of myrcene during storage is the subject of the present report.

Myrcene is a highly reactive compound and polymerizes spontaneously. Thus, Harries (*4*) found that myrcene heated in a sealed tube at 300° C. gave both an oil (boiling at 160-200° C., 12-16 mm.) and a viscous gum which he called "dimyrcene" and "polymyrcene", respectively. The nitrosite of dimyrcene he considered to be identical with a nitrosite he had prepared from rubber. Lebedev (*5*), upon polymerization of a rather impure myrcene at 150° C., found among the products a monomer not identical with myrcene; a dimer $C_{20}H_{32}$ (boiling point 183-184° C., 10 mm.; d_4^{20} 0.8763), and a viscous liquid polymer. The kinetics of the polymerization of myrcene at 150° C. was investigated by Gapon (*2*), who found that two processes occur—aromatization as well as polymerization.

It is well known that many conjugated diolefins, such as butadiene, undergo spontaneous polymerization to liquid polymers even at ordinary temperatures (*7*). It was not surprising, therefore, that myrcene was observed to deteriorate rapidly on storage at room temperature, as indicated by a marked increase in density and viscosity. The preliminary storage trials made during the present investigation indicated that loss of myrcene by polymerization during storage was due largely to thermal action. Thus, samples stored in a refrigerator at 3° C. for 6 weeks showed no detectable loss of monomer, on the basis of density or viscosity measurements. This was true whether the storage was carried out in bottles completely filled with myrcene, in bottles half filled with myrcene, or in bottles half filled with myrcene and with nitrogen replacing the residual air. On the other hand, myrcene stored at room temperature (24-30° C.) deteriorated badly; the rate of deterioration appeared to be the same whether or not air was excluded. When a sample of myrcene, to which had been

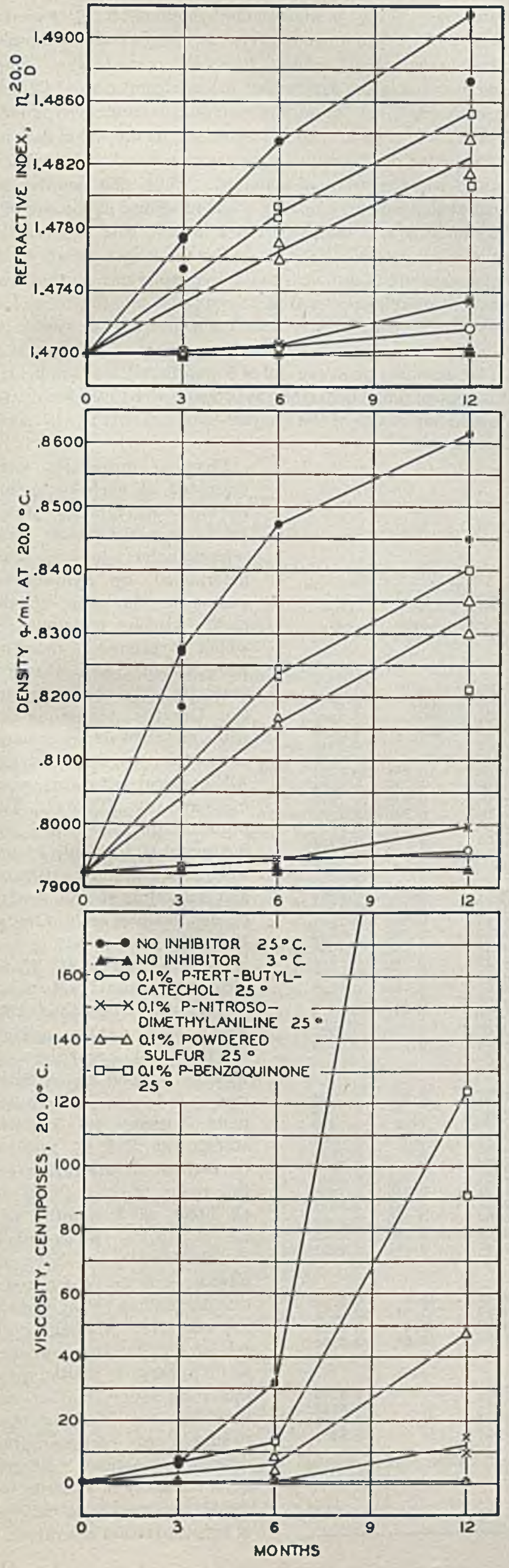

Figure 1. Effect of Temperature and Inhibitors on Physical Properties of Myrcene during Storage (Freshly Opened Samples)

Temperature is an important factor in the deterioration during storage of myrcene, a triolefin. At 25° C. approximately a third of the myrcene is lost by polymerization in only 3 months unless an inhibitor is used; at 3° there is no appreciable loss, even at the end of 12 months, with or without an inhibitor. At the higher temperature the use of 0.1% *p-tert*-butylcatechol will effectively inhibit polymerization; slightly less effective is the same percentage of *p*-nitrosodimethylaniline. More than one mode of polymerization is involved.

added 0.5% of *p-tert*-butylcatechol, was stored at room temperature, it deteriorated slightly more than did any of the samples stored without inhibitor at 3° C.

Following these preliminary observations, a storage test was conducted on myrcene over a period of a year. The results may be of interest not only for application in the storage of myrcene, but also in the storage of other polymerizable hydrocarbons.

In the 1-year storage test, the inhibitors included 0.1% *p-tert*-butylcatechol, 0.1% *p*-nitrosodimethylaniline, 0.1% *p*-benzoquinone, and 0.1% powdered sulfur. In each case 20-ml. samples of myrcene were placed in 60-ml. Pyrex-stoppered bottles. Samples were stored in the dark, either in a refrigerator at 3° C. or in an incubator at 25° C. Appropriate samples were removed periodically, generally after 3, 6, and 12 months. At the end of each inspection period, fresh samples were examined, and the previously examined samples were re-examined. Thus, the samples examined at the end of 3 months were re-examined at the end of 6 and 12 months, and the properties compared with those of the samples which had remained intact for the longer period. The samples were run in duplicate, with one exception; in that case one pair of samples removed at the end of 3 months differed so markedly in properties that removal of a third sample was necessary, and only a single fresh sample was then available in that series for examination at the end of 6 months. Results indicated that this exceptional behavior was probably due to the accidental contamination of one of the samples (No. 1, Table I) with some inhibitor.

TABLE I. EFFECT OF STORAGE ON PHYSICAL CONSTANTS AT 20.0° C. OF MYRCENE[a] SAMPLES, WITH AND WITHOUT INHIBITION

		3-Month Storage			6-Month Storage			12-Month Storage		
Sample No.	Storage Temp., ° C.	Refractive index, n_D^{20}	Viscosity, Centipoises	Density, g./ml.	Refractive index, n_D^{20}	Viscosity, Centipoises	Density, g./ml.	Refractive index, n_D^{20}	Viscosity, Centipoises	Density, g./ml.
No Inhibitor										
1	25	1.4754	5.97	0.8185	1.4800	22.0	0.8318	1.4885	293	0.8500
2	25	1.4774	6.58	0.8276	1.4837	37.3	0.8428	1.4934	580[b]	0.8657
3	25	1.4772	7.66	0.8269	1.4837	36.9	0.8431	1.4931	580[b]	0.8664
4	25	....	...	....	1.4835	32.3	0.8473	1.4922	486	0.8669
5	25	....	...	....	....	....	....	1.4873	.....	0.8449
6	25	....	...	....	....	....	....	1.4916	361	0.8615
9	3	1.4700	0.743	0.7923	1.4699	0.748	0.7931	1.4706	0.761	0.7935
10	3	1.4697	0.737	0.7923	1.4698	0.743	0.7927	1.4706	0.738	0.7929
11	3	....	...	....	1.4700	0.742	0.7927	1.4706	0.738	0.7926
12	3	....	...	....	1.4700	0.748	0.7934	1.4704	0.742	0.7928
13	3	....	...	....	....	....	....	1.4706	0.739	0.7928
14	3	....	...	....	....	....	....	1.4705	0.738	0.7929
0.1% *p-tert*-Butylcatechol as Inhibitor										
17	25	1.4702	0.759	0.7937	1.4706	0.762	0.7946	1.4717	0.792	0.7962
18	25	1.4702	0.761	0.7936	1.4706	0.771	0.7946	1.4717	0.789	0.7956
19	25	....	...	....	1.4705	0.769	0.7945	1.4716	0.798	0.7961
20	25	....	...	....	1.4706	0.762	0.7945	1.4717	0.792	0.7960
21	25	....	...	....	....	....	....	1.4718	0.788	0.7960
22	25	....	...	....	....	....	....	1.4717	0.786	0.7959
23	3	1.4700	0.746	0.7926	1.4699	0.754	0.7927	1.4705	0.725	0.7927
24	3	1.4701	0.747	0.7925	1.4697	0.748	0.7932	1.4705	0.740	0.7927
25	3	....	...	....	1.4698	0.749	0.7928	1.4706	0.738	0.7929
26	3	....	...	....	1.4698	0.744	0.7927	1.4706	0.738	0.7930
27	3	....	...	....	....	....	....	1.4708	0.740	0.7929
28	3	....	...	....	....	....	....	1.4706	0.737	0.7928
0.1% *p*-Nitrosodimethylaniline as Inhibitor										
29	25	1.4702	0.755	0.7937	1.4704	0.766	0.7938	1.4727	3.63	0.7989
30	25	1.4702	0.747	0.7937	1.4704	0.762	0.7938	1.4726	7.76	0.7989
31	25	....	...	....	1.4707	0.777	0.7945	1.4734	7.77	0.7989
32	25	....	...	....	1.4707	0.772	0.7945	1.4734	10.9	0.8004
33	25	....	...	....	....	....	....	1.4736	14.4	0.7996
34	25	....	...	....	....	....	....	1.4734	9.91	0.7996
35	3	1.4698	0.741	0.7925	1.4701	0.742	0.7929	1.4704	0.746	0.7930
36	3	1.4698	0.744	0.7925	1.4700	0.738	0.7928	1.4704	0.740	0.7929
37	3	....	...	....	1.4700	0.742	0.7929	1.4704	0.747	0.7925
38	3	....	...	....	1.4700	0.742	0.7929	1.4704	0.740	0.7927
39	3	....	...	....	....	....	....	1.4704	0.746	0.7925
40	3	....	...	....	....	....	....	1.4703	0.741	0.7927
0.1% Powdered Sulfur as Inhibitor										
41	25	....	...	....	1.4760	3.86	0.8167	1.4822	35.7	0.8285
42	25	....	...	....	1.4771	8.1	0.8159	1.4825	41.8[c]	0.8314
43	25	....	...	....	....	....	....	1.4837	48.6	0.8355
44	25	....	...	....	....	....	....	1.4815	41.8[c]	0.8301
0.1% *p*-Benzoquinone										
45	25	....	...	....	1.4788	13.6	0.8237	1.4882	152	0.8443
46	25	....	...	....	1.4792	13.7	0.8242	1.4862	147	0.8415
47	25	....	...	....	....	....	....	1.4808	91.2	0.8212
48	25	....	...	....	....	....	....	1.4854	124	0.8404

[a] Approximately 96% pure. Physical constants of the starting material were: n_D^{20} 1.4700; density 0.7924 g./ml., absolute viscosity 0.730 centipoise.

[b] Samples 2 and 3 combined.

[c] Samples 42 and 44 combined.

Physical properties were examined at each inspection period. Refractive index was determined on an Abbe refractometer; densities were determined by hydrometer, except in the case of the highly viscous materials for which pycnometer densities were taken; and absolute viscosity was measured by the Croxton technique (*1*) with an Ostwald viscometer as modified by Zeitfuchs (*9*). All physical constants were measured at 20.0° C. The physical data obtained are incorporated in Table I, and the refractive index, density, and viscosity of the freshly opened samples are plotted in Figure 1.

Samples stored at 3° C. showed practically no deterioration (less than 1%) over the entire period of the test regardless of whether or not an inhibitor was used. On the other hand, without an inhibitor storage at 25° C. resulted in serious deterioration (of the order of one third) in as little as 3 months. At 25° C. 0.1% *p-tert*-butylcatechol was an effective inhibitor, and 0.1% *p*-nitrosodimethylaniline was slightly less effective. Although both *p*-benzoquinone and powdered sulfur apparently exerted some inhibiting action, neither was very effective. The fact that products of corresponding density sometimes differed quite markedly in viscosity indicates that more than one type of polymerization is involved.

LITERATURE CITED

(1) Croxton, F. C., Ind. Eng. Chem., Anal. Ed., 14, 593 (1942).
(2) Gapon, E. N., *J. Gen. Chem.* (U.S.S.R.), 1, 502 (1931).
(3) Goldblatt, L. A., and Palkin, S., *J. Am. Chem. Soc.*, 63, 3517 (1941).
(4) Harries, C. D., *Ber.*, 35, 3259 (1902).
(5) Lebedev, S. V., and Merezhkovskiĭ, B. K., *J. Russ. Phys. Chem. Soc.*, 45, 1249 (1913); *J. Chem. Soc.* (Abstracts), 104, i, 1289 (1913).
(6) Power, F. B., and Kleber, C., *Pharm. Rundschau*, 13, 60 (1895).
(7) Robey, R. F., Wiese, H. K., and Morrell, C. E., Ind. Eng. Chem., 36, 3 (1944).
(8) Simonsen, J. L., "The Terpenes", 1st ed., Vol. 1, p. 10, Cambridge Univ. Press, 1931.
(9) Zeitfuchs, E. H., *Proc. Am. Petroleum Inst.*, III, 20, 104 (1939).

Composition of Vapors from Boiling Binary Solutions

APPARATUS FOR DETERMINATIONS UNDER PRESSURE

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The increase in the applications of distillation equipment and methods at elevated pressures made it desirable to modify the method and apparatus previously standardized for the determination of vapor-liquid equilibrium data at superatmospheric pressure. An apparatus was designed and built for use at pressures up to several hundred pounds per square inch. Data on the binary systems methanol-water and acetone-water are reported at pressures up to 200 pounds per square inch absolute. Correlations with each other and with data from the literature at atmospheric pressure are good. Acetone-water has a constant boiling mixture at higher pressures, as previously predicted from the shape of the atmospheric *X, Y* curve, since it is concave upward.

PREVIOUS articles (*6, 8, 9*) described a simple, rapid method for determining the vapor composition of a boiling binary solution. The equipment used was a self-contained glass apparatus in which samples of vapor and liquid, in substantial equilibrium with each other, may be obtained in a relatively short time throughout the entire range of compositions. Many modifications of this unit have been made in adaptations to special problems; and data taken by the method have been presented on numerous systems.

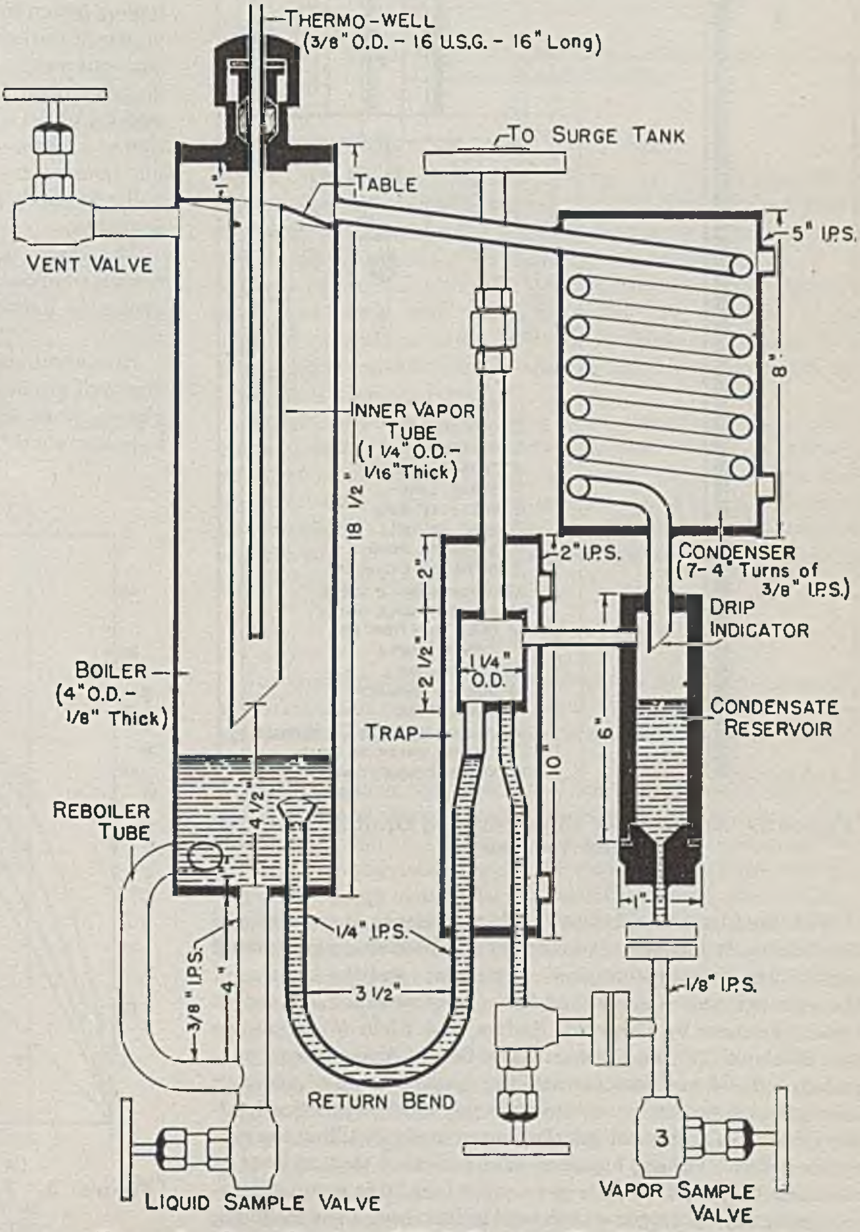

Figure 1. Cross Section of High Pressure Equilibrium Still

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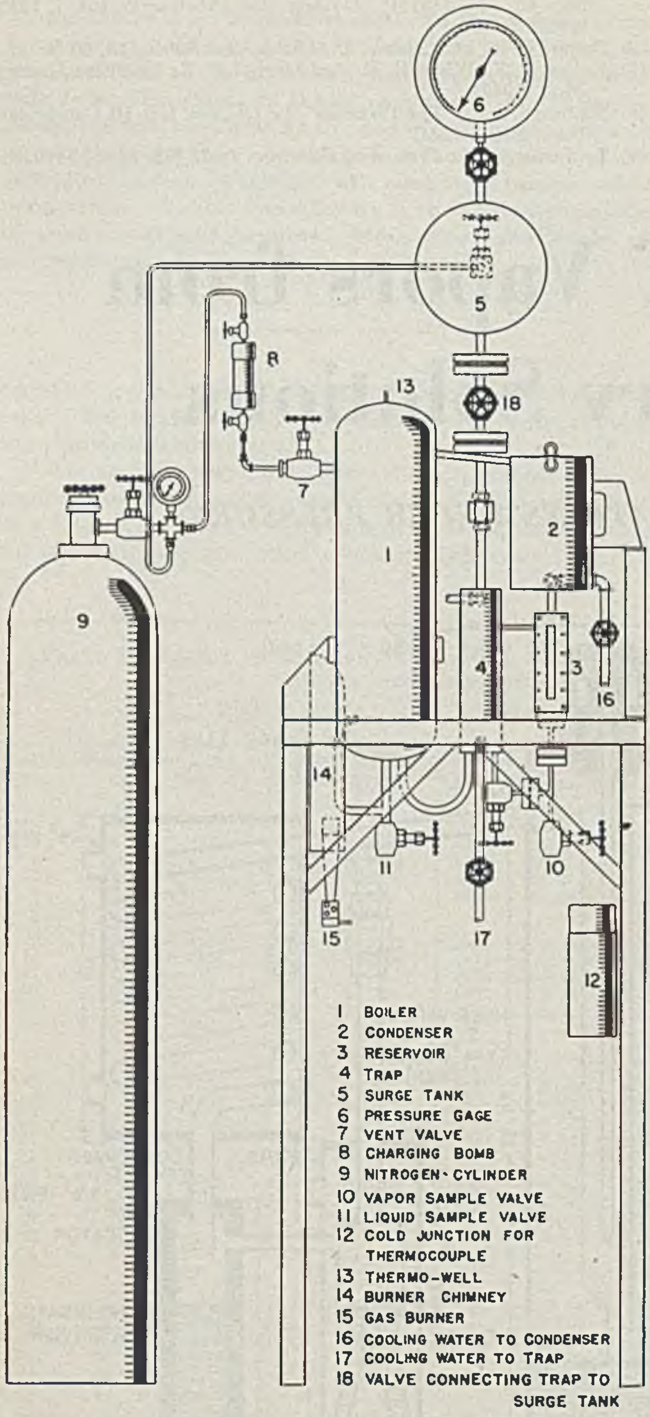

Figure 2. Assembly of High Pressure Equilibrium Still and Accessories

With the increase of interest in high pressure operations and distillations, it has become necessary to determine vapor liquid equilibrium at superatmospheric pressures; and the features of the previous unit and method have been modified for use at higher pressures by Griswold, Andres, and Klein (*5*), Scheeline and Gilliland (*12*), and others. The first of these writers suggested, but did not demonstrate, the disadvantages of using an inert gas to maintain a constant pressure, which is practically always done in commercial installations actually distilling the materials tested. Others, however, have indicated that, at least at pressures below 200 pounds per square inch, this is not an important error. Nitrogen was so used in this case; even assuming that it could have been completely dissolved to saturation in the condensate while the latter flows quickly through the reservoir system, this impurity would have amounted to only 0.7% under the worst conditions of the present investigation. The conclusions of others were substantiated that, up to at least 200 pounds per square inch, no abnormalities were noted which were traceable to this insignificant impurity; and consistent data for engineering purposes were obtained.

DESCRIPTION OF APPARATUS

A unit was designed, and built by the Vulcan Copper & Supply Company, for the determination of equilibrium data at pressures up to at least 500 pounds per square inch (Figure 1). The assembly, with essential accessories, consists of a boiler, condenser, trap, condensate reservoir, and surge tank (Figure 2). The unit is constructed entirely of stainless steel, and the various parts are fabricated from standard KA$_2$SMo tubes, pipes, sheets, bar or round stock, and valves. The individual parts were welded together.

BOILER AND CONDENSER. The boiler has a reboiler tube attached between the lower side wall and the drain tube. This is surrounded by an external chimney formed of thin sheet metal with a Bunsen burner supplying heat for the recirculating and boiling action inside the tube. The vapor tube is jacketed with vapors of the boiling solution after trapped air is expelled through the vent valve. The vapor tube is supported from a thin disk or table plate formed to allow drainage to the condenser. A packing gland is provided at the top of the boiler for the insertion of a thermowell through the center of the vapor tube. Liquid samples are withdrawn from the drain valve. The entire boiler assembly is covered with a 1-inch layer of 85% magnesia insulation.

The vapors pass from the top of the boiler through a condenser, composed of seven turns of ${}^3/_8$-inch iron-pipe-size stainless steel pipe jacketed by a condenser box made of standard iron pipe.

RESERVOIR AND TRAP. The reservoir is made of cast stainless steel and machined to accommodate full-length rectangular sight glasses, front and back, to allow for visual control. The drop indicator shows the rate of distillation. A pressure-equalizing

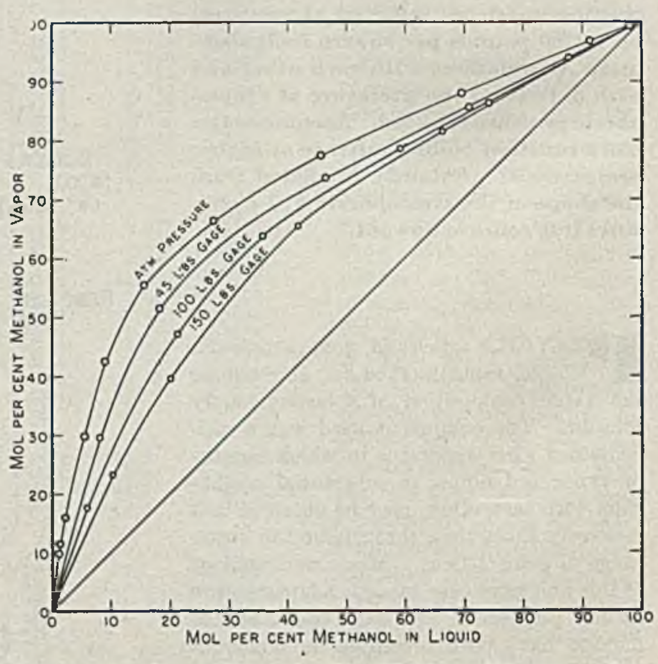

Figure 3. Vapor-Liquid Equilibrium Diagram for Methanol-Water System

Data for atmospheric curve are those of Cornell and Montonna (*4*)

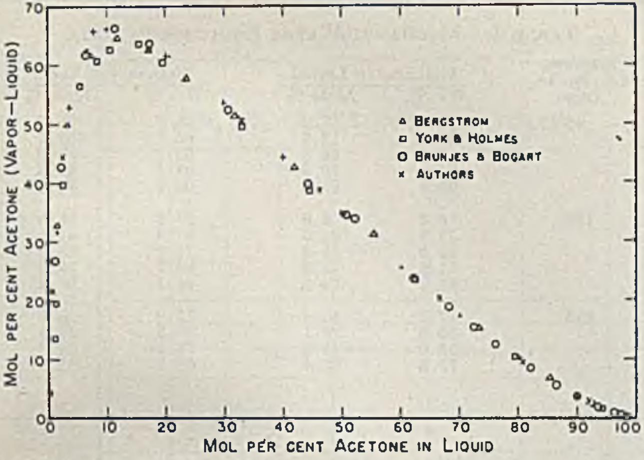

Figure 4. Comparative Vapor-Liquid Difference Plot, $(Y - X)$ vs. X, for Acetone-Water System at Atmospheric Pressure

tube passes from the reservoir to the trap. A drain line at the bottom is connected to a condensate valve and a 90° valve which allows the liquid to flow into the trap. This constant level trap is water-jacketed for cooling the condensate. It serves to maintain a constant level in the condensate reservoir and as a spill box to smooth out any minor fluctuations in boiling or liquid flow.

Pressure and Temperature Equipment. The surge tank is located above the apparatus and is connected through a valve to the vent line from the trap. It is fabricated from stainless steel, and is 8 inches in diameter and 36 inches long, rolled from $^1/_8$-inch sheet, and capped by $^1/_2$-inch heads. The tank is slightly inclined to return any possible condensate to the trap, the connection of which enters at the low point.

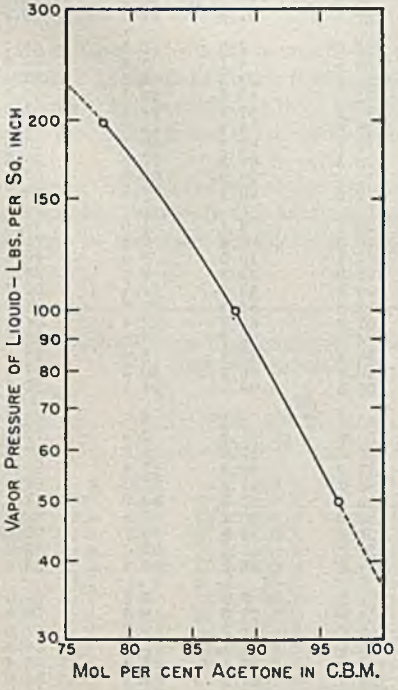

Figure 6. Variation of Pressure of C.B.M. of Acetone and Water with Composition

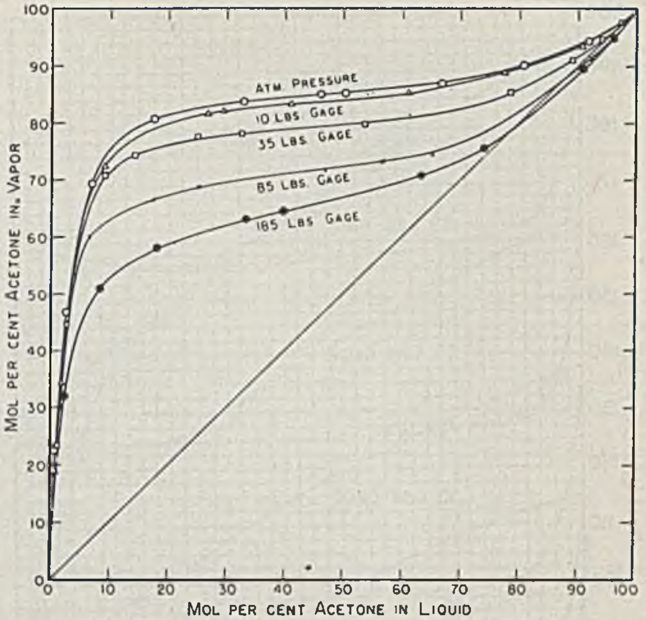

Figure 5. Vapor-Liquid Equilibrium Diagrams for the Acetone-Water System

A cylinder of nitrogen with a regulating valve serves as a means of applying pressure to the system and is connected through a shutoff valve to the surge tank. When the desired pressure is applied, a constant ambient pressure is maintained on the system, since the volume of the reservoir is very large compared to the internal volume of the rest of the apparatus.

The vent valve is also used for supplying feed by means of a small feed bomb, with valves on either end, attached to the nitrogen pressure system. This small bomb is identical with those used for withdrawing samples of liquid from the boiler and from the condensate reservoir.

Pressures were measured by an 8-inch Bourdon test gage, with graduations at $^1/_4$-pound intervals, and were calibrated against a standard dead-weight pressure assembly. Temperatures were measured by a Type K potentiometer, using a chromel-alumel thermocouple; the hot junction was placed in the thermowell, and the cold junction was placed in a thermos bottle containing cracked ice and water.

OPERATING PROCEDURE

The equilibrium apparatus is essentially the same in principle as the standard glass unit, and the method of operation is similar except for the special manipulations necessary in the use of pressure.

Before charging, the apparatus is thoroughly cleaned and boiled out with one of the pure components. The initial charge of approximately 600 cc. (rich in the low-boiling component) is then admitted to the unit through the vent valve. Both vent and vapor valves are closed, the gas burner is lighted, and condenser and trap cooling water are turned on. The valve connecting the distilling zone to the surge tank is then opened. The entire system is placed under nitrogen pressure in slight excess of the desired operating pressure which makes it easier to adjust the pressure later.

When the condensate of this vapor has filled the condensate reservoir and is recycling, the vent valve may be slightly cracked and thus vent off the trapped air from the annular space in the top of the boiling chamber. It is important that vapor condensate continues to form while venting. The vent valve should not be used to bleed off excess pressure. Pressure within the apparatus is reduced to the desired level by bleeding off the excess from an exhaust valve on the back of the surge tank.

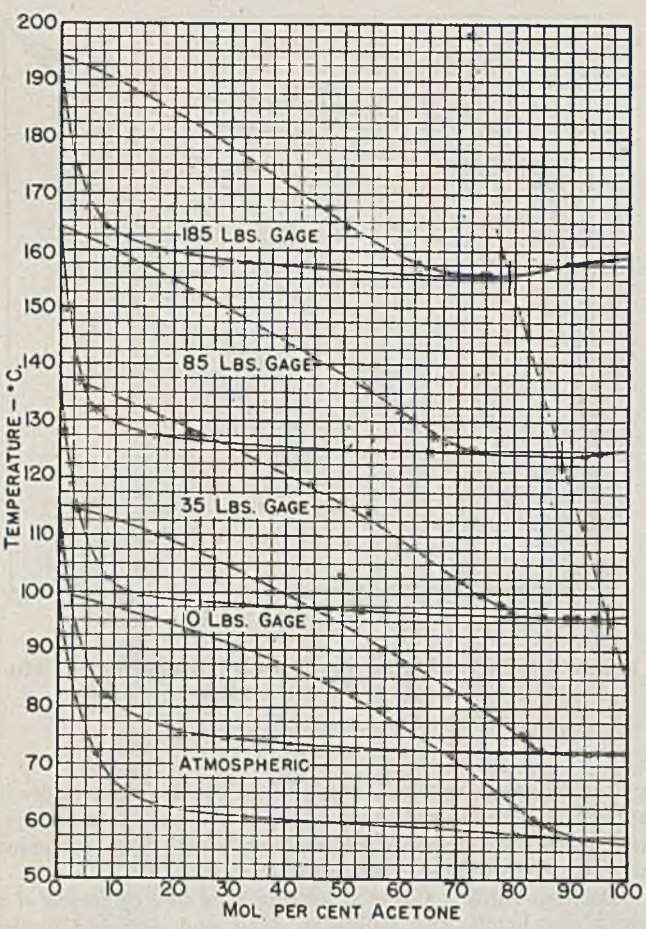

Figure 7. Boiling Point and Dew Point Curves of Temperatures *vs.* Composition for Acetone-Water

Frequent vapor temperature readings are made, and a steady state of operation is indicated when the temperature becomes constant. This takes a maximum of 2 to 3 hours to accomplish, depending on the components used, the respective amounts of the condensate and boiling liquid, and other factors (*8*).

In the case where the materials studied are liquids at room temperature, the condensate sample may be withdrawn directly from the reservoir to a sample bottle. In all cases the liquid sample will be at or above its atmospheric boiling point. A double-valve metal bomb was used as receiver. This was evacuated and attached to the liquid sample valve. By opening the valve on the bomb and the liquid valve, a true sample of the equilibrium boiling liquid is obtained. The bomb is then cooled down and the contents removed for analysis. In such a heavy apparatus it is difficult to stop the distillation completely when samples are taken; consequently, they should be withdrawn simultaneously and as rapidly as possible. Also, at the higher pressures a small drop in pressure as the samples are removed from the unit causes a slight amount of flashing to take place. This effect is minimized by rapid and simultaneous removal of samples.

In the second and succeeding runs, the unit is charged with additional liquid of somewhat different composition from a bomb used for taking the liquid sample from the boiler. The volume of material added to the boiler should be the same as that removed in order to maintain substantially the same amount of liquid in the boiler. If this is not done, the liquid level may drop too low or the level may get above the lower end of the inner vapor tube. Either situation would contribute toward false results. The charging bomb is filled by first evacuating it and then drawing in the liquid to be charged by opening one of the bomb valves

Table I. Methanol-Water Equilibrium Data

Pressure, Lb./Sq. In. Gage	Methanol in Liquid		Methanol in Vapor	
	Wt. %	Mole %	Wt. %	Mole %
45	13.7	8.2	42.7	29.5
	28.5	18.3	65.1	51.4
	60.8	46.5	83.3	73.8
	81.4	70.8	91.5	85.8
	92.8	87.8	96.7	94.0
100	10.2	6.0	27.8	17.8
	32.3	21.2	61.4	47.1
	49.8	35.8	75.9	63.8
	71.9	59.2	86.7	78.6
	84.2	74.1	92.1	86.5
150	17.1	10.4	35.0	23.2
	30.9	20.1	53.8	39.6
	56.0	41.9	77.1	65.3
	77.8	66.4	88.8	81.7

Table II. Data for Methanol and Water at Rounded Values of Liquid Composition

X, Mole %	*Y*		
	45 lb./sq. in.	100 lb./sq. in.	150 lb./sq. in.
0	0	0	0
5	18.6	14.9	12.1
10	34.5	27.9	22.6
20	53.3	45.5	39.3
30	63.4	58.2	53.0
40	70.2	66.9	63.7
50	75.6	73.4	71.2
60	80.6	78.9	77.8
70	85.5	84.3	83.6
80	90.4	89.5	89.0
90	95.2	94.7	94.4
95	97.6	97.4	97.2
100	100	100	100

Table III. Acetone-Water Equilibrium Data

Pressure, Lb./Sq. In. Gage	*T*, ° C.	Acetone in Liquid		Acetone in Vapor	
		Wt. %	Mole %	Wt. %	Mole %
Atm.	93.2	2.2	0.7	48.1	22.4
	85.1	7.3	2.4	73.8	46.6
	71.7	19.0	6.8	87.9	69.2
	63.0	40.8	17.6	93.0	80.5
	60.9	61.4	33.0	94.3	83.7
	59.8	73.4	46.1	94.7	84.8
	59.8	76.5	50.2	94.8	85.0
	59.0	86.7	66.8	95.2	86.2
	58.2	93.2	80.8	96.7	90.2
	57.1	97.4	92.0	98.2	94.4
10	110.0	1.6	0.5	41.1	17.8
	102.3	4.1	1.4	63.0	34.6
	81.7	23.7	8.8	89.4	72.3
	75.6	53.8	26.5	93.5	81.7
	74.5	57.1	29.2	93.6	82.1
	73.6	69.1	41.0	94.1	83.2
	72.7	83.3	60.8	95.0	85.5
	72.3	91.8	77.6	96.3	89.0
	72.2	96.9	90.8	97.9	93.6
	72.2	99.1	97.2	99.3	97.8
35	128.2	3.1	1.0	49.2	23.0
	119.0	6.8	2.2	71.9	44.2
	114.1	10.5	3.5	79.4	54.5
	102.3	23.3	8.6	88.7	70.9
	99.6	35.0	14.3	90.2	74.1
	98.2	51.5	24.8	91.7	77.5
	97.9	60.7	32.4	91.8	77.9
	96.8	78.7	53.3	92.6	79.5
	96.2	92.1	78.4	95.0	85.4
	96.1	96.5	89.5	97.1	91.1
	95.9	98.1	94.1	98.3	94.6
85	149.5	5.5	1.8	58.0	30.0
	136.8	11.2	3.8	79.2	54.2
	132.0	17.6	6.2	82.8	59.8
	127.3	40.4	17.4	86.4	66.4
	126.7	51.9	25.0	87.6	68.6
	125.5	77.0	50.9	89.7	73.0
	125.6	80.8	56.6	90.1	73.5
	124.8	85.8	65.1	90.4	74.4
	124.3	97.5	92.4	97.2	91.5
	124.8	98.7	95.8	98.4	95.0
185	177.2	7.3	2.4	60.0	31.8
	164.0	22.6	8.3	76.8	50.7
	160.3	41.7	18.2	81.6	57.9
	158.3	61.8	33.4	84.6	63.1
	157.3	68.1	39.8	85.4	64.4
	156.3	84.8	63.4	88.6	70.8
	156.0	90.3	74.3	90.9	75.6
	157.8	97.0	91.0	96.5	89.6
	157.5	98.9	96.6	98.6	95.6

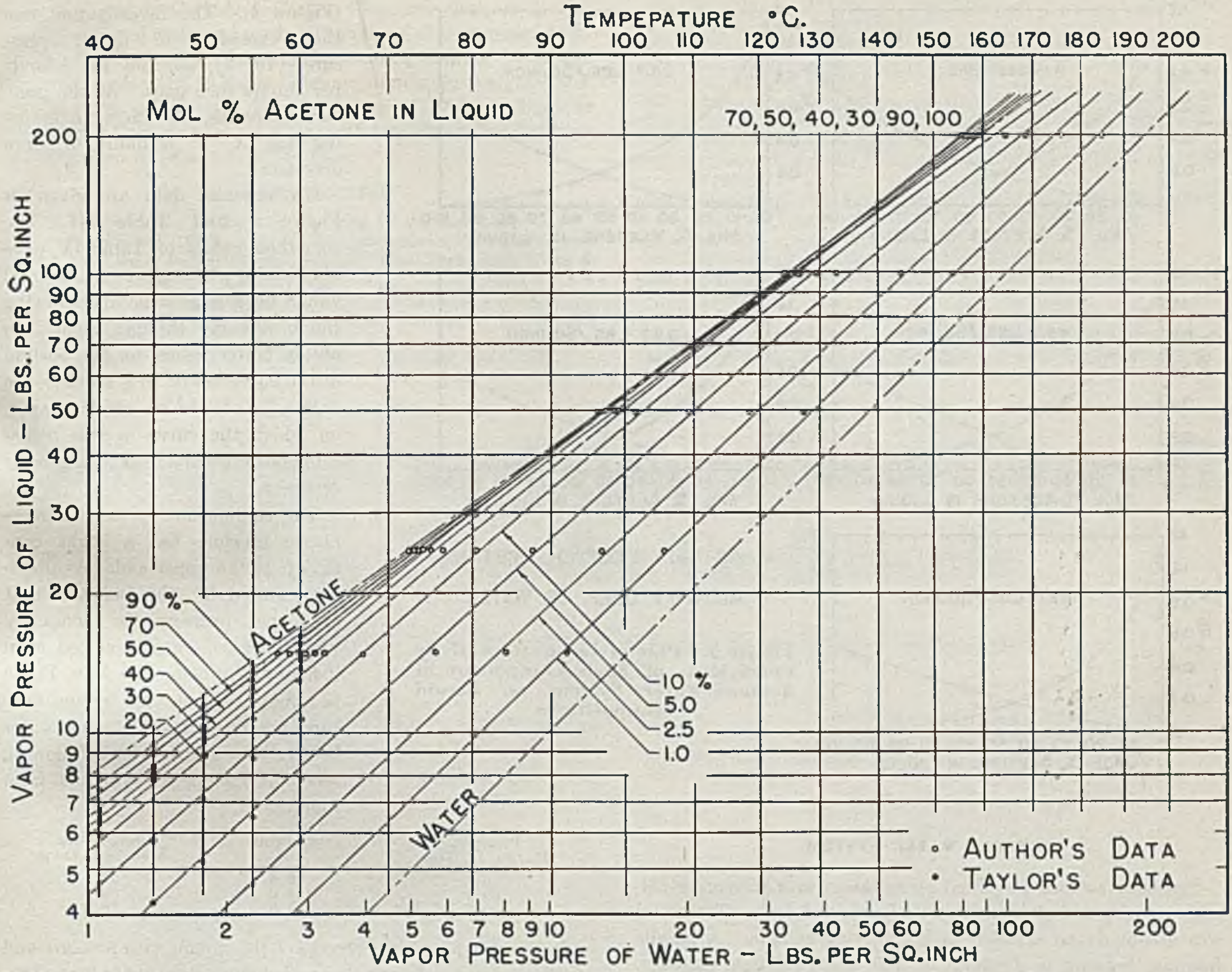

Figure 8. Plot of Total Vapor Pressure of Acetone-Water Mixtures *vs.* Vapor Pressures of Water at Same Temperatures

under the liquid surface. The bomb is attached to the vent valve in a vertical position as shown in Figure 1, and pressure is applied to the opposite end in excess of that in the apparatus. Vent and bomb valves are then opened, and the material flows into the still boiler.

If smaller samples than the volume of the reservoir are in keeping with the accuracy desired in the analytical procedure, the time of a run may be shortened considerably by decreasing the volume of the condensate reservoir. This may be accomplished in a given apparatus by filling the reservoir with glass beads and thus decreasing the volume available to the condensate. In the work reported here, analyses were made with precision pycnometers and tables of specific gravities. In the case of acetone-water, Squibb's data (*13*) were used.

TABLE IV. ACETONE-WATER EQUILIBRIUM DATA AT ROUNDED VALUES OF LIQUID COMPOSITION

	14.7 Lb./Sq. In.		24.7 Lb./Sq. In.		49.7 Lb./Sq. In.		99.7 Lb./Sq. In.		199.7 Lb./Sq. In.	
X, Mole %	*T*, ° C.	*Y*, Mole %	*T*, ° C.	*Y*, Mole %	*T*, ° C.	*Y*, Mole %	*T*, ° C.	*Y*, Mole %	*T*, ° C.	*Y*, Mole %
0.0	100.0	0.0	115.2	0.0	138.1	0.0	164.3	0.0	194.3	0.0
1.0	92.0	27.9	105.8	27.1	127.5	25.2	154.0	21.8	184.9	19.5
2.5	84.2	47.0	96.5	46.0	118.4	43.9	143.8	40.0	176.4	33.4
5.0	75.6	63.0	87.6	62.0	109.3	60.0	134.1	57.0	168.8	44.4
10.0	66.9	75.4	80.5	73.8	101.4	71.6	129.5	63.3	163.1	52.8
20.0	62.4	81.3	76.3	79.8	98.7	76.1	127.1	67.3	159.8	58.7
30.0	61.1	83.2	74.6	81.8	98.2	77.6	126.2	69.6	158.2	61.8
40.0	60.3	84.2	73.6	83.0	97.4	78.7	125.5	71.2	157.2	64.4
50.0	59.8	85.1	73.0	83.8	96.9	79.6	125.2	72.6	156.6	66.9
60.0	59.2	86.3	72.6	84.9	96.6	80.6	124.9	73.8	156.2	69.7
70.0	58.8	87.5	72.4	87.0	96.3	82.3	124.5	76.5	156.0	73.4
80.0	58.2	89.7	72.3	89.6	96.2	86.0	124.1	82.0	156.0	79.6
90.0	57.4	93.5	72.2	93.4	96.0	91.6	124.1	89.6	157.6	88.5
95.0	56.9	96.2	72.1	96.1	95.9	95.3	124.5	94.2	158.2	93.4
97.5	56.7	97.9	72.1	97.8	95.9	97.4	124.8	96.9	158.5	96.4
100.0	56.5	100.0	72.1	100.0	96.5	100.0	125.1	100.0	158.7	100.0

METHANOL-WATER SYSTEM

Distilled water and a commercial grade of methanol of above 99.5% purity were used. Temperatures were not recorded. The data are given in Table I and plotted in Figure 3; the equilibrium data of Cornell and Montonna (*4*) for atmospheric pressure are also plotted to show their relation. Experimental points are shown on Figure 3, and the best curves are drawn through them. Points at even values of liquid composition were then picked off the curves and are given in Table II. This "smoothing" is for convenience in using the data and is justified because of the close fit of the curves to the experimental data.

Data were presented by Bredig and Bayer (*2*), taken at constant temperatures up to 180° C. (at which the vapor pressure of pure methanol is 26.35 atmospheres). These data vary so much among themselves that they are worthless except to indicate general trends.

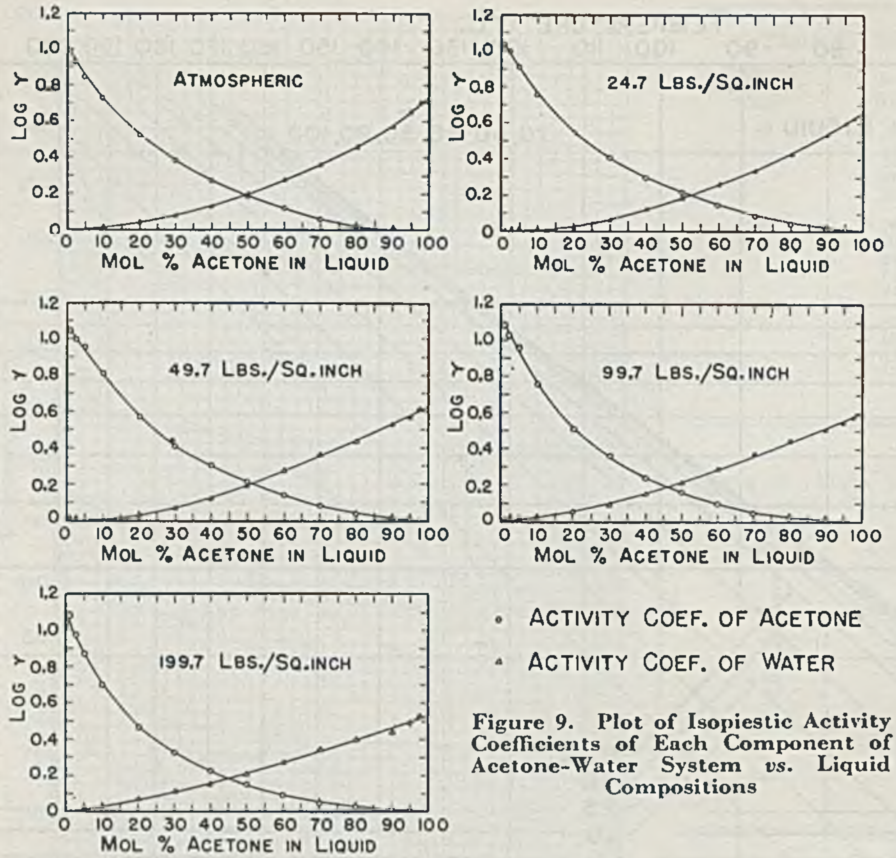

Figure 9. Plot of Isopiestic Activity Coefficients of Each Component of Acetone-Water System vs. Liquid Compositions

ACETONE-WATER SYSTEM

Synthetic acetone was dried by agitation with anhydrous calcium chloride and allowed to stand for several days. The liquid was decanted and distilled in a rectifying column. A middle fraction, distilling in the range of 56.5° C. at 760 mm. mercury, was collected. It was filtered through fuller's earth, and again distilled and collected in the same way. A middle fraction was used which boiled at 56.5° C. at 760 mm. and had a specific gravity (d_{25}^{25}) of 0.7861. Laboratory distilled water was used.

Equilibrium data for atmospheric pressure have been reported in the literature by several investigators, including Bergstrom (*1*), York and Holmes (*15*), Brunjes and Bogart (*3*), and Othmer and Benenati (*10*). Comparison of the atmospheric equilibrium data determined in this work with the reported values of the preceding investigators showed that all were in close agreement (Figure 4). The investigation was then extended to higher pressures—10, 35, 85, and 185 pounds per square inch gage. As the pressure increases, its effect in lowering the *X*, *Y* equilibrium curve decreases.

Experimental data are given in Figure 5 and Table III. The smoothed values of Table IV were obtained by plotting the experimental values on a large scale and drawing the best curve through them. To obtain better values for the portion of the curve below 10% acetone, the data were plotted on semilog paper, on which the curve in this region could be drawn and read with greater accuracy.

The equilibrium curve at atmospheric pressure has a slight concavity at the upper end. As previously stated (*7*), this indicates that at higher pressure the concavity will become more pronounced until it finally dips below the $X = Y$ line to produce a constant boiling mixture (c.b.m.). Acetone and water behave thus and form the following series of c.b.m., as obtained from Figure 5:

Pressure, Lb./Sq. In. Abs.	Temperature, ° C.	Composition, Mole % Acetone
49.7	95.8	96.5
99.7	124.0	88.4
199.7	155.8	78.0

Figure 6 indicates the change of this c.b.m. with pressure and its disappearance below about 37 pounds per square inch absolute. Figure 7 presents the data of the boiling point and dew point curves at constant pressure plotted as temperatures against composition.

Figure 8 is a total vapor pressure plot against the vapor pressure of water by the method previously described (*7*, *11*). The lines are fairly straight and are extended into the subatmospheric region by making use of Taylor's data on total pressure (*14*). This is an interesting application of this method of plotting and shows the relation of the representation of data taken at constant pressure to those taken at constant temperature. The correlation is good. Lines are shown which cross and are higher than the vapor pressure line of pure acetone. This is due to the formation of the c.b.m. of minimum boiling point. Figure 8 is of additional value in that the slope of any line is the ratio of the molar latent heat of the mixture to the latent heat of water at the same temperature. This provides a method of readily obtaining latent heat data for the system.

The apparent isopiestic activity coefficients are presented on Figure 9. These are the ratios of the products of total pressure and vapor composition to the product of vapor pressure of one pure component and liquid composition.

Table V. Apparent Activity Coefficients of Acetone-Water at Various Pressures

	14.7 Lb./Sq. In.		24.7 Lb./Sq. In.		49.7 Lb./Sq. In.		99.7 Lb./Sq. In.		199.7 Lb./Sq. In.	
X, Mole %	Acetone	Water	Acetone	Water	Acetone	Water	Acetone	Water	Acetone	Water
1	9.60	0.94	10.76	1.01	12.00	1.03	11.80	1.03	12.20	1.00
2.5	8.31	0.96	9.21	1.10	10.22	1.04	10.72	1.06	9.65	1.02
5	6.85	1.01	7.90	0.90	8.71	1.03	9.40	1.02	7.39	1.05
10	5.27	1.02	5.76	1.02	6.35	1.02	5.81	1.05	4.86	1.06
20	3.24	1.07	3.51	1.05	3.62	1.08	3.25	1.14	2.90	1.16
30	2.36	1.18	2.54	1.17	2.50	1.16	2.29	1.24	2.08	1.27
40	1.86	1.32	1.99	1.33	1.94	1.32	1.78	1.40	1.65	1.42
50	1.51	1.58	1.65	1.56	1.60	1.54	1.46	1.61	1.39	1.61
60	1.31	1.88	1.40	1.83	1.36	1.86	1.25	1.95	1.22	1.86
70	1.16	2.24	1.24	2.14	1.20	2.28	1.11	2.36	1.10	2.19
80	1.05	2.77	1.12	2.57	1.10	2.72	1.05	2.82	1.05	2.52
90	1.01	3.75	1.04	3.28	1.04	3.29	1.02	3.27	1.00	2.73
95	1.03	4.48	1.02	3.88	1.03	3.70	1.01	3.49	0.99	3.08
97.5	1.01	5.00	1.04	4.37	1.02	4.09	1.00	3.70	0.98	3.33

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Bergstrom, H., "Aftryk ur Bihang til Jernkontorets Ann.", Stockholm, 1912; also in E. Hausbrand's "Principles and Practice of Industrial Distillation", New York, John Wiley & Sons, 1928.
(2) Bredig, G., and Bayer, R., *Z. physik. Chem.*, 130, 1 (1927).
(3) Brunjes, A. S., and Bogart, M. J. P., Ind. Eng. Chem., 35, 255 (1943).
(4) Cornell, L. W., and Montonna, R. E., *Ibid.*, 25, 133 (1933).
(5) Griswold, J., Andres, D., and Klein, V. A., *Trans. Am. Inst., Chem. Engrs.*, 36, 243 (1943).
(6) Othmer, D. F., Ind. Eng. Chem., 20, 734 (1928).
(7) *Ibid.*, 32, 347 (1940).
(8) *Ibid.*, 35, 614 (1943).
(9) Othmer, D. F., Ind. Eng. Chem., Anal. Ed., 4, 232 (1932).
(10) Othmer, D. F., and Benenati, R. F., Div. of Ind. Eng. Chem., 108th Meeting of ACS, New York, N. Y.
(11) Othmer, D. F., and Gilmont, R., Ind. Eng. Chem., 36, 1061 (1944).
(12) Scheeline, H. W., and Gilliland, E. R., *Ibid.*, 31, 1050 (1939); 32, 48 (1940).
(13) Squibb, *J. Am. Chem. Soc.*, 17, 187 (1895).
(14) Taylor, H. R., *J. Phys. Chem.*, 4, 367 (1900).
(15) York, R., Jr., and Holmes, R. C., Ind. Eng. Chem., 34, 348 (1942).

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Nomograph for Calculation of Over-all Heat Transfer Coefficients

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IN CALCULATIONS dealing with the rate of heat transfer from one fluid to another separated from it by a solid wall, it is customary to define the over-all heat transfer coefficient, U, as

$$U = \frac{1}{AR} = \frac{1}{A(r_i + r_{if} + r_w + r_{of} + r_o)} \tag{1}$$

where A = area of specified surface normal to direction of heat flow, sq. ft.
R = total resistance to heat flow, (hr.)(° F.)/(B.t.u.)
r_i = resistance to heat flow offered by fluid film on inside surface of wall, (hr.)(° F.)/(B.t.u.)
r_{if} = resistance to heat flow due to fouling on inside surface of wall, (hr.)(° F.)/(B.t.u.)
r_w = resistance to heat flow offered by wall itself, (hr.)(° F.)/(B.t.u.)
r_{of} = resistance to heat flow due to fouling on outside surface of wall, (hr.)(° F.)/(B.t.u.)
r_o = resistance to heat flow offered by fluid film on outside surface of wall, (hr.)(°F.)/(B.t.u.)
U = over-all heat transfer coefficient, B.t.u./(hr.)(sq. ft.)(° F.)

The individual resistances are further expressed as

$$r_i = \frac{1}{h_i A_i};\quad r_{if} = \frac{1}{h_{if} A_i};\quad r_w = \frac{L_w}{k_w A_w};\quad r_{of} = \frac{1}{h_{of} A_o};\quad r_o = \frac{1}{h_o A_o}$$

where A_i = area of inside surface of wall, sq. ft.
A_o = area of outside surface of wall, sq. ft.
A_w = mean area of solid wall normal to direction of heat flow, sq. ft.
h_i = film coefficient of fluid in contact with inside surface of wall, B.t.u./(hr.)(sq. ft.)(° F.)
h_{if} = fouling coefficient of inside surface of wall, B.t.u./(hr.)(sq. ft.)(° F.)
h_{of} = fouling coefficient of outside surface of wall, B.t.u./(hr.)(sq. ft.)(° F.)
h_o = film coefficient of fluid in contact with outside surface of wall, B.t.u./(hr.)(sq. ft.) (° F.)
k_w = mean thermal conductivity of solid wall, B.t.u./(hr.)(ft.)(° F.)
L_w = thickness of solid wall, ft.

Depending upon the configuration of the wall through which heat is being transmitted, A takes on different values. In case the solid wall is bounded by (*a*) parallel plane surfaces,

$$A = A_i = A_o = A_w$$

(*b*) concentric cylindrical surfaces,

$$A_w = \frac{A_0 - A_i}{\ln \frac{A_o}{A_i}} \text{ and } A = A_o$$

(*c*) concentric spherical surfaces,

$$A_w = \sqrt{A_o A_i} \text{ and } A = A_o$$

The resistance of the wall, r_w, is often negligible in comparison with r_i, r_{if}, r_{of}, and r_o, so that Equation 1 becomes:

$$U = \frac{1}{A\left[\frac{1}{A_i}\left(\frac{1}{h_i} + \frac{1}{h_{if}}\right) + \frac{1}{A_o}\left(\frac{1}{h_{of}} + \frac{1}{h_o}\right)\right]} \tag{2}$$

If, further, A is always designated as A_o, then U may be called U_o, the over-all heat transfer coefficient based upon the outside surface, and the following expressions result: (*a*) for parallel planes,

$$U_o = \frac{1}{\left(\frac{1}{h_i} + \frac{1}{h_{if}}\right) + \left(\frac{1}{h_{of}} + \frac{1}{h_o}\right)} \tag{3A}$$

(*b*) for concentric cylinders,

$$U_o = \frac{1}{\left(\frac{1}{h_i} + \frac{1}{h_{if}}\right)\left(\frac{D_o}{D_i}\right) + \left(\frac{1}{h_{of}} + \frac{1}{h_o}\right)} \tag{3B}$$

(*c*) for concentric spheres,

$$U_o = \frac{1}{\left(\frac{1}{h_i} + \frac{1}{h_{if}}\right)\left(\frac{D_o}{D_i}\right)^2 + \left(\frac{1}{h_{of}} + \frac{1}{h_o}\right)} \tag{3C}$$

All three of these cases can be generalized in the form

$$U_o = \frac{1}{\left(\frac{1}{h_i} + \frac{1}{h_{if}}\right)\left(\frac{D_o}{D_i}\right)^n + \left(\frac{1}{h_{of}} + \frac{1}{h_o}\right)} \tag{3}$$

where D_i = diameter of inner (smaller) cylinder or sphere, ft.

D_o = diameter of outer (larger) cylinder or sphere, ft.

n = 0, 1, 2, respectively, for parallel, cylindrical, and spherical surfaces

NOMOGRAPH

Figure 1 shows a nomograph capable of solving all three forms of Equation 3. The following problems illustrate its use.

PROBLEM I. Determine the value of the over-all heat transfer coefficient for heat transfer from steam to water through a copper wall, if the value of h for the steam is 1000 B.t.u./(hr.)(sq. ft.) (° F.) and that for the water is 300 B.t.u./(hr.)(sq. ft.)(° F.), the fouling resistances on both sides are negligible (that is, $h_{if} = h_{of} = \infty$), and if: (*a*) the wall is a flat sheet 0.5 inch thick; (*b*) the wall is a pipe with 1-inch o.d. and 0.64-inch i.d., the steam being on the inside; (*c*) the wall is a sphere with 10-foot o.d. and 9-foot i.d., the steam being on the outside.

PROBLEM II. Repeat problem I if the values for h_f for the water and steam sides are 500 and 250 B.t.u./(hr.)(sq. ft.)(° F.), respectively.

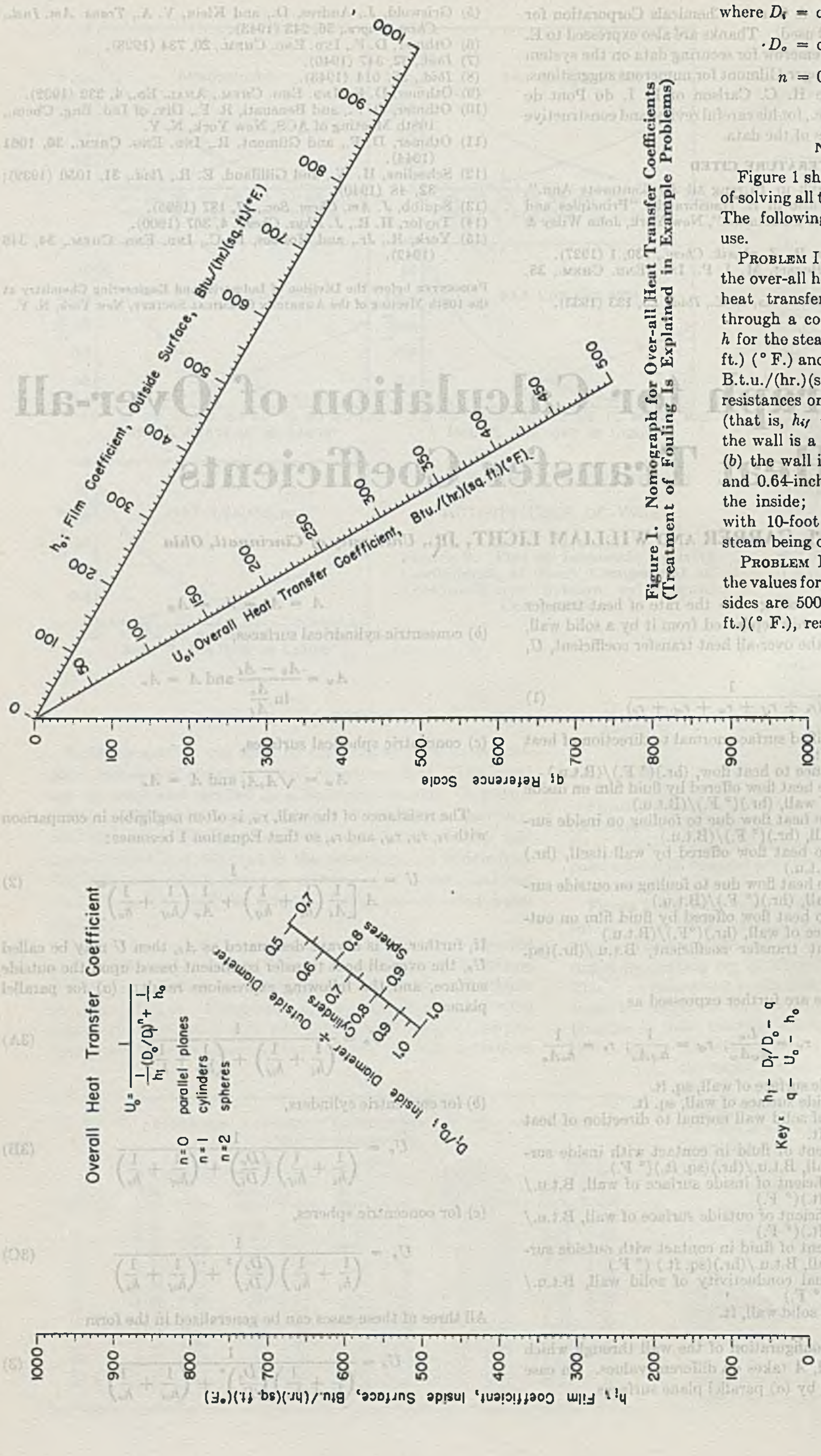

Figure 1. Nomograph for Over-all Heat Transfer Coefficients (Treatment of Fouling Is Explained in Example Problems)

SOLUTIONS

Assuming r_w to be negligible, the problems are solved by making the following alignments:

For problem I*a*, align h_i = 1000 on the q-scale with h_o = 300 on the h_o-scale to give U_o = 230.

For problem I*b*, align h_i = 1000 on the h_i-scale with D_i/D_o = 0.64 on the cylinder scale to give q = 645 on the q-scale; and align this, in turn, with h_o = 300 on the h_o-scale to give U_o = 204.

For problem I*c*, align h_i = 300 on the h_i-scale with D_i/D_o = 0.9 on the sphere scale to give q = 240 on the q-scale; and align this, in turn, with h_o = 1000 on the h_o-scale to give U_o = 195.

As constructed, the nomograph is capable of solving problems which include fouling resistances at the inside and outside surfaces in addition to film resistances. The scales can be made to serve a double purpose. From an algebraic standpoint, alignment of the right-hand set of scales (q, U_o, and h_o) adds resistances in series and gives the answer in the form of the equivalent conductance of the heat transfer path. Thus the equivalent conductance, including fouling and fluid film resistances, may be calculated separately for both the inside and outside surface by making a pair of alignments on the right-hand set of scales (q, U_o, h_o). The U_o value obtained from the h_i and h_{if} pair is $(r_i + r_{if})^{-1}$; the U_o value calculated from the h_o and h_{of} pair is $(r_o + r_{of})^{-1}$. When these two values, together with that of D_i/D_o are used to make the alignments as specified on the key of Figure 1, the resulting U_o is the over-all heat transfer coefficient for the system, including fouling.

For problem II*a*, align $h_i = 1000$ on the q-scale with $h_{if} = 250$ on the h_o-scale to give $U_o = 200$ on the U_o-scale; this is the value of $(r_i + r_{if})^{-1}$. Align $h_o = 300$ on the q-scale with $h_{of} = 500$ on the h_o-scale to give $U_o = 188$ on the U_o-scale; this is the value of $(r_o + r_{of})^{-1}$. Finally, align $h_i = 200$ on the q-scale with $h_o = 188$ on the h_o-scale to give $U_o = 97$ on the U_o-scale. This is the over-all heat transfer coefficient for the flat sheet, including fouling.

For problem II*b*, align $h_i = 1000$ on the q-scale with $h_{if} = 250$ on the h_o-scale to give $U_o = 200$ on the U_o-scale; this is the value of $(r_i + r_{if})^{-1}$. Align $h_o = 300$ on the q-scale with $h_{of} = 500$ on the h_o-scale to give $U_o = 188$ on the U_o-scale; this is the value of $(r_o + r_{of})^{-1}$. Align $h_i = 200$ on the h_i-scale with $D_i/D_o = 0.64$ on the cylinder scale to give $q = 125$ on the q-scale, and align this, in turn, with $h_o = 188$ on the h_o-scale to give $U_o = 76$ on the U_o-scale. This is the over-all heat transfer coefficient for the pipe, including fouling.

For problem II*c*, align $h_i = 300$ on the q-scale with $h_{if} = 500$ on the h_o-scale to give $U_o = 188$ on the U_o-scale; this is the value of $(r_i + r_{if})^{-1}$. Align $h_o = 1000$ on the q-scale with $h_{of} = 250$ on the h_o-scale to give $U_o = 200$ on the U_o-scale; this is the value of $(r_o + r_{of})^{-1}$. Align $h_i = 188$ with $D_i/D_o = 0.90$ on the sphere scale to give $q = 150$ on the q-scale, and align this, in turn, with $h_o = 200$ on the h_o-scale to give $U_o = 86$ on the U_o-scale. This is the over-all heat transfer coefficient for the sphere, including fouling.

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CHEMISTRY OF WESTERN PINES

Effect of Solvents on Extractives from Ponderosa Pine

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Solvent extraction of green lumber indicates that it is possible simultaneously to remove and recover extractives as well as remove water. If this solvent-seasoning process proves practical, the treated lumber will be upgraded and at the same time will establish a new source of extractives heretofore unavailable. Solvent choice will be governed by a number of factors; one may be its extractive action for the extraneous components in the wood. This report deals with the extractive action of various solvents for ponderosa pine extractives as well as the nature of each solvent extract.

PREVIOUS chemical analyses of one of several commercially important western pines indicated that ponderosa pine (*Pinus ponderosa*) is relatively rich in extractives (*1, 2*). Since extractives do not appear to be an integral part of wood, the problem consists in the possible economical removal and recovery of these extractable products from lumber, as well as from forest and mill wood waste. While not a major component of the tree, the extractives may play an important role in the chemical utilization of wood. Since so little is known regarding the distribution and nature of extractives in the wood of western pines, this and previous investigations (*1, 2*) were undertaken. This study deals with the effect of seven different solvents and one mixed solvent on the quantity and nature of the extractives from both the heartwood and sapwood of ponderosa pine.

Dore (*3*) investigated the extractives from ponderosa pine sapwood. He concluded that, although benzene extracted slightly more material than ether, petroleum ether, or carbon tetrachloride, and slightly less than chloroform, acetone, or carbon disulfide, the differences were not marked. He stated that the chief substances of economic value extracted by benzene are resins and essential oils, and that if the benzene-extracted wood was subjected to an alcohol extraction, this fraction would contain any tannins and coloring matter present in the wood. The heartwood extractives were not investigated. A previous article (*2*) on the distribution and nature of the acetone-soluble extractives from ponderosa pine indicated that the sapwood extractives of this wood contained, in addition to resin acids, essential oils, and tannins, a considerable proportion of free fatty acids, together with smaller amounts of esters and unsaponifiable material. Further, the analysis showed that the acetone-soluble extractives consisting of resin acids, fatty acids, volatiles, esters, and unsaponifiables from the heartwood are similar to those from the sapwood, but the proportion of these extractives differs from those in the sapwood.

Kurth and Sherrard (*7*) investigated extractives from southern slash pine, and found that petroleum ether boiling from 40° to 60° C. had less extractive action than ethyl ether. The petroleum ether extract was 10.9 to 18.2% smaller than the ether extract, and the difference was apparently in the amount of saponifiable material removed. Later Kurth (*5*) showed that ethanol-benzene had greater extractive action than ethyl ether for both longleaf and shortleaf pine extractives.

EXTRACTION AND ANALYSIS

Composite samples of ponderosa pine heartwood and sapwood were used in this investigation. The authenticity of the samples was verified by microscopic identification. The results reported here are not necessarily representative for this species but rather show an analysis of random samples of ponderosa pine. The representative composition of ponderosa pine extractives from various stands has already been reported (*2*). The segregated wood was reduced to sawdust to pass a 2-mm. screen in a Wiley mill. The ground samples were stored in sealed glass jars, in

Table I. Approximate Composition of Ponderosa Pine Extractives[a]

	Ethanol-Benzene		Ethanol		Methanol		Acetone		Ethylene Dichloride		Benzene		Ethyl Ether		Petroleum Ether	
	H	S	H	S	H	S	H	S	H	S	H	S	H	S	H	S
H_2O + ether insol.	5.9 0.66	21.0 0.82	4.7 0.50	10.8 0.41	5.4 0.57	5.7 0.22	2.8 0.30	4.7 0.14	1.3 0.14	3.5 0.11	0.0 0.00	0.0 0.00	0.0 0.00	0.0 0.00	0.0 0.00	0.0 0.00
H_2O sol.	2.1 0.24	4.1 0.16	2.8 0.30	10.4 0.40	3.2 0.34	16.8 0.64	1.8 0.19	10.5 0.38	0.8 0.08	1.9 0.06	0.6 0.06	1.0 0.03	1.3 0.13	4.1 0.13	0.0 0.00	0.0 0.00
Resin acids	56.1 6.28	23.1 0.90	57.0 6.10	24.0 0.91	58.2 6.17	24.5 0.93	57.6 6.11	25.7 0.93	59.8 6.28	29.3 0.94	58.5 5.85	29.8 0.94	59.2 5.86	27.2 0.87	56.5 4.80	28.4 0.80
Fatty acids	10.8 1.21	31.6 1.23	11.5 1.23	34.3 1.30	10.8 1.15	34.7 1.32	13.4 1.42	40.1 1.46	12.5 1.31	40.6 1.30	12.1 1.21	42.8 1.32	11.4 1.13	41.6 1.33	13.2 1.12	47.7 1.34
Volatile	5.1 0.57	2.4 0.09	2.9 0.31	2.5 0.10	2.7 0.29	2.4 0.09	5.4 0.57	2.7 0.10	5.5 0.58	2.9 0.09	5.6 0.56	3.0 0.09	5.7 0.56	2.9 0.09	6.6 0.56	3.3 0.09
Esters	9.8 1.10	10.2 0.30	9.0 0.96	9.6 0.36	7.7 0.82	8.4 0.30	7.2 0.76	7.2 0.26	10.0 1.05	12.3 0.39	12.0 1.20	13.0 0.40	9.8 0.97	12.4 0.40	11.4 0.97	12.1 0.34
Unsaponifiable	10.1 1.13	7.6 0.30	11.9 1.27	8.3 0.32	11.8 1.25	7.5 0.29	11.7 1.24	9.0 0.32	10.0 1.05	9.5 0.30	11.1 1.11	10.2 0.32	12.5 1.24	11.8 0.38	12.3 1.05	8.5 0.24
Extractives[b], %	11.2	3.9	10.7	3.8	10.6	3.8	10.6	3.6	10.5	3.2	10.0	3.1	9.9	3.2	8.5	2.8
Decrease in extractives, %	0.0	0.0	4.5	2.6	5.4	2.6	5.4	7.7	6.2	17.9	10.7	20.5	11.6	17.9	24.1	28.2

[a] Upper figure in each case is per cent, based on weight of extractives; lower figure, per cent based on weight of moisture-free wood. H = heartwood: S = sapwood.

[b] Based on weight of moisture-free wood.

which the air had been displaced with carbon dioxide, to retard the seasoning of the more labile components in the extractives.

The solvents chosen for this study include ethanol, methanol, acetone, ethylene dichloride, benzene, ethyl ether, petroleum ether (boiling at 30-75° C.), and the mixed solvent ethanol-benzene (in the ratio 1 to 2). The solvents were of C.P. grade; no attempt was made to purify those containing traces of impurities, since this study was concerned with solvents which might serve in the commercial solvent extraction of wood. Ground heartwood (150 grams) and ground sapwood (300 grams) having 18.1 and 23.7% moisture, respectively (based on green weight of wood), were extracted with each of the solvents in large all-glass Soxhlet extractors for 12 hours. The extraction liquid in the Soxhlet flask was transferred to a 250-cc. volumetric flask and diluted to mark with the particular solvent used. The amount of extractives removed was determined by pipetting 10-cc. aliquots, in duplicate, into tared flasks, removing solvent on water bath, and drying the extract for 16 hours in an oven at 105° C. This gave the weight of extractives less volatiles. The percentage of extractive reported here includes the volatile fraction, and the quantity of the latter component was computed from the yield of volatile obtained from each extract analyzed. The moisture content of the green sawdust was determined by the toluene method (*8*).

The 230 cc. of extraction liquid remaining in the volumetric flask were transferred to a distillation flask, and the solvent was removed on a water bath. The extractive which remained was resolved into its approximate major chemical entities—namely, water and ether insolubles, water solubles, resin acids, free fatty acids, volatiles, esters, and unsaponifiables by the procedure described previously (*2*).

QUANTITY OF EXTRACTIVES

The approximate order of color of heartwood extractives removed by each of the solvents follows, the first being the darkest: (1) ethylene dichloride, (2) ethanol-benzene, (3) ethanol, (4) acetone, (5) methanol, (6) benzene, (7) ethyl ether, and (8) petroleum ether. In the case of the color of sapwood extractives, the order of color intensity was: (1) ethanol-benzene, (2) ethanol, (3) methanol, (4) acetone, (5) ethylene dichloride, (6) benzene, (7) ethyl ether, and (8) petroleum ether. Table I shows that, in the case of sapwood, the color intensity is approximately indicative of the extractive action of the solvent employed. This does not appear to hold true, however, for the heartwood extractives except for the last three solvents—i.e., benzene, ethyl ether, and petroleum ether.

Each solvent is listed in Table I in order of extractive action. Thus the mixed solvent ethanol-benzene has the greatest extractive action and petroleum ether has the least; the latter removes 24.1 and 28.2% less extractives than ethanol-benzene from heartwood and sapwood, respectively. Ethanol, methanol, acetone, and ethylene dichloride removed practically the same amount of extractives from heartwood. Benzene and ethyl ether extracted comparable amounts from heartwood, as well as from sapwood. The water-miscible solvents ethanol, methanol, and acetone are more effective extracting agents than the water-immiscible type employed here.

HEARTWOOD AND SAPWOOD EXTRACTIVES

The composition of the extractives which are removed by the different solvents from ponderosa pine may be summarized as follows (Table I):

Water and Ether Insolubles. According to Kurth (*6*) the water- and ether-insoluble material would probably include phlobaphenes and natural pigments. Ethanol-benzene appears to have the greatest solvent action for this fraction. The water-immiscible hydrocarbons did not remove this component from the wood. While the water-miscible solvents extracted a larger quantity of water and ether insolubles from the heartwood than from the sapwood, the mixed solvent, ethanol-benzene, removed more of this fraction from the sapwood than it did from heartwood.

Water Solubles. Kurth (*6*) includes tannins, soluble carbohydrates, cycloses, and salts if present. All solvents, except petroleum ether, removed from traces to relatively large proportions of this entity. Among the solvents investigated, methanol appears to be the most effective solvent for this fraction. Sapwood contains more of this fraction than heartwood.

Resin Acids. The richest fraction in ponderosa pine heartwood extract is resin acids; it is the second most abundant component in sapwood extractives. Benzene, ethyl ether, and petroleum ether have less extractive action for this fraction than the water-miscible solvents and ethylene dichloride; the latter apparently is most effective.

Free Fatty Acids. These are the predominating component in the sapwood extractives and the second richest fraction in heartwood. While acetone removed the larger quantity of this fraction, in general, the remaining solvents extracted comparable amounts.

Volatiles. Heartwood contains more essential oils than sapwood. Here again, the extractive action of most of the solvents for this fraction was comparable; methanol and ethanol apparently removed slightly less from the heartwood than did the other solvents.

Esters. Larger quantities of this fraction are found in the heartwood than in the sapwood. Benzene appears to be the most effective solvent for this component.

Unsaponifiables. Heartwood contains more of this component than sapwood. Ethanol appears to be the best solvent for the unsaponifiables in heartwood; sapwood unsaponifiable seems to be more thoroughly removed with ethyl ether.

In the ethyl ether-soluble material from longleaf and shortleaf pine sapwood, Kurth (*5*) found that its composition differed materially from that in the heartwood. In sapwood the percentage of resin acids was relatively low, 22-30%, and the fatty acid ester content was correspondingly high, 58-71%. On the other hand, in the heartwood the reverse was true. The resin acids predominated (64-68%) and fatty acids, largely as esters, were present from 17 to 21%. The ethyl ether-solubles isolated from ponderosa pine sapwood also contain a predominance of fatty acids, mostly, however, in the form of free acids (42%) and of esters (12%); the resin acid content was correspondingly lower, amounting to about 27%. In ponderosa pine heartwood the resin acids predominated to the extent of about 59%, free fatty acids approximately 11%, and fatty acid esters 10%.

Hibbert and Phillips (*4*) isolated and analyzed the ethanol-benzene extract from mixed sapwood and heartwood of jack pine, and found that resin acids predominated, averaging about 43%; free fatty acids amounted to about 25%, and fatty acids as glycerides, about 6%. The ethanol-benzene extract from whole ponderosa pine wood likewise follows this same percentage composition trend of resin acids, free fatty acids, and esters.

SUMMARY

Since initial investigations by this laboratory have indicated that it is possible to remove extractives from green lumber by solvent extraction, the solvent choice would probably be governed, among other things, by its extractive action for the extraneous components in the lumber. This preliminary investigation indicated that solvents may vary materially in their ability to remove extractives from ponderosa pine sawdust. The order of extractive action of the solvents investigated thus far is: (1) ethanol-benzene, (2) ethanol, (3) methanol, (4) acetone, (5) ethylene dichloride, (6) benzene, (7) ethyl ether, and (8) petroleum ether. The last and least efficient solvent was approximately 75% as effective as ethanol-benzene. Ethyl ether and the low-boiling petroleum ether are laboratory solvents and not generally applicable to commercial extraction processes; of the remaining commercially feasible solvents, the water-miscible type appears to be most effective for removal of extractives.

The solvents exhibited varying selective extraction action for the various extraneous components in the wood. Thus, the mixed solvent ethanol-benzene was the most effective solvent for removing the water- and ether-insoluble fraction. The water-soluble component was most efficiently removed with methanol. Ethanol-benzene and ethylene dichloride were about equal in their ability to remove resin acids; acetone was most efficient in extracting free fatty acids. The amounts of volatile removed by the various solvents, in the main, were comparable. Benzene extracted the largest quantity of esters, and the unsaponifiable fraction was most effectively removed by ethanol and by ethyl ether. The exact nature of the various components of ponderosa pine extractives will have a bearing on their commercial value, and this identification is under investigation by this laboratory.

LITERATURE CITED

(1) Anderson, Ind. Eng. Chem., 36, 662 (1944).
(2) *Ibid.*, 38, 450 (1946).
(3) Dore, *Ibid.*, 11, 556 (1919).
(4) Hibbert and Phillips, *Can. J. Research*, 4, 1-34 (1931).
(5) Kurth, Ind. Eng. Chem., 25, 192 (1933).
(6) *Ibid.*, Ind. Eng. Chem., Anal. Ed., 11, 203 (1939).
(7) Kurth and Sherrard, Ind. Eng. Chem., 23, 1156 (1931).
(8) Wise, "Wood Chemistry", ACS Monograph 97, pp. 563-4, New York, Reinhold Pub. Corp., 1944.

Dealkylation of Dialkylbenzenes

USE OF SUPERATMOSPHERIC PRESSURE AND ALUMINA-SILICA CATALYST IN THE PRESENCE OF BENZENE

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THE dealkylation of polyalkylbenzenes has been studied for many years, but practically all of the work has been done with aluminum chloride as catalyst (*9*). In the absence of benzene the theoretical yield of monoalkylbenzene is one mole per mole of polyalkylbenzene, but in the presence of sufficient benzene it is theoretically possible to obtain as many moles of monoalkylbenzene as there are alkyl groups in the original polyalkylbenzene:

$$C_6H_{6-n}R_n + (n-1)\,C_6H_6 \longrightarrow nC_6H_5R$$

Radziewanowski (*10*) was the first to recognize the importance of benzene as an acceptor of alkyl groups from polyalkylbenzenes, and this method of dealkylation, consisting in the transfer of alkyl groups to benzene molecules, has been utilized by numerous investigators (*1, 2, 3, 4, 6, 7, 8, 12*). The dealkylation of xylene and other polyalkylbenzenes received considerable attention during World War I because of the unsatisfied demand for toluene. Interest in the dealkylation of polyalkylbenzenes has again revived because of the recent large scale production of ethylbenzene and isopropylbenzene and the desirability of dealkylating by-product diethylbenzene and diisopropylbenzene.

Because of the recent publication of a paper by Hansford, Myers, and Sachanen (*6*) on the dealkylation of polyalkylbenzenes over alumina-silica catalyst at ordinary pressure and rela-

Diethylbenzene was dealkylated under pressure over an alumina-silica catalyst in the presence of a large excess of benzene to produce monoethylbenzene. Operating at 400° C., 500 pounds per square inch, and 2 liquid hourly space velocity on a mixture of 1 mole of diethylbenzene and 10 moles of benzene, the yield per pass was 1 mole of monoethylbenzene, and the ultimate yield was 1.8 moles of monoethylbenzene as compared with the theoretical ultimate yield of 2 moles of monoethylbenzene. Compared with diethylbenzene, xylene was more difficult to dealkylate, whereas diisopropylbenzene plus 10 moles of benzene gave 1.6 moles of monoisopropylbenzene per pass. A study was made of the effects of the operating variables of time, temperature, pressure, and amount of benzene. Operation at superatmospheric pressure was found to be preferable to operation at ordinary pressure with regard to conversion per pass, ultimate yield, and catalyst life.

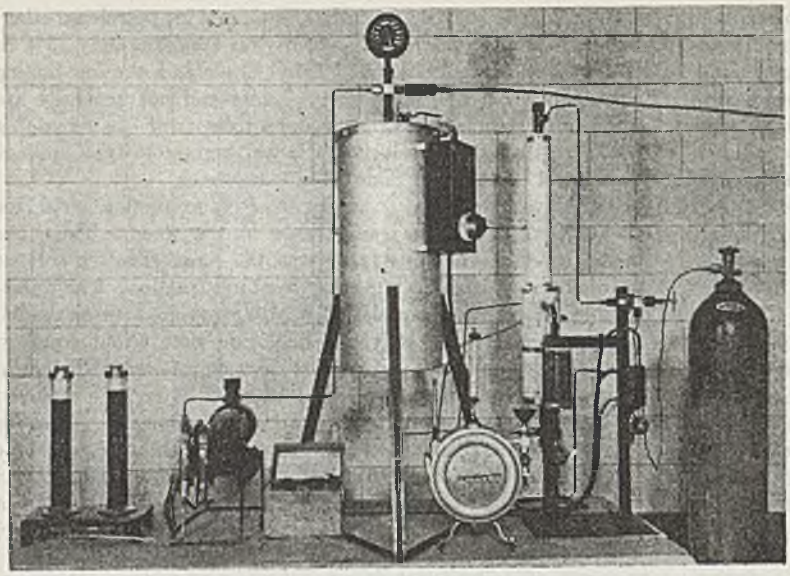

Figure 1. Dealkylation Plant

tively high temperatures, data are presented here which were obtained several years ago on the same reaction under completely different conditions.

The conditions used by the previous investigators were 15 pounds per square inch, 454-538° C., and 0 to 3 moles of benzene per mole of dialkylbenzene. Under these thermally drastic conditions the ultimate yield of monoalkylbenzene was low as a result of destructive cracking, and it was impossible to employ a sufficiently long contact time to obtain a high conversion per pass. No definite information was given on the catalyst life for the dealkylation of diethylbenzene, but it was implied that the optimum time on-stream was less than 2 hours, and that it was preferable to operate with 15-minute life cycles. The standard length of our experiments was 12 hours.

Our much less drastic thermal conditions of 400° C. and a large excess of benzene (10-15 moles per mole of dialkylbenzene) repressed destructive cracking reactions and thereby favored the ultimate yield. Superatmospheric pressure made it possible to employ a sufficiently long contact time to obtain high conversion per pass and also considerably lengthened the life cycle of the catalyst because of the washing effect of the dense hydrocarbon phase. Even with 36 hours of continuous operation, the average conversion per pass of diethylbenzene to monoethylbenzene was 42% of the theoretical, and the average ultimate yield over the 36-hour period was 92%; the highest yields reported by Hansford, Myers, and Sachanen (*6*) were 29% per pass and 63% ultimate, with a much shorter catalyst life between regenerations.

A patent by Sachanen and Hansford (*11*) describes dealkylation under superatmospheric pressure, but the chemical composition of the feed stock was not specified (boiling range, 150-250° C.) and the conditions were so drastic (482° C. and 40 minutes of contact time) that the product gave little information as to the nature of the reaction.

EXPERIMENTAL DETAILS

MATERIALS. The benzene was nitration grade. The xylene contained about 65% of *m*-xylene and 35% of *p*-xylene. The diethylbenzene and diisopropylbenzene were prepared by the alkylation of benzene by ethylene and propylene, respectively. The amounts of the various isomers were not determined. The dialkylbenzenes were distilled through a fifteen-plate Fenske column with a reflux ratio of 10 to 1 to give products with the following constants:

	B.P., ° C. (760 Mm.)	n^{20}_D	d^{20}_4
Xylene	138-9	1.4963	0.863
Diethylbenzene	180-3	1.4958	0.866
Diisopropylbenzene	206-8	1.4888	0.856

CATALYST. The 90% silica-10% alumina catalyst was made by dispersing freshly prepared, washed silica gel in dilute aqueous aluminum chloride and adding aqueous ammonia with stirring. The intimate mixture of silica and alumina gels was washed five times with distilled water, and the filter cake was slurried each time in the water wash. The washed cake was dried at 100° C., crushed, screened to 20-30 mesh, and pelleted in the form of 0.32

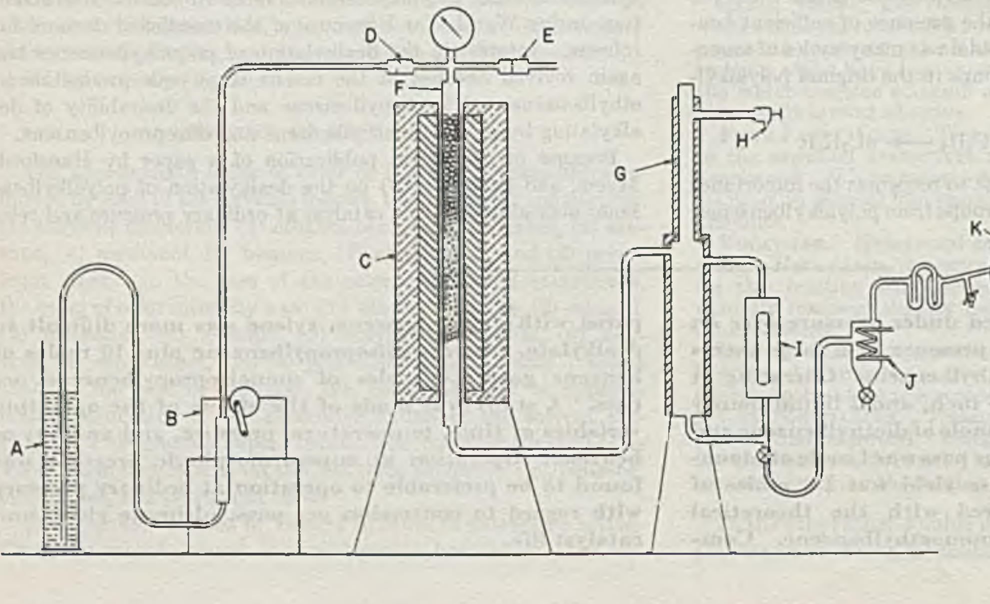

Figure 2. Flow Sheet of Dealkylation Process

A. Charger
B. Pump
C. Furnace
D. Check valve
E. Rupture plate assembly
F. Catalyst tube
G. High pressure receiver
H. Inlet for nitrogen
I. Jerguson sight glass
J. Low pressure receiver
K. Gas meter

Table I. Study of Variables in the 12-Hour Dealkylation of Diethylbenzene

Conditions			Charge[a]			Product[a], Grams				EB Yield, % of Theoretical	
T ° C.	L.H.S.V.[b]	Lb./sq. in. gage	Mole ratio, B/DEB	B, g.	DEB, g.	EB	DEB	> DEB	C on Catalyst, Grams	Per pass	Ultimate
A. Effect of Benzene Concentration											
400	2	500	5	1562	538	289	337	21	1.11	33.9	91
400	2	500	10	1769	303	247	137	14	0.59	51.6	94
400	2	500	15	1895	217	229	66	11	1.52	66.7	96
B. Regeneration and Catalyst Life											
400	2	500	10	1769	303	247	137	14	0.59	51.6	94
400	2	500	10	1777	305	265	125	15	....	55.0	93
400	2	500	10	1765	303	181	179	15	....	37.8	92
400	2	500	10	1714	294	151	187	14	1.97	32.5	89
C. Effect of Temperature											
300	2	500	10	1779	306	25	285	11	0.02	5.2	75
350	2	500	10	1733	297	118	212	13	0.16	25.2	87
400	2	500	10	1769	303	247	137	14	0.59	51.6	94
450	2	500	10	1718	295	265	96	15	1.97	56.8	84
D. Effect of Pressure											
350	1	250	5	793	272	113	192	10	0.78	26.1	89
350	1	500	5	789	271	123	185	10	0.84	28.7	91
350	2	500	10	1733	297	118	212	13	0.59	25.2	87
350	2	900	10	1801	313	114	231	13	0.18	23.0	88
400	2	15	10	1750	300	17	282	5	0.68	3.6	60
400	2	250	10	1810	310	139	213	14	0.52	28.3	90
400	2	500	10	1769	303	247	137	14	0.59	51.6	94
400	2	900	10	1793	308	220	155	14	0.61	45.1	91
E. Effect of Space Velocity											
400	1	500	10	867	149	151	48	7	1.01	64.2	94
400	2	500	10	1769	303	247	137	14	0.59	51.6	94
400	3	500	10	2637	453	367	202	10	0.74	51.0	92
F. Recycling of Recovered Diethylbenzene											
400	2	500	10	1748	300	268	112	18	0.88	56.3	90

[a] B = benzene, EB = monoethylbenzene, DEB = diethylbenzene.

[b] L.H.S.V. (liquid hourly space velocity) is volume of liquid fed per hour through an equal volume of catalyst.

× 0.32 cm. ($^1/_8$ × $^1/_8$ inch) pills with 4% of aluminum stearate as die lubricant. The pills were heated in a stream of air at 600° C. to remove carbon before being used as catalyst.

The silica gel used was precipitated from dilute aqueous water glass by hydrochloric acid and washed six times with distilled water (filtering by suction after each wash and slurrying the filter cake in each subsequent wash) until the sodium content of the gel was lowered to 0.1%. The final silica gel cake contained about 12% of silicon dioxide.

Apparatus and Procedure. Figures 1 and 2 show the actual setup and the flow diagram of the process. The furnace consisted of a vertical 10 × 61 cm. (4 × 24 inch) insulated stainless steel block, electrically heated and thermostatically controlled within ±3° C. of the desired temperature, and containing a longitudinal hole (2.5 cm. or 1 inch in diameter) for the catalyst tube and a parallel hole (4.8 mm. or $^3/_{16}$ inch in diameter) for the thermocouple. The catalyst tube was of stainless steel, 2.06 cm. i.d. and 94 cm. long ($^{13}/_{16}$ and 37 inches). The 100-cc. (80-gram) catalyst bed (about 30 cm. or 12 inches long) was held in place in the middle of the heated zone by plugs of steel wool, and the upper volume of the catalyst tube was packed with broken quartz for preheating.

The liquid feed (benzene and dialkylbenzene) was pumped into the top of the catalyst tube by a Hills-McCanna type SA pressure pump. Nitrogen was used to maintain the pressure in the plant. The catalyzate (liquid and gas) was taken off through a high-pressure needle valve which was followed by a water-cooled condenser. The liquid product was stabilized, and the liberated gas was measured and analyzed. The gas was mainly nitrogen which was carried over dissolved in the liquid. The gas was analyzed by absorption and combustion, and the weight of the gas was approximated from these data. The stabilized liquid product was heated under a fifteen-plate Fenske column to remove benzene, and the concentrate was distilled through a semimicro column (5). Very little material boiled between the distillation plateaus, and therefore no intermediate fractions were taken; for example, the cut point between benzene and monoethylbenzene was 107° C. and that between monoethylbenzene and diethylbenzene was 158° C. The distillation cuts were identified by boiling point, refractive index, and density. At the end of each experiment the catalyst was flushed (at the temperature of the experiment) with nitrogen to remove adsorbed hydrocarbon, cooled, and ground to a fine powder. The carbon on the used catalyst was determined by burning a 5-gram sample in a dry air-oxygen stream (1 volume of air, 2 volumes of oxygen) at 650–700° C., and collecting the carbon dioxide in an Ascarite tube which was preceded by a drying tube. In one experiment (Table IB) where the regenerated catalyst was needed for other runs, the total catalyst (in pill form) was burned at 600° C. in air for 3 hours, and the carbon dioxide was collected.

CALCULATION OF RESULTS

Yield Figures. The percentage yields were calculated on the assumption that one mole of dialkylbenzene can produce two moles of monoalkylbenzene:

$$C_6H_4R_2 + C_6H_6 \longrightarrow 2C_6H_5R$$

These yields are not to be confused with the "weight yields" reported by Hansford, Myers, and Sachanen (6) which regard, for example, a yield of 134 grams (1.264 moles) of monoethylbenzene from 134 grams (1 mole) of diethylbenzene as a 100% yield; it really corresponds to only 63.2% of the amount theoretically possible. Weight yields also vary in significance as a function of the size of the alkyl group. For example, a 100% weight yield of monoalkylbenzene corresponds to 57.6%, 63.2%, or 67.5% of the theoretical yield from xylene, diethylbenzene, or diisopropylbenzene, respectively.

Conversion per Pass vs. Ultimate Yield. When the conversion per pass was low, the ultimate yield was also low. The explanation of this relationship is probably the comparatively greater loss of product by adsorption in the low-conversion experiments and the condensation reactions; the latter always take place, even when there is little dealkylation, to form high boiling, nonrecyclible hydrocarbons from the product or from the starting materials. Both of these effects would diminish the ultimate yield more for the low conversion than for the high conversion runs.

DISCUSSION OF RESULTS

Negligible Gas and Carbon Production. Gas was collected and analyzed in all runs, but it was always less than 1

Table II. Dealkylation of Xylene and Diisopropylbenzene

(500 lb./sq. in., 2 l.h.s.v., mole ratio $C_6H_6/C_6H_4R_2$ = 10; 12-hr. runs)

$C_6H_4R_2$	Temp., ° C.	Charge, Grams		Product, Grams			C on Catalyst, Grams	Yield of C_6H_5R, % of Theoretical	
		C_6H_6	$C_6H_4R_2$	C_6H_5R	$C_6H_4R_2$	$>C_6H_4R_2$		Per pass	Ultimate
$C_6H_4(CH_3)_2$	400	1884	256	8	234	11	0.67	1.8	21
$C_6H_4(CH_3)_2$	450	1814	246	23	230	11	1.94	4.7	83
$C_6H_4(C_3H_7)_2$	400	1728	359	419	42	20	1.24	79	89

gram per 12-hour run (after subtracting the nitrogen used to pressure the plant). It was of the order of 0.3% of the weight of the dialkylbenzene charged or 0.04% of the total hydrocarbon charged. The carbon production for the superatmospheric pressure runs was of the same order, ranging from 0.02 to 0.1% of the total hydrocarbon charged. This 0.04% gas yield and 0.02 to 0.1% carbon production are to be compared with 0.3 to 8.4% gas yield and 0.4 to 2.0% carbon production reported by Hansford, Myers, and Sachanen (*6*) for the catalytic dealkylation of diethylbenzene.

Effect of Benzene Concentration. Table I*A* lists data obtained at three different benzene concentrations. Fifteen moles of benzene per mole of diethylbenzene gave a 66.7% conversion per pass of diethylbenzene to monoethylbenzene; 5 moles of benzene per mole of diethylbenzene gave a 33.9% conversion per pass. The ultimate yields in all cases were at least 90% of theoretical.

Regeneration and Catalyst Life. The first experiment in Table I*B* shows the performance of fresh catalyst; the three subsequent experiments show the behavior of the regenerated catalyst during three consecutive 12-hour periods. Regeneration consisted in burning in situ at 600° C. in a stream of air for 3 hours. The regenerated catalyst gave a somewhat higher conversion per pass during the first 12 hours than the fresh catalyst, the conversion falling from 55% during the first 12 hours to 32.5% during the third 12 hours. The final catalyst contained about 2% of carbon (after 36 hours of continuous operation), which corresponded to 0.2% of the diethylbenzene charged or 0.03% of the total hydrocarbon charged.

Effect of Temperature. Under the conditions used (pressure, feed rate, reactant ratio, and length of run) the optimum temperature was about 400° C. (Table I*C*). Operation at 300° and 350° C. gave only 10 and 50%, respectively, as much conversion per pass as at 400° C.; operation at 450° C. gave a somewhat higher conversion per pass but a lower ultimate yield and higher carbon formation.

Effect of Pressure. The rate of carbon deposition on the catalyst at 400° C. with respect to time was the same at 15, 500, and 900 pounds per square inch, but the rate of carbon production with respect to ethylbenzene production was about 15 times as much at 15 as it was at 500 and 900 pounds (Table I*D*). The usual explanation involving the more effective washing by the denser phase hydrocarbon is probably applicable. At 350° C. doubling the pressure from 250 to 500 pounds had little effect on the conversion, whereas doubling it at 400° C. from 250 to 500 pounds almost doubled the conversion. Raising the pressure seventeen fold (from 15 to 250 pounds) at 400° C. raised the conversion eight fold, but raising the pressure from 500 to 900 pounds, both at 350° and 400° C., slightly decreased the conversion per pass.

Effect of Space Velocity. A 300% increase in liquid hourly space velocity (from 1 to 3) decreased the percentage conversion per pass by less than 20% (from 64.2 to 51%), which indicated that economical conversions could be obtained at considerably higher space velocities (Table I*E*).

Recycling of Recovered Diethylbenzene. The physical constants (boiling point, d^{20}_4, n^{20}_D) of diethylbenzene recovered from the first pass were the same as those of the original diethylbenzene (Table I*F*). The recovered diethylbenzene was dealkylated on the second pass to the same extent as on the first pass; this showed that there was no preferential dealkylation in the first pass to give a more refractory isomeric mixture for recycling.

Dealkylation in Absence of Catalyst. When a mixture of 1 mole of diethylbenzene and 10 moles of benzene was passed over Pyrex beads 3.2 mm. (1/8 inch) in diameter at 400° C., 500 pounds per square inch, and 2 l.h.s.v. for 12 hours, the conversion to monoethylbenzene was less than 1% as compared with approximately 50% in the presence of alumina-silica catalyst. Carbon production on the beads was essentially zero. Hansford, Myers, and Sachanen (*6*) reported that thermal treatment at ordinary pressure gave zero yield of monoethylbenzene even at 510° C.

Higher Boiling Hydrocarbons Recovered from Dealkylated Diethylbenzene. Claisen flask distillation of a composite residuum (boiling point > 185° C.) from the dealkylation of diethylbenzene gave the following data:

Fraction	B.P., ° C. (Mm.)	Volume % Over	n^{20}_D	d^{20}_4
1	185–205 (760)	3	1.4990	0.875
2	205–230 (760)	42	1.5183	0.905
3	90–230 (8)	55	1.5573	0.985

The two high boiling fractions seemed to contain considerable amounts of polycyclic hydrocarbons as evidenced by refraction and density.

Dealkylation of Xylene and Diisopropylbenzene. As Table II shows, xylene was dealkylated very little at 400° and 450° C. at 500 pounds per square inch. Hansford, Myers, and Sachanen (*6*), using 538° C., 15 pounds per square inch, 1.13 l.h.s.v., and 2 moles of benzene per mole of xylene, obtained a 16% yield of toluene per pass; at 0.36 l.h.s.v. their yield per pass was 23%, compared with our yield of 1.8% per pass at 400° C. and 4.7% at 450° C., using 2 l.h.s.v. with 10 moles of benzene per mole of xylene. Diisopropylbenzene, on the other hand, was more easily dealkylated than diethylbenzene; the per pass yield at 400° C. and 2 l.h.s.v. was 79% of theoretical.

ACKNOWLEDGMENT

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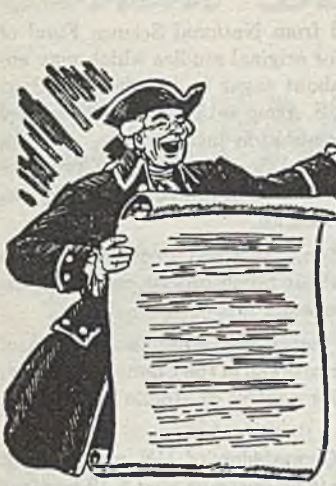
LITERATURE CITED

(1) Berry and Reid, *J. Am. Chem. Soc.*, 49, 3142 (1927).
(2) Boedtker and Halse, *Bull. soc. chim.*, 19, 444 (1916).
(3) Cline and Reid, *J. Am. Chem. Soc.*, 49, 3150 (1927).
(4) Corson and Ipatieff, *Ibid.*, 59, 645 (1937).
(5) Glowacki, "Determination and Examination of Light Oil in Gas", New York, Am. Gas Assoc., 1941.
(6) Hansford, Myers, and Sachanen, Ind. Eng. Chem., 37, 671 (1945).
(7) Milligan and Reid, *J. Am. Chem. Soc.*, 44, 206 (1922).
(8) Nametkin and Pokrovakaya, *J. Gen. Chem.* (U.S.S.R.), 8, 699 (1938).
(9) Nightingale, *Chem. Rev.*, 25, 329 (1939).
(10) Radziewanowski, *Ber.*, 27, 3235 (1894).
(11) Sachanen and Hansford, U. S. Patent 2,222,632 (1940).
(12) Zal'kind and Arbuzova, *Plasticheskie Massy, Sbornik Statei* No. 3, 249–55 (1939); *Khim. Referat. Zhur.*, 1940, No. 3, 90.



JUNE'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ **June 1.** U. S. Senate unanimously passes McMahon bill for national civilian control of atomic energy.

¶ **June 2.** American Viscose conducts "advanced seminar on rayon" for deans and instructors of eight textile schools.~~War Assets Administration offers for sale Louisville, Ky., synthetic rubber plant, operated by B. F. Goodrich Chemical Co. during war.

¶ **June 3.** Reynolds Metals Co. announces successful completion of its first shipment of aluminum by water and says it was much less expensive than by rail.~~Blaw Knox acquires assets and business of Buflovak Northwest Co.

¶ **June 4.** At hearing before House Committee on Patents, R. J. Dearborn, chairman Committee on Patents and Research, National Association of Manufacturers, says government-owned patents should be made available to citizens of U. S.~~War Department announces contract with GE for atomic energy research and development including transfer of operation of $347,000,000 government-owned plant at Hanford, Wash., from du Pont to GE.~~Henry Ford II reveals plans for construction of $50,000,000 research and engineering center on 500-acre tract in Dearborn, Mich.[1]~~Security Council Subcommittee that investigated Spain says exclusion of Franco regime from UN bars effective international control of atomic energy.

¶ **June 5.** Vannevar Bush, president Carnegie Institute, proposes Army ground and air forces and Navy be required to unify their military research and development.~~Spencer Chemical Co. takes over Jayhawk Ordnance Works, a wartime nitrogen plant near Pittsburg, Kans., for production of basic industrial and agricultural chemicals.~~Air Reduction Co. and U. S. Industrial Chemicals, Inc., announce plans to build new chemical research laboratory in Stamford, Conn.[1]

¶ **June 6.** Leaders of American chemical industry at annual meeting of Manufacturing Chemists' Association at Skytop, Pa., see several years of record sales after 1946.~~Harry L. Derby, president American Cyanamid & Chemical Corp., tells MCA in annual meeting that if permitted to rehabilitate its chemical industry and retain plant facilities to provide munitions, Germany may become a threat to world peace.

¶ **June 7.** State Department officials say reciprocal trade pacts with foreign countries will not be issued until after the UN preliminary trade conference.~~American Viscose announces acquisition of Sylvania Industrial Corp.~~Robert E. Wilson, chairman of board Standard Oil Co. of Ind., is elected to life membership in the Corporation of MIT.

¶ **June 8.** J. M. Jardine, president University of Wichita, reveals discovery of new strain of penicillin by Wayne Simmonds, which has potentialities possibly greater than those now used commercially.

¶ **June 9.** Office of Publication Board reports German research workers claim to have developed experimental plant which simultaneously pasteurizes and enriches vitamin D content of milk by ultraviolet light.~~Frank H. Kelley, Jr., representative Bell Aircraft Corp., says newly developed "bug bomber", a specially equipped helicopter, will be tested on a crop spraying and dusting project in the Yakima Valley, Wash.~~Rear Admiral A. C. Read, Sr., says potential defenses against atomic bomb are already in outline stage.

¶ **June 10.** WAA says Spencer Chemical Co. has leased government-owned ammonium nitrate plants at Parsons, Kans., MacGregor, Tex., and Baxter Springs, Kans., and Lion Oil Co. those at Minden, La., and Texarkana, Tex., for production of fertilizer.~~WAA recommends sale of 10 government-owned synthetic rubber plants.~~National Fertilizer Association, in response to a special message from President Truman, pledges increased help to farmers by supplying fertilizers for production of more food to satisfy world needs.

¶ **June 11.** Secretary of War Patterson urges House of Representatives to pass McMahon bill for control of atomic energy.~~Socony Vacuum Oil markets Mobil-flame, a liquid petroleum gas.

¶ **June 12.** Fred C. Shaneman, president Pennsylvania Salt Mfg., says company has begun construction of new $1,000,000 chemical plant on Willamette River near Portland.~~War Department officials say $2,500,000 atomic power plant at Oak Ridge, Tenn., is expected to be ready for experimental operation by January 1.~~Navy joins Army in endorsing Senate legislation to create 5-member civilian commission for domestic control of atomic energy.

¶ **June 13.** War Department discloses by-products from atom plants will be distributed to schools, hospitals, and laboratories of science and industry.~~Senator Connally says any agreement for international control of atomic energy must be bound in a treaty from which no signatory country could deviate.~~U. S. District Court grants defendants in antitrust suit against American Petroleum Institute and major oil companies an extension of time to July 22.~~Military officials of Army-Navy Petroleum Board at Annapolis witness successful demonstration of synthetic gasoline and Diesel fuel from natural gas.~~Glenn L. Martin Co. announces plans to construct first units of a $1,500,000 chemical plant near Painesville, Ohio.

¶ **June 14.** Linus Pauling receives Willard Gibbs Medal for outstanding research at meeting of Chicago Section, ACS.~~Representatives of 12 nations convene in attempt to insure development of atomic energy will advance, instead of destroy, mankind.~~Bernard M. Baruch, at first meeting of UN Atomic Energy Commission, says U. S. will tell bomb secret, and destroy bomb, if UN establishes controls and bans veto.~~Senate passes amended legislation approving Bikini atoll

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[1] *Chem. Eng. News.*, 24, 1680 (June 25, 1946).

atomic bomb tests.∼∼Civilian Production Administration places 30-day inventory limits on synthetic rubber and zinc.

¶ June 15. Senator Eugene D. Millikin demands speedy Allied agreement on peace treaties before U. S. moves to entrust atomic secrets to international control, but Senator McMahon, chairman of Senate Atomic Energy Committee, disagrees and believes atomic decisions reached in N. Y. will have greater bearing on future peace than agreements made in Paris.

¶ June 16. Senator Mitchell asserts government agencies are blocking development of a competitive aluminum industry.∼∼ Pennsylvania Salt Co. is producing new insecticide, hexachlorocyclohexane, which has 10 times the killing power of DDT, on experimental basis.∼∼Universal Match Corp. introduces new Aqua-Pruf water-resistant strike-any-where match which corporation claims will light after indefinite exposure to moisture.∼∼ Board of Directors, American Viscose, approves appropriation for preparation of plant site of company's new plant at Radford, Va.∼∼R. J. Dearborn urges prompt Senate action on five bills designed to bring about constructive changes in patent system. ∼∼John Steele, national commander, American Legion, says Legion opposes giving atomic power secrets to UN until Big Four have shown they have no "imperialistic aims".∼∼J. T. Shotwell, chairman committee on Atomic Energy, Carnegie Endowment for International Peace, issues proposal for international control of atomic energy similar to Baruch proposal but retaining veto power and leaving to Security Council primary responsibility for punishment of violations of atomic bomb regulations.

¶ June 17. Interagency Policy Committee on Rubber in report to War Mobilization and Reconversion recommends early disposal of 25 synthetic rubber plants which would be unessential to a national rubber program.∼∼King George, opening Empire parley, cites atom values and warns against curbs on study.∼∼ Federation of American Scientists announces formation of Committee for Foreign Correspondence to re-establish prewar international scientific collaboration.∼∼R. J. Dearborn says Atomic Energy Control bill as recently passed by Senate is so unduly restrictive as "to jeopardize our system of private initiative and free enterprise".∼∼Monsanto announces plastic that puts new life in old oil wells, accomplishing what is believed to be far greater efficiency and economy than any material previously used.

¶ June 18. House Military Committee rejects Senate proposal to place domestic development of atomic energy in 5-man civilian commission and votes military two places.∼∼Interior Secretary J. A. Krug names 85 men to new National Petroleum Council, an industry committee which will advise him on oil and gas.∼∼Du Pont establishes new nylon section in chemical division of ammonia department to centralize research and development work on chemicals used in making nylon.∼∼Johns Hopkins establishes Institute for Cooperative Research to work with Government and industry on scientific projects, President Isaiah Bowman announces.

¶ June 19. Soviet Union offers substitute plan for outlawing atomic bombs which would ban their use or retention but would keep Big-Power veto.∼∼House Military Affairs Committee votes to strengthen Army's control over atomic bomb production by giving it power to make its own weapons.∼∼Bakelite Corp. announces acquisition of former Inland Rubber Co.'s plant near Ottawa, Ill., for manufacture of Vinylite plastics.∼∼M. D. Coulter, Goodyear's research staff, announces F. F. Pliofilm, a frozen foods packaging material which will remain flexible at −20° F.

¶ June 21. J. C. Turrells, director Cluett Peabody's sanforizing division, announces new chemical process said to stabilize viscose rayon fabrics so they can be washed without danger of appreciable shrinkage or stretch.∼∼W. Z. Hassid, M. Doudoroff, and H. A. Barker, research workers at University of California, receive first intermediate $5000 award from National Science Fund of National Academy of Science for original studies which may enable scientists to learn more about sugar in the diet.∼∼Brig. Gen. William H. Draper says U. S. Army authorities have stopped dumping captured German ammunition into the sea, and are salvaging it for fertilizer.∼∼Royal Society (London) proposes at least £1,000,000 be spent on research in fundamental subjects, excluding cost of buildings or salaries.

¶ June 22. Sir Alfred Egerton, at Royal Society's Empire Science Conference, suggests atomic bomb pits be used as reservoirs for water distilled from the sea.

¶ June 24. Dummy atomic bomb falls amid fleet in Bikini dress rehearsal.∼∼*Pravda*, official organ of the Communist party, flatly rejects U. S. proposals for control of atomic bomb as instrument of war.

¶ June 25. Atomic Energy Commission of UN unanimously approves proposal by H. V. Evatt of Australia that a 12-member committee be formed to take up suggestions made during general discussions.∼∼CPA grants Diamond Alkali Co. permission to construct a $5,750,000 electrochemical plant at Houston, Tex. ∼∼L. W. Chubb, director Westinghouse Research Laboratories, announces plans for big atomic research program with conversion of atomic energy into a useful source of power for peacetime use. ∼∼UN Atomic Energy Commission sets up "committee of the whole" to draft plan for world control and development of atomic energy.∼∼Atomic Trades and Labor Council, AFL, petitions National Labor Relations Board for representation elections in three principal plants working on atomic energy.∼∼Rutgers University gets 20 prefabricated aluminum buildings originally intended for use of troops in South Pacific.

¶ June 26. J. Oostermeyer, president Shell Chemical Co., says company will begin soon to produce petroleum-derived chemical, glycerin epichlorohydrin, for use in manufacturing plastics, fumigants, and industrial solvents.∼∼CPA says 9 industrial alcohol plants, representing almost total facilities of the industry, have shut down because of lack of molasses. ∼∼WAA offers for sale or lease complete silica alumina catalyst manufacturing plant with rated capacity of 10,800 tons a year.∼∼Attorney General Clark announces filing in U. S. District Court at Cleveland civil action charging 3 lecithin manufacturers with violation of antitrust laws.∼∼Bernard M. Baruch drafts J. R. Oppenheimer, director of Desert Laboratory where first atomic bomb was produced, for post in U. S. Delegation to UN Atomic Energy Commission, Chas. G. Ross, President Truman's secretary, says.∼∼House Appropriations Committee approves appropriation of $660,000 for U. S. Delegation to UN Atomic Energy Commission.

¶ June 27. Industry through it advisory committee, asks CPA to remove use controls on oils in paint and varnish manufacture.∼∼Farrington Daniels, director Metallurgical Laboratory, University of Chicago, in report to ACS points out uranium might be substituted for gold in our monetary system. ∼∼Federal Grand Jury in Denver returns indictment charging 6 corporations and 5 individuals with antitrust violations in vanadium industry.

¶ June 28. E. D. Bransome, president Vanadium Corp., denies charges of conspiracy to monopolize and fix vanadium prices. ∼∼P. Cherenkov, writing in *Izvestia*, says work of Alexander P. Zhdanov on new aspects of atom splitting, which won him a Stalin prize, opens a new page in nuclear physics.∼∼Empire Scientific Conference, Cambridge, England, adopts resolution calling for UN International Organization to control airborne pests.

¶ June 30. OPA price controls end at midnight.∼∼Atomic bomb explodes over Bikini fleet, sinking 5 ships, damaging 31, and with relatively few, if any, of remaining ships escaping some damage.

Current Developments in
EQUIPMENT AND DESIGN

Are new standards possible with metals produced by modern metallurgical science?

Discussed by Charles Owen Brown

In last month's column (June, Advertising page 69) the subject of loading chemical equipment to capacity was discussed as an introduction to the subject of the potential possibilities of modern metals. A few generalities about their strength, hardness, machinability, and resistance to heat and atmosphere is worth while to the user of equipment. Most heat-resistant equipment or highly stressed equipment is fabricated from ferrous metals and alloys.

Primitive iron was made in furnaces which were really crude. A two-man four-cylinder "blowing engine" produced iron for the ancients of Egypt, Assyria, and China, and a well reduced metal reached Europe, in small quantities at least, before Caesar. For generations the problem was mainly production, and any kind of material could be sold. Then came knowledge of more exact methods for improving the properties by regulation of carbon, and heat treatment followed. For many years the metallurgical world focused its research on the role of carbon as the basis of all special steels, but it came to be known almost automatically that many other elements in small quantities could impart valuable properties to steels. For several generations the best materials for making steel have been steel scrap, and it is used as far as the supply will permit. Scrap steel looks rough and rusty, but actually it is the purest raw material, even better than the best pig iron. The large use of scrap in steel making has resulted in a great deal of unplanned alloying and blending. Most steels today contain an appreciable content of metal which has been returned to the furnace many times. Therefore, eventually a run of steel will contain fractions of a per cent of several alloying agents resulting from the impurities in the scrap; investigations of the effect of these small additions as well as of carbon on the properties of steels have been forced with the programs of metallurgical research.

For a long time it has been recognized that a small amount, such as 1% of any of the important alloying metals, produces an effect approximately half as great as 5 or 6% of the same element. The possibilities of steels containing a total of 2% of nickel, chromium, molybdenum, tungsten, and manganese, together with the usual carbon, had to be investigated because as far back as the first World War the scrap had become mixed up. Well known steels of this type are the 8600 and 8700 types; each has remarkable properties, although the total of alloying metals plus carbon is approximately 2%. These steels are evidence that trace metals are even more important than carbon as a basis for the development of physical properties by heat treatment. Early in the century, Kent's Handbook contained a table labeled "Effect of Carbon on Physical Properties of Steel", the carbon content listed ranged from 0.05 to 0.85% (pearlite), and the reported ultimate tensile strength of the untreated steel ranged from 45,000 to a maximum of 140,000 pounds per square inch, with 27,000 to 78,000 as the corresponding yield points. In one modern steel of the 8600 type, having 0.40% carbon and 2% of the four alloying metals, the Brinell hardness was developed to 430, the ultimate tensile was 214,000 pounds with an elastic limit of 185,000 pounds per square inch, and 16% elongation in 2 inches produced a reduction in area of 48%. This is a striking example of the value of elements other than carbon in producing a steel of much wider usefulness with good machinability.

The yield point of the 8600 type just described is 85% of the ultimate tensile strength of 214,000 pounds per square inch. It would make little difference in this case whether the designer based a factor of safety on the usual "ultimate" or, more logically, on the yield point, and thus avoided the use of any data signifying deformation. In every-day carbon steel, however, there is a marked difference. The usual steel plate, bars, and shapes have a yield point of 34,500 pounds (at 0.15% carbon) with an ultimate tensile of 57,000 pounds per square inch. The Code requires a factor of safety of 4 (American Petroleum Institute) or 5 (American Society of Mechanical Engineers) applied to the ultimate tensile. The designer may therefore use a stress of 14,250 pounds per square inch. It should be noted, however, that the purchaser of such steel must accept material having a tensile of 51,300 pounds with a yield point of 32,000 pounds per square inch. If the same stress is based on the more scientific yield point, a safety factor of 2.25 is obtained. Many designers use a safety factor for ordinary carbon steel of 2.5 based upon the yield point, which is more logical and conservative. There are other factors to be considered when this principle is used with five-element 8600 and 8700 type steels. The yield point, especially

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with cold working, disappears into the ultimate tensile strength. Even in the hot-worked material the yield point is very high, but the proportional limit (the stress beyond which the change in length is no longer proportional to the stress applied) does not follow either the high yield point or ultimate tensile. A safety factor of 5, based upon 214,000 pounds would permit a design stress of 42,800 pounds per square inch. A safety factor of 2.5, based on the yield point of 185,000 pounds, would indicate the rather high stress of 74,000 pounds per square inch; but if the proportional limit of 110,000 pounds is substituted for yield point, then the 2.5 factor of safety gives almost the same design stress of 44,000 pounds per square inch.

There are further important variations in these two physical properties. In carbon steels the ultimate tensile strength increases in a straight line proportion to the carbon content, up to maximum pearlite content corresponding to 0.80% carbon, which gives an ultimate tensile strength of 140,000 pounds per square inch. The yield point values do not increase in the same proportion and at 0.80% carbon reach only 70,000 pounds, a ratio to ultimate of only 50%. A safety factor of 4, based on the ultimate value, would permit design stresses of 35,000 pounds per square inch which is only a safety factor of 2.0 based on the yield point. Of course there are other rules limiting the designer who uses high carbon steels with a reduction in area of 15% and an elongation of 10% in 2 inches, such as the change in properties at low and elevated temperatures.

The designer should employ physical properties based upon the hot-rolled mill materials and not upon the results of tests after cold working, since the yield point is raised by cold working sometimes up to the tensile strength. After the same steel is annealed, the yield point is restored. The values of these properties for carbon steels which have been cold-worked can be raised as much as 70%; this indicates the dangers of using yield point data which depart too widely from the proportional limit.

Not every chemist or chemical engineer is faced with the problems of designing equipment, but it is somewhat essential to all users of equipment to appreciate the approximate values of the chief physical properties of common steels. One often stresses the properties of a special alloy in determining its fitness for a certain problem. The excellent possibilities and high strength of present carbon steels are often overlooked. The use of carbon steel of 75,000 pounds per square inch tensile strength in vessel manufacture will decrease the weight and cost of the completed vessel considerably more than the slight premium required for plates of the higher tensile strength.

Current Developments in INSTRUMENTATION

Sensitive dial-type absolute pressure indicators and slide rule calculators.

Discussed by Ralph H. Munch

On various occasions we have described devices for measuring absolute pressures in the range from zero to a few hundred millimeters. These devices included both manually operated and recording types of ionization gages, Pirani gages, and McLeod gages for the low range, the float or DuBrovin gage for intermediate pressures, and the closed-end, U-tube manometer for higher pressures (advertising section page 37, March, 1945, and page 91, November, 1945).

Gages with Bourdon tubes, bellows, or diaphragms are often used for measuring pressures below atmospheric. Usually these measure gage pressure—that is, the difference between the actual and atmospheric pressure. When low pressures are being measured, variations in atmospheric pressure become of the same order of magnitude as the low pressure; for this reason atmospheric pressure is not a suitable reference standard. It becomes necessary, therefore, to use another reference point. The most practical solution of this problem is to use, as a standard, a vessel evacuated to such an extent that the pressure within it can be considered zero for the purposes of the measurement. The gage should then be arranged to measure the difference in pressure between the evacuated space used as standard and the space containing the unknown pressure. A gage of this type measures absolute pressure.

Various manufacturers have been building absolute-pressure measurement and control equipment for some time. The lower limit for full scale range is usually in the vicinity of 100 mm. of mercury. Wallace & Tiernan Products, Inc., Belleville, N. J., now makes absolute pressure indicators with ranges as low as 0 to 20 mm. of mercury. The mechanism of one of these indicators is shown in Figure 1. The pressure-sensitive element is constructed of beryllium copper diaphragms soldered together. Beryllium copper is used because of its excellent fatigue-resisting properties, which minimize the effect of hysteresis.

The capsule formed by the diaphragms is evacuated and sealed so that the pressure inside is practically zero. The top of capsule *A* is firmly clamped to the back supporting plate. The bottom is free to move and is connected to rod *C* which moves longitudinally as the capsule expands. The opposite end of the rod is connected through a flexible link to a lever attached to sector gear *F*, which rotates about flexure pivot *E*. The sector gear engages pinion *H* on the pointer shaft and thus causes it to rotate as the capsule expands and contracts as a result of pressure changes in the case. Counterweight *G* is provided to balance the lever system and minimize position error.

Backlash is eliminated by the following arrangement: A sheave of the same pitch diameter as pinion *H* is mounted on the

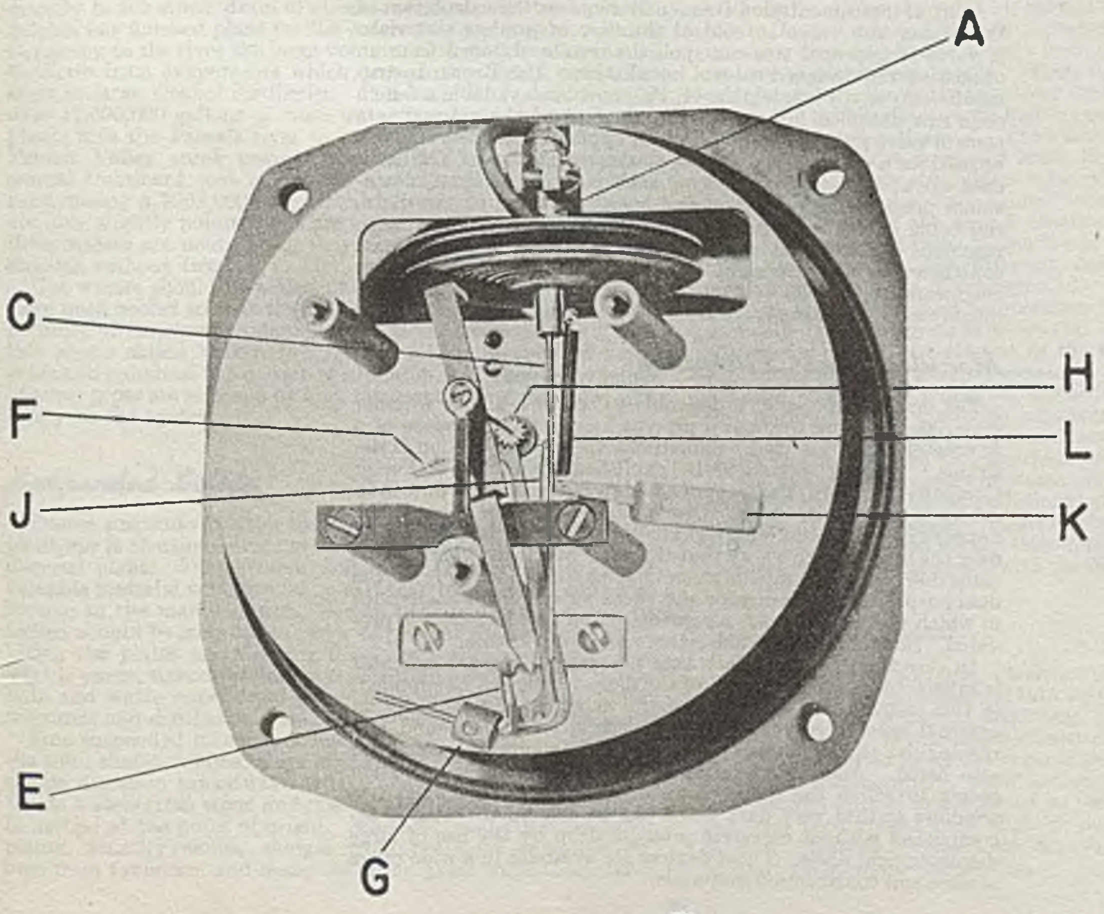

Figure 1. Absolute Pressure Indicator

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Instrumentation

pointer shaft directly under the pinion. (This is not visible in the photograph.) A nylon thread is wrapped around the sheave and fastened to a wire spring, *J*, affixed to the sector. This spring puts tension on the nylon thread and keeps the sector and pinion firmly meshed. When the capsule expands and thus moves the sector to the right, the thread unwinds and the pressure of the sector against the gear remains the same. This arrangement, according to the manufacturers, is superior to a conventional hair spring, for the latter causes tension which changes with rotation of the sector. Lever *K* is the zero adjustment which changes the tension on spring *L* connected to the capsule.

The mechanism is mounted in a vacuum-tight case, $3\frac{7}{8}$ inches in diameter and 3 inches deep. The vacuum to be measured is applied to the case through a $\frac{1}{8}$-inch female pipe connection on the rear of the case. If the vacuum is within the range of the instrument, it will cause the capsule to expand and move the pointer. The pointer indicates the difference in pressure between the evacuated interior of the capsule and the pressure in the case. The instrument is therefore an absolute pressure indicator. The capsule is provided with internal stops so that neither capsule nor lever system is distorted or otherwise damaged when the instrument is exposed to atmospheric pressure, even if the exposure is sudden, such as when a leak occurs in a vacuum system.

The absolute pressure indicator is available in the ranges 0 to 20, 50, 100, and 200 mm. of mercury. The scale can be provided with a hundred graduations. The makers state that the instrument is sensitive to 1 part in 500 of the range, and accurate to 1 part in 300. Gages covering these ranges with such sensitivity and accuracy should find many uses in plant and laboratory. Most of us are not accustomed to thinking of dial-type pressure gages sensitive to 0.04-mm. variations in pressure with ranges as low as 20 mm.

Wallace & Tiernan also supplies a similar gage for differential pressure measurements. The type of construction just described is employed. The minimum range, sensitivity, and accuracy are also the same as those for the absolute pressure indicator.

Slide Rule for Control Valve Size

Control instrumentation frequently requires the calculation of the proper size valve to control the flow of process materials. A valve of improper size can spoil the results obtained from an otherwise well designed control installation. The Brown Instrument Company, Philadelphia 44, Pa., now has available a 6-inch slide rule designed for quick determination of the approximate control valve size required for various applications. The rule can be used for a wide range of liquid, steam, or gas flows. The usual data about operating conditions, such as pressure drop, downsteam pressure, temperature, and specific gravity of the material being controlled, are required. This small calculator is an ingenious device for storing a large amount of information on control valve characteristics in compact, readily portable form. Engineers working on control problems will find it valuable for quickly approximating valve sizes.

Manufacturers' Literature

For many purposes it is desirable to see at a glance whether material is flowing through a process line, yet the expense of a flowmeter is not justified. Sometimes visual examination is desirable. Catalog section 93-B, published by Fisher & Porter Company, Hatboro, Pa., covers a wide variety of sight flow indicators to meet such needs. One of the simplest of these is the flapper type, a conventional sight flow glass with a flapper pivoted over the inlet in such a way that the angle at which it hangs indicates flow. A slight modification enables the device to serve the dual purpose of flow indicator and check valve. For installations in which visibility is poor, a rotating-wheel flow indicator is provided. Simple drip flow indicators are also available.

In case the fluid is so dark that no type of internal indicator is satisfactory, a modification of the flapper type can be supplied; in this instrument the motion of the flapper is indicated by an external pointer coupled to it magnetically. Both round and rectangular sight windows to be installed in process vessels are also listed. Another variation is the thin-stream observation fitting in which the liquid flows in a thin layer between two windows so that very dark fluids can be examined. This is accomplished without excessive pressure drop by the use of large diameter sight disks. These devices are available in a wide range of sizes and construction materials.

Current Developments in WASTE UTILIZATION

The effect of effluents from industrial plants upon sewage treatment processes

Discussed by Harold R. Murdock

Last month we discussed the rental of municipal sewer systems by industry. It was shown that many cities are already cooperating with industry by handling trade wastes with their sewage. In setting up policies and regulations, one must understand the effect that various liquid effluents from commercial operations has upon sewage treatment processes. It is also essential that means be developed for processing these industrial residues which are incompatible with domestic sewage and equipment. The biological processes commonly used by public sewage treatment plants are often seriously abused by some industrial wastes. Sewer systems and equipment are frequently seriously damaged by substances which enter from factories. Such incompatability of wastes increases the operation cost of municipal disposal plants. In most cases these difficulties can be overcome by pretreatment and by balancing the rate at which the spent products are added to the sewer system.

Volume of Waste

The total volume of waste materials entering the sewage system determines, to a large degree, the size of the treatment plant needed. It is important, therefore, that industry should not purge into the sewer system such waters as are discharged from cooling condensers, refrigerating systems, etc., for these waters are clean or only slightly polluted. They should be added directly to the storm drain or stream. It is reported that Philadelphia has finished plans for the construction of separate drains to convey to the river the large volumes of slightly contaminated distillate from evaporators which process the highly pollutable slops in large alcohol distilleries. Paterson, N. J., has diverted over 11,000,000 gallons of rinse water per day from textile dye plants into the Passaic river in order to relieve the overloaded Passaic Valley trunk sewer system. This saved Paterson an annual treatment cost of $35,000 and eliminated the need for constructing a $908,000 relief trunk sewer. Some waste waters are only slightly polluted but are either acid or alkaline. When these waters are neutralized, they can be added directly to the streams without trouble.

Hot waters should be added to sewer systems only after they have been cooled so that they do not appreciably raise the temperature of the sewer contents. High sewer temperatures stimulate septic action within the system, which releases offensive gases and enhances the danger of explosion. The asphaltic joints of sewer pipes are softened by high temperatures, with consequent injury to the system.

Suspended Solids

Coarse suspended matter should be removed at the industrial plant, for it obstructs sewer systems and overloads screens at the disposal plant. Furthermore, solids usually indicate a loss of valuable material which could be salvaged to provide a source of income to the manufacturer. Screen floor plates which can be locked should be installed in order to prevent the workmen from lifting the plates and flushing floor waste into the sewer line. Textile yarns, strands of flesh and hide from meat packing plants, pulp and waste paper from paper mills, and spent grains from breweries and distilleries are often troublesome in sewer systems.

Fine suspended matter overloads the grit chambers, increases the total sludge volume, clogs pipe lines, and accumulates in the sludge digestion tanks when it is a heavy inorganic substance. Waste waters from stone and marble plants, for instance, should be settled at the point of origin. Similarly, coal ash from boiler plants, foundry sands, sludges from acetylene manufacture, lime from tanneries, and many other inorganic suspensions have caused trouble by clogging sewer systems. Organic suspended matter is also troublesome. Brewery wastes are notorious for disturbing the operation of activated sludge plants. At Akron, Ohio, rubber reclamation wastes are reported to carry more suspended solids into the sewers than all the domestic sewage within the city. Paper mill cities have reported similar relationships.

Grease, tar, and oil not only create a fire hazard at the sewage treatment plant but disturb sludge digestion operations when they become incorporated with settling solids. Garages and service stations, machine shops, hotels, and restaurants are common sources of such objectionable matter. Some municipalities have placed strict supervision over the entrance of these wastes into the sewer system. Alert operators have, in turn, found economic uses for these by-products. In Los Angeles a planned program of industrial waste control makes it illegal to discharge into sewers an industrial waste having a temperature exceeding 100° F., or one containing more than 1000 parts per million of suspended solids or more than 600 p.p.m. oil. The wastes discharged must be within the range of pH 5.5 to 9.0.

Colloidal and Soluble Materials

Plants which process milk usually produce effluent waters having a biological oxygen demand of about 1000 p.p.m., which is about five times the value for normal sewage. Excessive foaming in Imhoff tanks has been reported as due to milk wastes in many disposal plants. Casein from milk is used in the manufacture of water-base paints. When such a product enters the sewage system, the finely powdered mineral filler does not settle out in the primary treatment and imposes a serious solid loading on the activated sludge unit. The waste from vegetable canneries has a B.O.D. which is usually much higher than that of sewage alone and, consequently, places seasonal burdens on the disposal plant. Cherry and tomato cannery wastes are reported to have caused difficulty at the sewage treatment plant at North East, Pa. Dissolved and colloidal matter in brewery wastes contributed to operating difficulties at Jeannette, Lancaster, and Norristown, Pa. In Washington, D. C., yeast plant wastes, high in both sulfur and temperature, have been reported responsible for disintegration of sewers. In Gastonia, N. C., textile wastes colored the effluent of the treatment plant and disrupted the activated sludge process.

Large commercial laundries, particularly in small communities, intermittently discharge substantial quantities of soapy water that seriously disrupt sensitive sewage treatment processes. Institutional laundries are notorious for upsetting the operation of the biological processes of waste digestion. Laundry wastes are considerably higher in pollutional characteristics than is the average dyehouse waste. Paper mills in Kalamazoo, Mich., process old papers and empty their waste waters into the sewer; they are reported to interfere with the disposal of normal sewage.

Toxic Substances

Various types of solvents, which are used in many small industrial operations, are discharged into public sewer systems. Their effect upon the biological treatment processes, particularly in sewage digestion, is sometimes disastrous. Because the solvents are often adsorbed upon the organic sludge, their effect is most notable in this digestion. Small amounts of methyl, ethyl, butyl, and isoamyl alcohol are reported to produce greater volumes of gas, but they retard only slightly the destruction of organic matter. Acetone increases the liquefaction of organic matter without affecting gas production.

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Large amounts of toluene and carbon tetrachloride retard digestion, but xylene is reported to be toxic to both liquefying and gas-producing organisms. When only 1 p.p.m. of ethylene dichloride is present, gasification is retarded, and 10 p.p.m. reduces gas production by 50%. Such chemicals from dry cleaning establishments can become a serious deterrent to smooth operation of disposal plants.

Cyanides wasted from metal plating operations are toxic to biological activity when present in the sewage in dilutions as low as 1 p.p.m. A considerable amount of research has been conducted on the effect of copper upon sludge digestion. Sewage containing 0.5 p.p.m. copper produces a sludge containing over 100 p.p.m. and decreases the efficiency of sludge digestion. A similar disturbance is reported when sewage contains about 1 p.p.m. chromium. At Muskegon Heights, Mich., copper and cyanides from plating operations practically stopped sludge digestion. At Lancaster, Pa., excessive discharge of phenolic wastes from a gasworks disrupted the activity of the activated sludge plant.

Acid Wastes from Industry

The city of Worcester, Mass., treated its sewage by the chemical precipitation method from 1890 to 1925. This method was adopted because the sewage contained spent, acid-pickling liquors from steel wire mills. Lime was added to the sewage and the sewage was then put through sand filters. In 1910 these filters required 72.5 acres, according to reports. In 1919 the city had to construct a new sewage plant. Experimental units had shown that the Imhoff tank trickling filter method treated this iron-containing sewage successfully; consequently such a plant was constructed and placed in operation on June 25, 1925. The plant produced a better effluent than did the chemical precipitation method; the average annual operating cost varied from $5.50 to $6.50 as compared to $8 to $10 per million gallons for the chemical precipitation method. No serious operation difficulties were experienced during nearly eighteen years of operation. The first indication that the character of the sewage had changed was noticed in the Imhoff tank sludge drawn early in April, 1943. The pH was 5.6 as compared with the usual 6.8 or 6.9, according to report. The March average pH was 6.9 and the April average, 6.0. Samples taken hourly proved that the sewage was acid throughout the 24 hours and extremely acid during the night. Conferences held with the four industrial plants concerned brought out the important point that the increased acidity of the sewage was attributable to partly used acid which was being dumped to increase compensation of piecework employees as well as to increase war production.

We cite this experience as published by Worcester's supervising chemist in order to bring out an important point in evaluating the compatability of trade wastes with sewage. Until war activities increased the ratio of spent pickling liquor to normal sewage, Worcester would have reported that this industrial waste was not incompatible in their treatment process. It was the expansion of industrial activity which seriously upset the smooth operation of the trickling filter. If Worcester had obtained a new industry during the war period, which would have purged an alkaline waste into the sewer system, the system might still be operating smoothly.

Compatibility of any industrial waste to sewage plant operation depends upon the tolerance of the sewage disposal unit. This tolerance varies with every chemical entering the system. It also depends on the nature of other industrial wastes entering the sewer. Phenolic wastes, for instance, are readily oxidized to completion on biological filters if the concentration of phenol is kept below 30 p.p.m.; but concentrations above 200 p.p.m. rapidly destroy the organisms necessary for the action of the filter. We should not, therefore, condemn indiscriminately those industrial wastes which enter sewer systems; we must consider the degree of dilution of the waste with respect to the total volume entering the receiving system. When the diluting volume is insufficient, attention should be given to a uniform rate of adding the waste throughout the 24-hour period. If difficulties persist, the industrial plant producing the waste should be compelled to process it before sending it into the sewer or stream, to a degree which allows the municipal treating plant to operate normally.

Current Developments in

PLANT MANAGEMENT

Various problems confront chemical manufacturers who wish to enter foreign trade.

Discussed by Walter von Pechmann

Most chemical manufacturers have expanded their production facilities during the war. Realizing that the domestic market will be unable to absorb the increased output of the chemical industry, many concerns for the first time are exploring the possibilities of selling their goods to foreign countries. The difficulties entailed in establishing foreign trade are not generally recognized. International good-will organizations, trade groups, and semiofficial agencies often point enthusiastically to the advantages of foreign trade, but neglect to mention the complications which may arise when one enters this phase of business without being fully prepared. Present day seller-market conditions are abnormal and should not be taken as a measuring stick to determine where and in what quantities goods can be sold in the future. As soon as conditions have returned to normal, we must expect competition from within the countries to which we are now selling.

The prospective foreign trader, therefore, will have to plan on a long range basis. He must be convinced that if he goes into the foreign field, it will be on a permanent basis. He must be willing to put up with many difficulties at first and, above all, be prepared to support his program wholeheartedly. The fact that a manufacturer has faith in the fundamental good quality and salability of his products does not entitle him to neglect the analysis and evaluation of essential factors which may affect the introduction of his products to foreign markets.

Before a manufacturer attempts to engage in foreign trade, he should assure himself that he has sufficiently exploited the domestic market. Foreign trade usually involves additional work and risks which should not be underestimated. The sale of goods to foreign countries almost invariably calls for changes in product specifications and, simultaneously, the revamping of production facilities. Since many foreign countries use the metric system, different units of weight and measure have to be used. Also, empty containers are often re-used for other purposes abroad, and the foreign buyer, therefore, is inclined to purchase his goods from a source which supplies him with a package of metric dimensions.

The product to be sold in foreign trade must be in constant demand and must comply with the customs, manners, habits, buying power, and living conditions of the country in which it is to be distributed. The application of American standards and taste to goods sold abroad may be possible at the present time because of the general shortage of merchandise. When conditions return to normal, however, foreign countries will demand that we respect their way of living by producing our goods in a form which caters to their tastes. This will naturally involve special product design, different methods of advertising, and the adoption of sales policies foreign to us.

Foreign trade may also make it advisable to have a middleman in the United States who has the know-how of the country in which the goods are to be sold. The novice in foreign trade will find that many of his most perplexing problems are routine with those concerns whose business it is to assist United States manufacturers in exporting goods. Exporters, particularly those located inland, frequently employ freight forwarders to attend to the details of clearance, cargo space, delivery of goods to vessels, certificates of origin, and other formalities connected with the delivery of goods aboard ship. The names of exporters, forwarders, and organizations offering services in the field of foreign trade can be found in various directories, two of which are: Foreign Trade Associations in the United States (available without charge from the Bureau of Foreign and Domestic Commerce, Washington 25, D. C.) and Foreign Trade—Basic Information Sources (available on request to the Commercial Intelligence Division of the Bureau of Foreign and Domestic Commerce, Washington 25, D. C., and also Department of Commerce field offices).

Tariffs, foreign government regulations, and United States regulations have to be taken into consideration. The local duties on imported goods in many instances represent a substantial portion of the cost of manufacturers' goods to the consumer, and this has a direct bearing on his ability to compete in a given market. It is important that the manufacturer understand his responsibility and liability under the laws of the land in which he is trading. Laws governing the collection of debts, the protection of property, and the registration of trade-marks should be known. The successful prosecution of the war made it essential for the United States to impose controls over foreign trade, financial transactions, communications, and shipping. These are constantly being adjusted to meet current conditions. A careful study and thorough understanding of these regulations is a "must" for every foreign trader.

Many factors enter into the cost of exporting. Foreign trade cannot always be connected on an f.o.b.[1] factory basis. It might be necessary to quote rates f.a.s.[1] United States or even c.i.f.[1] port of destination. This naturally requires that means of collecting be established. The following factors are recommended as considerations in a cost analysis for foreign trade: packing, transportation, documentation fees, selling, registration fees, insurance, discounts, commissions, advertising, terms of payment abroad, trade-marks, and licenses.

The United States Government has ample facilities for assisting the prospective foreign trade. The Bureau of Foreign and Domestic Commerce, Department of Commerce, will supply, on request, statistics, market surveys, names of selling outlets, sources of raw materials, information on credit, collection, and exchange conditions, tariffs and local regulations, laws pertaining to commerce, credit terms, and prevailing trade practices, competition, local tastes, buying power, and similar data concerning foreign trade analysis and promotion. Matters pertaining to economic studies may be re-

(*Continued on page 88*)

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[1] f.o.b., freight on board; f.a.s., free alongside ship; c.i.f., cost, insurance, and freight.

Plant Management

ferred to the Bureau's Division of International Economy. Commodity information can be obtained through the Division of Industrial Economy. The Division of Commercial and Economic Information provides prompt and easy access to existing reports relating to various business problems, including those of foreign trade. The inquiry and Reference Service of the Commercial Intelligence Unit has extensive files containing thousands of useful abstracts, digests, studies, and references pertaining to international trade. This unit also provides classified lists of foreign importers, dealers, agents, industrial firms, and local exporters of native products. Information can be supplied promptly concerning a firm's method of operation, reputation, size, number of employees, capital, annual turnover, ownership or management, representatives or principals in the United States or other countries. The Commercial Intelligence Unit is also the government source of information concerning political characteristics of foreign firms, "black lists", and wartime trade.

Literature

The following government publications are recommended for study:

Export and Import Practice. Trade Promotion Series 175. 310 pages. Bureau of Foreign and Domestic Commerce, Washington 25, D. C. 1938. 40 cents.

Foreign Commerce Yearbook. Bureau of Foreign and Domestic Commerce, 1939 and 1942. $1.00.

Foreign Commerce and Navigation of the United States for the Calender Year 1941-1944. Superintendent of Documents, Washington 25, D. C. $2.50.

Foreign Trade Reports. Bureau of the Census, Washington 25, D. C.

Foreign Trade Associations in the United States. Bureau of Foreign and Domestic Commerce. 1945. No charge.

Foreign Trade—Basic Information Sources. Commercial Intelligence Unit, Bureau of Foreign and Domestic Commerce. 1944.

Nongovernment publications which might be of interest to the prospective trades follow:

How to Import and Export. Postwar Foreign Trade Bulletin 1, World Trade Department, Los Angeles County Chamber of Commerce. 1944. No charge.

Exporters' Encyclopedia. 1800 pages, maps. Published annually by Thomas Ashwell and Company, Inc., 20 Vesey St., New York 7, N. Y. $20.00.

Phelon's New York City Export Buyers List. Published annually by J. S. Phelon and Company, 32 Union Square, New York, N. Y. $5.00.

The writer would like to call attention to a new publication, *The Industrial Engineer.* This magazine is published monthly by the National Industrial Engineering Society (1 North LaSalle St., Chicago 2, Ill.). It contains feature articles written by industrial engineers well known in the chemical industry, on various phases of management. Last month's issue covered wage incentives, job evaluation, better trained personnel for industry, delegation of authority, overspecialization, and labor-hour budgeting. It is edited by William P. Hinkel, who started the publication as a hobby. He is supported by a staff of volunteers who contribute their time free of charge to make this paper a success. Our best wishes for the continued success of *The Industrial Engineer.*

From the Editor's Desk

★ A satisfactory substitute for cloth tags is obtained by using melamine-resin-treated paper. This resin increases both the wet and dry strength of the tag stock.

★ Farm cash income from crops has risen from nearly 3 billion dollars in 1911 to almost 10 billion in 1945. During the same period expenditures for fertilizer rose from approximately 175 million to an estimated 475 million dollars.

★ The passenger tire output for this year is estimated at 69,150,000 which is 1,300,000 tires under the industry's March estimate. Replacement tires are not expected to be plentiful until late this year.

★ Many long bolts of large diameter are hollow and contain a resistance heater. In use, the bolt is screwed tight while hot; then when it cools, shrinkage develops the required tension.

★ A strong metal with half the weight of aluminum is now available. It is made up of 75% beryllium and 25% aluminum. The cost, however, is high.

★ Silicone derivatives are now being sprayed into dies to prevent molding materials from adhering to the die surface.

★ Despite 1945 shortages in the supply of labor and raw materials, the fuel briquetting industry has continued steady expansion of its production since 1938. Output in 1945 reached a total of 2,762,204 net tons—73% of the total capacity of the thirty-two plants in operation.

★ The new weed killer called "2,4-D" (2,4-dichlorophenoxyacetic acid) is undergoing extensive application research for an evaluation of its lethal power in killing weeds without harming adjacent crop plants.

★ Output of soybean oil may be somewhat less than in 1945 because the 1946 soybean crop may be the lowest since the beginning of the war.

★ Penicillin production, continuing its upward curve, marked up a new record of 1838 billion units for March. This is 12% greater than the 1944 total production.

★ An insecticide deadlier than DDT has been announced by a British chemist. It comprises a mixture of DDT and pyrethrum. This activated DDT passes through the chitin of the insect and destroys the nervous system more efficiently than does ordinary DDT.

★ Transparent Plexiglas is now used for making minutely calibrated slide rules which defy temperature changes, humidity, and all other factors that formerly affected old-fashioned wooden rules.

★ The United States production of crude petroleum has reached a new peak—4,990,610 barrels per day.

★ Temperature-indicating crayons are available that make a chalklike mark below their indicating temperature, but melt and glisten when it is reached. Temperatures from 125° to well over 1000° F. may be measured with the crayon grades available.

★ The Ethyl Corporation can no longer be associated solely with the marketing of tetraethyllead. A concentrated "soapless soap" solution now is being sold under the Ethyl trade-mark, and other products may follow.