



# Industrial and Engineering Chemistry

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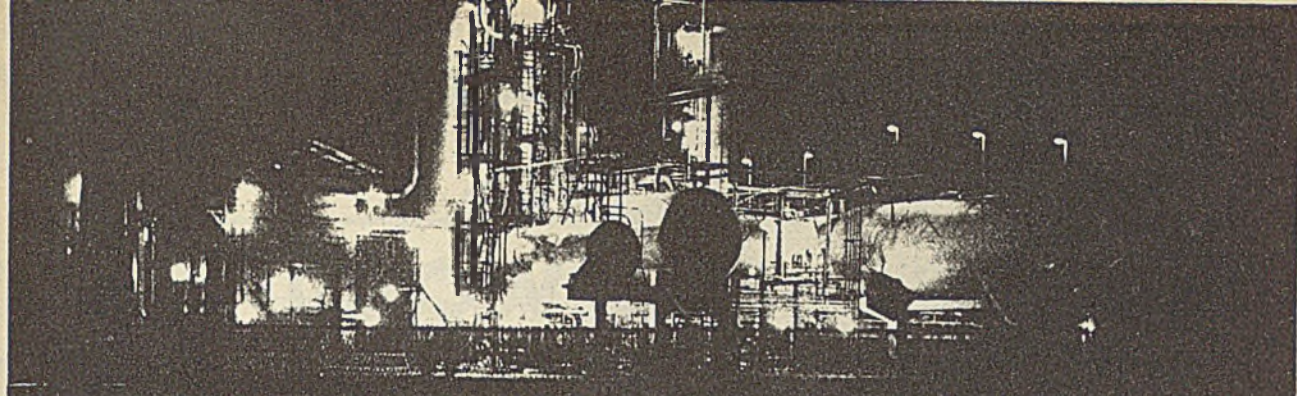
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# INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

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Above is a night view of a solvent-refinery lubricating oil plant, built by The Lummus Company.

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# INDUSTRIAL AND ENGINEERING CHEMISTRY

## REPORTS

### ON THE CHEMICAL WORLD TODAY

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#### *Technology*

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**Paper Shortage.** With paper in expanding use as a substitute for other scarce materials, a rapidly developing shortage is cause for concern. Paper cans and bags replacing metal cans and burlap are still available for essential purposes, but newsprint, printing papers, and others have ceased to be plentiful and measures adopted to reduce requirements have scarcely eased growing stringencies. The trouble, we learn, starts with man power in the woods. Stocks of pulpwood at mills have been seriously depleted to a point far below the industry's normal safe reserve, as men have been drawn from the woods into military service or enticed to more remunerative jobs in industrial plants. The problem is also associated with Canadian internal politics. Most woodcutting is done in the province of Quebec, and deferred farmers at present lose their deferment status if they cut wood. With the spring of raw material thus drying up and reserve stocks dwindling, other bottlenecks, no less serious, lose some of their significance. Recent years have seen a growing use of motorized equipment to bring logs out of the forests, and this transport has naturally suffered from scarcities of gasoline and rubber. In the paper mills themselves labor forces have shrunk in the face of other pressing demands. In all, the revival of waste paper collection is a natural consequence. Little likelihood appears that the present urgency of this need will peter out as did its predecessors two years ago. At that time accumulated stock of waste paper clogged warehouses and threatened to overwhelm mills, using waste, with a flood of raw material. Meanwhile the growing scarcity of new pulp has forced greater use of reworked stock wherever possible, and demand for waste paper has soared in consequence. Waste paper collecting agencies, Salvation Army, Boy Scouts, and others will find that their activities assume new importance.

**De-inking Newsprint.** The paper shortage and curtailment of newsprint revive interest in the de-inking processes. Problem of separating the extremely fine particles of carbon in the ink from the fibers of the paper so that the latter can be used again for their original purpose seems still to be unsolved. Innumerable processes have

been proposed, but none of them has seemingly met the twin requirements of efficiency and cheapness requisite to success. Meanwhile the demand for waste paper for less exacting purposes, which do not require whiteness, considerably exceeds present supply. De-inking is clearly not urgent now.

**Re-use of Packages.** Increasing burden on package makers and a scarcity of raw materials for this use have developed into a situation where all concerned are being urged by WPB to re-use every possible shipping container and package. Clearly the useful life of most one-trip containers is by no means exhausted by the normal single use. Conservation of metals, paper, lumber, and textiles in this way can readily become significant when and if the movement gains substantial headway. Chemical industry, most of whose containers are specially constructed at a relatively high cost in both material and man-hours, can profit particularly by this conservation. Indeed, many chemical products now in reasonably good supply cannot reach consumers promptly for lack of packages in which to ship them. Instances cited of this new bottleneck extend from sulfa drugs to caustic soda. Obviously something must be done about it. It is of more than passing interest to note the prominent part chemists are playing in the packaging field. New resins, new plastics, new waxes, new bonding agents, etc., are revolutionizing packaging practice. Full utilization of these products of chemical research will mean in the future products of greater purity, better physical condition upon arrival, and lower costs.

**Arctic Oil.** Newest oil field to be exploited in North America is the Canol field centering around Fort Norman, Northwest Territories, Canada. Discovered some twenty-two years ago, the new field is given special value and importance by the development of the Alcan Highway and the utilization of Alaskan bases as vital outposts on the way to Japan. Construction of pipe lines from the field to refineries in Whitehorse, Yukon Territory, and from there

*(Continued on page 8)*

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

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to Fairbanks, Alaska, to carry finished products, puts the newly developed oil at the disposal of the military in that theater of war at a cost substantially lower than the freight on oil from the United States proper. Estimated cost of supply adequate for expected military needs in Alaska is placed at \$1.25 per barrel delivered at Whitehorse. The development is being carried out by Imperial Oil Company of Canada, Ltd., subsidiary of Standard Oil Company of New Jersey, in cooperation with the U. S. Army, and is being financed by U. S. Government funds. The military importance of development is great, but the problem of its utilization in peace remains to be solved, particularly in view of the sparse population of the area and consequent minor demand for oil and its products.

**Tin's Future.** Political rumblings already suggest that American smelting of tin is solely and completely a war baby, that it will not long survive the peace. A single major smelter operating on Bolivian ore represents our entire primary production of this important metal. Secondary production from scrap tin cans has attained significance in areas where the collection of sufficient quantities permits the operation of recovery plants. It is not possible yet to foresee a time when tin will no longer be necessary to us, but clearly our future requirements of the metal will never again be so great as in the past. Development of electrotin-plate processes has already cut deeply into the amount of tin needed as a protective coating. Tin-less and tin-poor alloys serve well other purposes formerly dependent on the white metal. Silver-coated bearings are proving superior to babbitt in numerous applications. The collapsible tube industry, deprived of most of its tin, is finding plastics useful in many but not all places where metal served before. Paper cans meet growing acceptance in industry as fabrication and materials improve. To both nationalists, who insist on complete protection of American industries, and international thinkers, whose views are directly the opposite, the subject of tin may be vital. Its industrial significance is dwindling.

**Electrolysis of Tungsten.** Recovery of tungsten from its ores has involved special problems of beneficiation to separate other metals and of reduction because of the extremely high melting point of the metal itself. At the recent 84th meeting of the Electrochemical Society, Fink and Ma described a new development. The electrolysis of metallic tungsten directly as powder from a fused bath of alkaline salts (borax, phosphates, or mixtures) was reported in successful operation on lower grade ores than have heretofore been worked economically. Itself significant, the new method attains special importance in the continuing search for economically practicable methods of utilizing the relatively abundant low grade ores of many vital metals. Chromium, manganese, tungsten, vanadium are among the important alloying metals whose ores in the United States have been considered too poor to be

*(Continued on page 10)*

economically worked in competition with richer ores imported from distant deposits. During the present emergency and huge war demand, the development of methods of utilizing low grade domestic ores has proceeded apace. Now tungsten appears to have joined manganese as a metal that can be practicably recovered from more abundant low grade ores.

**Lard for Soapmaking.** To many it may come as a surprise that soapers are now using edible oils and fats, especially lard. In an era when economics is at sixes and sevens in most fields, there is nothing of the "sacred cow" about edible oils and fats that should cause any hesitancy on our part to add them to the soap kettle if by so doing we head off soap rationing. Lard supplies have accumulated to the point where government officials believe it advisable to divert approximately 100,000,000 pounds to soapmakers. Plans are under way to make available still further quantities, possibly 300,000,000 pounds more, in the next twelve months. Future allocations will naturally depend upon civilian ration allowances and Lend-Lease requirements. The amount already allotted to soapers represents about 3 per cent of the present annual rate of production. Two behind-the-scene reasons are given for the recent action of the War Food Administration: Lard made into soap replaces an equivalent amount of tallow needed in production of synthetic rubber; and increased soap production will provide larger quantities of badly needed glycerol. A possible third reason may be that the Government is loathe to ration soap. There seems to be a psychological repugnance to soap rationing that, for some unknown and strange reason, does not apply even to food. Many believe that curtailing supplies of soap would destroy morale, for the lay public is well aware of Germany's predicament in World War I. And speaking of switches on oils and fats, it is interesting to note that domestic supplies of linseed are going to Russia for edible purposes under Lend-Lease. Russians like the peculiar taste, but so far no attempt has been made to introduce linseed oil into American diets.

Turning back momentarily to lard. It may not be available in such large quantities a year hence, for WFA is asking farmers to raise fewer hogs and to market them with less fat on them in the interest of conserving feed grains.

**Sulfa Sufficiency.** With shortages in increasing number and new severity plaguing industry and consumers, there is comfort in the announcement made by Fred J. Stock, of WPB's drug and cosmetics section, to the National Wholesale Druggists Association that supplies of sulfa drugs are sufficient to meet both military and civilian needs. Sulfanilamide, sulfadiazine, and sulfathiazole were specifically mentioned as available in satisfactory quantities. The further statement was made that production of sulfas will exceed 10 million pounds in 1943, the eighth year of the sulfonamide era in chemotherapy in the United States.



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

*Industry  
and  
Commerce*

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**Metals Problems.** Almost simultaneous are announcements of a new concerted drive to collect more ferrous metal scrap and of the transfer of several metals from the stringently critical list to a lesser degree of stringency. It is all thoroughly confusing and quite characteristic of this democracy earnestly at war.

Zinc, mercury, and certain ferrous alloys are in a somewhat improved position, justifying slight relaxation of restrictions but not enough to affect other than war-connected uses of secondary importance. Meanwhile, depletion of scrap stocks available at steel furnaces requires that they be replenished. Thus relaxation and increased stringency go hand in hand as they will until a major break occurs in the military situation.

**Milk Bottle Shortage.** Much publicity has been given to the shortage of milk bottles, said to be due to the lack of adequate manufacturing facilities. Another novel reason given us recently was that penicillin manufacturing was using a large quantity of milk bottles, because bottling and sterilizing equipment is available to handle these standardized sizes.

Swift development of the penicillin program already suggests that the bottle technique may soon be out of date, and thus relieve whatever part of this shortage is chargeable to the new miracle drug.

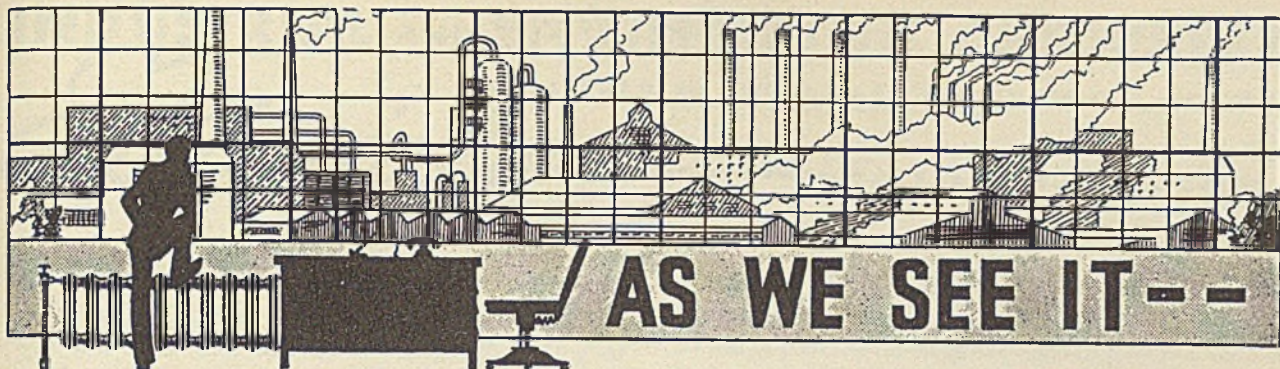
**Tissue from Rope.** Formerly the tissue paper used by the electrical industry as a covering for wire and as a backing for mica tape, came from Japan, being a product principally of the mulberry tree. Like silk, another mulberry tree monopoly, science has come up with a substitute which seems to be everything the original was. Now from manila rope, American companies are making tissue paper which is serving extremely well in the business of insulating wire.

**Aluminum.** Remember the aluminum drive early in the war? Pots, pans, and countless other kitchen gadgets were collected, under impetus of the thought that soon they would metamorphose into bombers. After the collection was over, nothing more was heard of the flying pots and pans except for a statement by Tom C. Clark, Assistant Attorney General of the United States, that the "monumental junk heaps of aluminum pots and pans commandeered from the housewives of America" were memorials to the role monopoly has played in this war.

The facts are these: The aluminum collected could have been used in the manufacture of airplane-grade sheet, but the collection was so badly handled that all the pots and pans wound up by being used in steel production as a deoxidizer. In Pittsburgh, home of aluminum, a steam roller was used to flatten the heap of kitchen utensils, and in so doing the wooden handles and other foreign substances were ground into the metal, rendering it useless for sheet fabrication.

*(Continued on page 122)*





▶ **PETROLEUM** supplies for the future provide bases for discussion from several points of view. Like most disagreements, this one will be cleared up by consideration of the facts given us in thoughtful detail by Frolich (page 1131). Interest in this paper stems not only from its subject matter, important as that is in its comprehensive view of the problem, but at the same time from the personality of its author. One might expect the President of the AMERICAN CHEMICAL SOCIETY to be a remote, perhaps an august, person. But no one could think in these terms of the warm friendliness of Per Frolich. His Norwegian nativity and rearing account for the thoroughness and the modesty which characterize the man. On two successive days in May of this year he received honorary doctorate degrees from two leading universities "in recognition of his distinguished achievements in organic chemistry, with special reference to the technology of petroleum and synthetic rubber", yielding "far-reaching results for the good of civilization".

▶ **NITRATION OF PARAFFINS** has lately provided an important new family of chemical products of varied and widening usefulness, largely through the researches of Hass (page 1146) who brings us up to date on progress in this field. Although many of the compounds stemming from the new technique were known before, the ease of their production by the methods pioneered by Hass places them in a new class of potential abundance and cheapness. Like many other developments of the war period, these await release of productive equipment and raw materials at war's end to reach full fruition. Interesting side light on nitro-paraffins is the cooperation in their development between university and industry which has put the new products rapidly into service.

▶ **GLUTAMIC ACID**, used in the form of the sodium salt as a meat-flavoring condiment, occurs in the Steffen's waste of beet sugar manufacture. Variations in yield of this by-product, which interfere with its recovery, have been investigated by O'Day and Bartow (page 1152) to learn something of their causes with a view to placing the production of the material on a sounder basis.

▶ **WAXY CORNSTARCH**, found in special hybrids of the maize family having properties superior in many applications to imported tapioca, has been studied by Schopmeyer, Felton, and Ford (page 1168). Properties of the new starch, already grown on 3000 acres expected to yield some 4.5 million pounds, are given and indicate its important usefulness.

▶ **SULFUR COMPOUNDS** in petroleum products have constituted a continually vexing problem in the refining industry. Sulfur removal becomes particularly important now through its bearing on susceptibility of fuel to tetraethyllead additions. Byrns, Bradley, and Lee (page 1160) describe an efficient process for this purpose using hydrogen with cobalt molybdate as a catalyst. Results through the semipilot plant stage indicate the value of the method in treating high-sulfur distillates.

▶ **GRAIN ALCOHOL DISTILLERIES** consume some 700 gallons of water per bushel of grain converted to 95 per cent alcohol. Boruff, Smith, and Walker (page 1211) detail the requirements.

▶ **TUNG OIL EXTRACTION** has been studied by Freeman, Pack, and McKinney (page 1156) who compare thirty-three solvents employing two types of extractors. Variations in quality of oil are noted, depending on the solvent used.

▶ **DEHYDRATED SPINACH** undergoes changes in color during processing and storage through chemical changes in the pigments present, and these may parallel reduction in vitamin potency, according to Dutton, Bailey, and Kohake (page 1173).

▶ **DEHYDRATION OF MEAT** has been studied by Ritchell, Piret, and Halvorson (page 1189) to determine the effects of variable conditions on rate of drying.

▶ **SPRAY-DRIED WHOLE EGGS** have been found by Klose, Jones, and Fevold (page 1203) not to lose vitamin potency during processing but to suffer loss, particularly of vitamin A, during storage.

▶ **PORTLAND CEMENT** has been examined with the electron microscope by Sliepcevich, Gildart, and Katz (page 1178), and crystal forms of the products of hydration are pictured.

*D. H. Killeffer*

AS WE SEE IT, an I. & E. C. feature of long standing (introduced in 1932 as The Listening Post), has been strictly a D. H. Killeffer institution. Reluctance on his part to discuss over his signature the background of his article on chemical industry's part in the problems of the postwar world (page 1139) prompts his editorial associates "to take over" here. Several months ago Killeffer was mildly amused and then slightly annoyed at a series of articles on postwar developments in one of our prominent national publications for the simple reason that the author seemed to be concerned only with the external appearances of our after-the-war automobiles, refrigerators, and other gadgets. While streamlined bodies and/or modernistic effects unquestionably intrigue the lay mind, it is the inner workings of these and other machines that are of greatest importance to the chemist and chemical engineer. Determined to do something practical, Killeffer questioned hundreds of key individuals in a variety of fields and geographical locations with better than a 70 per cent return. Surprisingly, many first replied that little if any thought had been given to postwar problems but that detailed statements would follow. "Problems and Promise of Peace" represents more than two months of study, and discusses postwar probabilities in a way to stimulate planning for the part chemical and related industries will play in what, we all hope, will be a bright new world.







### Synthetic Rubber's Tomorrow

NO MORE serious problem has arisen out of this war than that of rubber. Although getting off to a late start, our synthetic rubber industry has come into being with unparalleled speed. Consumers generally have just grounds for complaint that its beginning was so long delayed. Yet now the prospect daily brightens for a plentiful ultimate supply of synthetics of several varieties to meet the manifold needs formerly filled by rubber. With this situation progressing so well, those responsible for the program gasp in amazement at the announcement of a policy that no protection be given this industry at war's end, that the American people be again left at the mercy of foreign growers of rubber. The reason given for this stand is that tires of synthetic are expected to be more expensive than those made of plantation rubber. The whole action seems to us to be based on incomplete information and erroneous reasoning.

No one can with any assurance predict the state of the plantation rubber industry after victory. Obviously, any surmise as to future production and costs of rubber must depend upon a guess at the state of the plantations at the future date. Just what steps the Japanese have taken and will continue to take to protect the plantations as productive units are hidden beyond the enemy's battle lines. The conquerors of Malaya and Singapore came into sudden possession of rubber stocks far beyond their capacity to fabricate and consume. In this situation no reason existed for them to exercise the painstaking care necessary to keep the trees in continuing productive health. Hevea trees now grown, although selected as resistant to blights and pests, are not completely immune and, we are reliably informed, require constant care lest they succumb. Furthermore, the tropical nature of rubber growing country fosters the growth of jungle plants of other kinds and creates a constant imminent threat of return to the jungle of any cultivated land. These two dangers to plantations can well combine to destroy the productive capacity of any lacking proper and continuous care. Neglect for even the short period since the fall of Singapore is enough to destroy a substantial share of their value, and as the period stretches out into the future, the hazard becomes increasingly great. One need only recall the difficulty of clearing tropical jungle land, and the fact that rubber trees first come into production at an age of seven to ten years to realize the gravity of this situation.

Our new synthetic industry, still approaching completion, cannot properly be asked at this early stage in its life to forecast its costs even one or two years hence. Processes now operated have been chosen solely on the basis of assured speedy production. No one familiar with the problems involved would be willing to hazard a guess at what changes in process will be effected in two or three years of experience and certainly not at production costs at a future date. Thus it becomes fatuous to forecast future tire costs. Often overlooked in such discussion, too, is the far larger share in the cost of tires to consumers of other items than rubber itself, notably fabric, labor of fabrication, and distribution.

Throughout the recent history of synthetic rubber no phase has received more vocal attention than the bugaboo of cartel control. When this specter arose in a clothing of patents, its effects were awesome in the extreme. Yet when, as now, its raiment is the monopoly which through the Stevenson plan of the 20's forced crude rubber prices up above ten times normal, the haunting spectral form becomes in some way impossible to understand, a benign visitation.

Thus it is apparent that political and not economic or technological consideration govern the attitude of many officials toward our synthetic rubber industry and its future. The industry itself must assume the burden of proof of its right to continued existence. One recalls the fight after the first World War to preserve our then infant organic industry, especially the dye field, by political means. Perhaps similar measures should be undertaken now to ensure permanence of our newest important synthetic industry. But it seems probable that much more effective insurance is to be found in another direction. Already the industry of rubber fabrication is diligently at work developing and perfecting applications of synthetic elastomers. Technologists in and outside this field are daily improving the position of the new products. Not only is GR-S, the present major synthetic, being developed to economic superiority, but other compounds, some still cloaked with secrecy, are undergoing similar swift development. Time to prove the case of the synthetics is limited, and the continuing success of our arms tends to shorten the period available, but the redoubled efforts of American scientists and technologists can and will answer political arguments on this important question. We must reach a point technologically and economically where the return of plantation rubber is a matter of indifference to us. That point is not far ahead.



## Reconversion as of What Year?

TWO diametrically opposed schools of thought are developing in recent discussions on postwar plans. One is emphatic in its belief that it is advisable to revert to 1942 models, at least during the first several months of reconversion; the other is equally insistent that such a policy will fail to attract the public to the point of spending freely when the shooting ends. The latter group do have a point in their favor for the buyers of automobiles, refrigerators, or washing machines may hesitate to invest in 1942 versions while daydreaming of super-streamlined models suggested in present-day advertising copy.

Those favoring temporary freezing of 1942 models of consumer goods point out that a sharp break between the war and the peace on the industrial front is unlikely; that reconversion will occur gradually as the war goes on, especially if Germany is defeated a year or more before Japan. Claims are made that if manufacturers become jittery over what competitors are doing to prepare postwar models, production of war matériel may be demoralized.

Any program of freezing would require stringent governmental controls for an indeterminate period following cessation of hostilities, and would impose hardship on progressive research-minded manufacturers. It will diminish competition. Indeed, it will develop a form of cartelization. Research and product development, whether of automobiles or chemicals, cannot be treated as a glorified race to stake home-steads with all the contestants lined up awaiting the starting signal.

The problem is difficult. Output of war matériel must not suffer, for, as far as any one knows now, the war is far from won. Nevertheless, we should not, in fact dare not, wait until the day of victory to undertake development of postwar products. Proper assignment of a small fraction of one per cent of our raw materials as they become available to research for development of new models and pilot plant operation would hardly jeopardize the war effort. Only a minimum of control would be necessary to ensure that materials assigned for this purpose are not improperly used.

## Accidents, the Saboteur of Production

ALTHOUGH the chemical manufacturing industry, in common with others, has been forced to employ large numbers of new and inexperienced help at a time when old plants are operating equipment at full capacity or above, and new processes are being introduced and vast new productive capacity hurriedly brought into operation, its accident record is still excellent.

At the recent meeting of the Chemical Section of the National Safety Council in Chicago, the frequency record for the industry as a whole was reported as 9.90 and the severity figure at a new low of 1.29. In the

past six months considerable improvement has been achieved in reducing accidents in plants where the Chemical Warfare Service is directly cooperating.

In the spring of this year the War Production Board conducted a survey of requirements for safety equipment in war industries and essential civilian manufacturing industries. The Government learned for the first time, as a result of this survey, how much money manufacturing industries spend for safety equipment. It is gratifying to learn that the chemical industry stands at the top of the list with \$6.00 per capita employment in 1942. All industries surveyed spent an average of \$3.80. Mining was fifth in the list of sixteen industries with \$4.53; petroleum, seventh with \$3.98; and rubber, eleventh with \$1.76 per capita. Highly significant is the close correlation between amounts expended for safety equipment and frequency of accidents. The chemical industry, which spends most, enjoys one of the lowest frequency rates of the major industries.

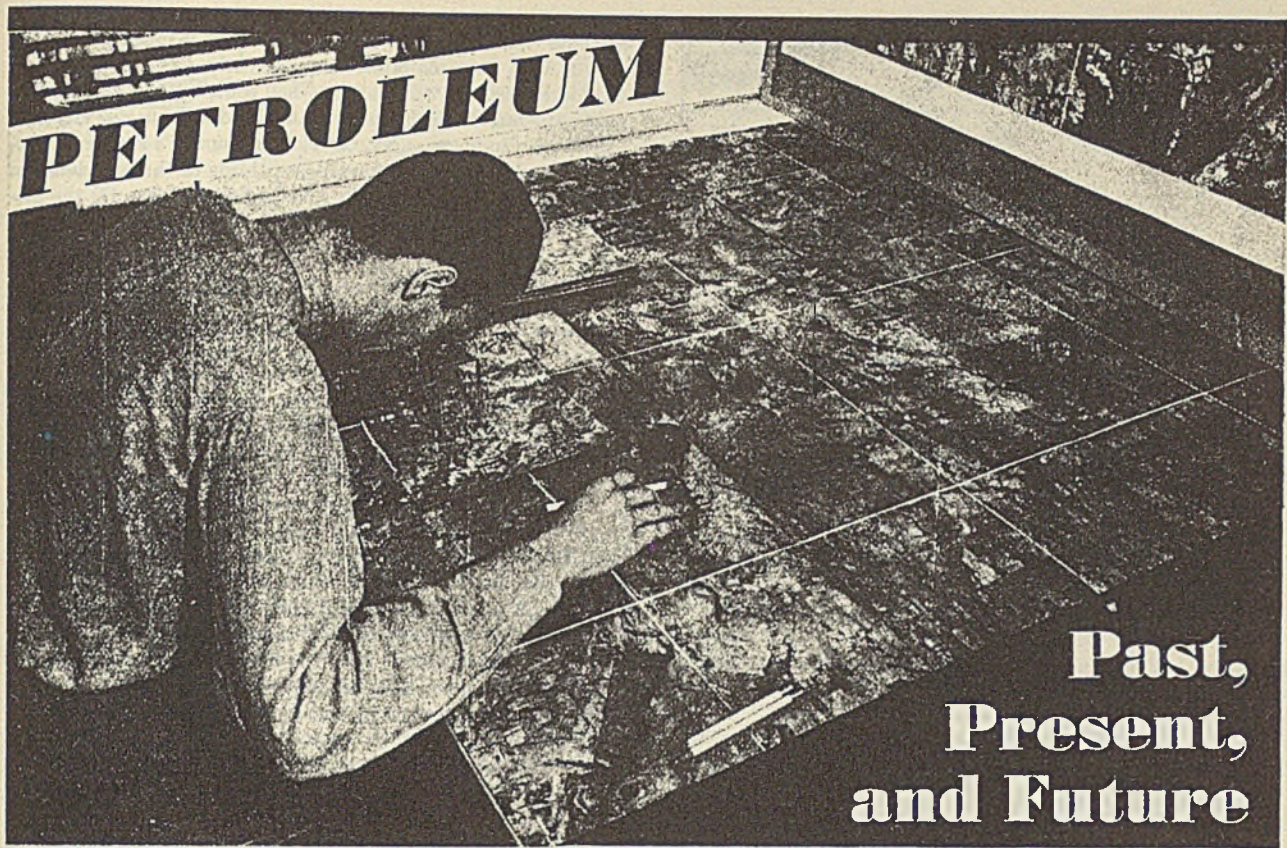
According to the Office of War Information, there is simply not enough industrial safety equipment available today to meet all demands. As authority for this statement, OWI quotes the Safety Equipment Section of the War Production Board's Safety and Technical Equipment Division. Manufacturers of such equipment have exhibited great ingenuity in improvising materials for ones usually employed but now available only in small quantities if at all. They have even done an excellent job in developing substitutes for substitutes. It may come as a surprise to many to learn that production of safety equipment sold to industry in 1943 will total more than \$100,000,000.

All manufacturers requiring safety equipment can assist by not ordering in excess of actual needs, and by insisting upon observation of the general rules laid down for the care and maintenance of safety equipment.

## The Container Problem

THE shortage of containers for packaging chemicals is critical. Production of all types of containers is running between 15 and 25 per cent behind consumption demands. The extent to which WPB will issue further orders curtailing use of containers will be determined by the economies effected through the re-use of such packages. Further curtailment will affect first deliveries of chemicals destined for civilian consumption. It will be a pity if an increase in allotments of chemicals for civilian needs is denied because of a container shortage. It is possible to re-use certain packages considered "single-trip" containers, provided such action does not conflict with ICC regulations. Further expansion in the program to eliminate cross-hauls is still another opportunity. Manufacturers who are farsighted will give serious study to the packaging problem now.





## Past, Present, and Future

Per K. Frolich

ESSO LABORATORIES,  
STANDARD OIL DEVELOPMENT COMPANY,  
ELIZABETH, N. J.

A GREAT deal of attention is currently being devoted to the petroleum situation. Until a short while ago we were primarily concerned with the transportation problem. The question of getting available petroleum products to where they were needed seemed to overshadow all other considerations. Now that the transportation difficulties gradually are being overcome, our interest is turning to the question of the country's ability to produce crude oil to supply the present and future demands for petroleum products.

Our industrialized civilization is fundamentally based on the utilization of mineral resources. It is therefore not surprising that, in the forty-year period of industrial expansion in this century, the world's mineral production has been greater than in all preceding history (9). In the United States petroleum and its by-products in terms of dollar value account for 40 per cent of the total mineral production (13). Half of the crude oil used to date in this country has been taken out of the ground in the last twelve years.

The importance of petroleum in relation to other available sources of energy is brought out by Figure 1; it is seen that some 40 per cent of our energy (B. t. u. equivalence basis) comes from crude oil and natural gas. A peak of 43.5 per cent was actually reached in 1938. Some of the remarkable growth indicated for this energy source represents a shift from coal, but most of the gain in the recent

twenty-year period is due to the development of new forms of transportation based on the use of liquid fuels.

This trend toward motorized transportation has not only been responsible for a greatly increased production of crude oil, but has also resulted in the conversion of a gradually increasing proportion of the crude into gasoline. According to Figure 2, the yield of gasoline on crude increased from 25 per cent in 1919 to some 45 per cent in 1932. How the technological developments in cracking made this rise possible is so well known to chemists that it requires no further discussion.

That the average gasoline yield has leveled off in the 43-45 per cent region during recent years is purely a matter of relative demand for the various products from petroleum. From a technological standpoint there is nothing to prevent it from going higher. Indeed, it is entirely feasible by catalytic cracking under high pressure of hydrogen to convert crude oil to gasoline, volume for volume.

Along with the increase in yield of gasoline there has also been a marked improvement in quality. One of the important factors as far as quality of motor fuel is concerned is octane number. The progressive increase in octane rating shown in Figure 3 may be taken as evidence of the petroleum industry's ability to control the chemical composition of its fuels; it can also be seen from this figure that the improvement in octane number, by and large, parallels

Much surface geological work is done from aerial maps which are studied with the aid of a stereoscope and an ordinary magnifying glass. The maps in the photograph above are copyrighted by the Edgar Tobin Aerial Surveys, San Antonio, Texas.



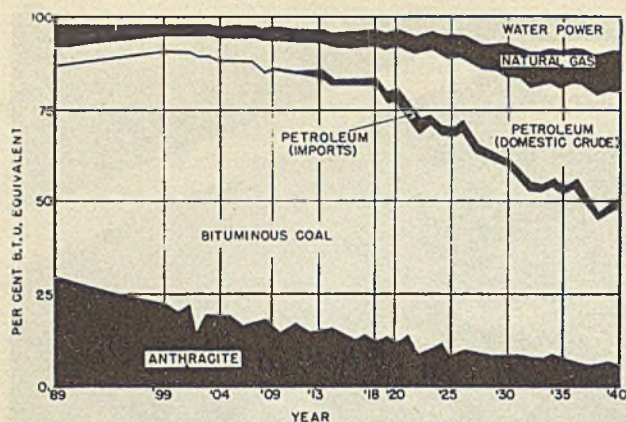


Figure 1. Percentage of Total B.T.U. Equivalent Contributed by the Several Sources of Energy, Counting Water Power at Constant Fuel Equivalent, 1889-1940

If water power is counted at the prevailing fuel equivalent of central stations in each year, its proportion is 3.2 per cent in 1889 and 3.5 in 1940, and the proportions of other sources of energy are affected accordingly (reproduced from Bureau of Mines Minerals Year Book Review of 1940, page 776).

the engine builder's increase of compression ratio, which in turn is a criterion of the power output that can be obtained per unit of fuel.

AS A RESULT of the progress made by both the petroleum and automotive industries, the American public has become increasingly dependent upon motorized transportation. Figure 4 shows the growth in number of passenger cars registered, as well as in the average gasoline consumption per car. The depression of the 30's brought home to all of us how dependent modern society has become upon the automobile. It was frequently stated then that the last thing the average man was willing to give up was his private means of transportation. The family car stood out as ranking with shelter, food, and clothing as a necessity of life. Many were the instances related in which the car seemed to head the list. This situation is brought out in Figure 4 which shows an inconceivably small sacrifice in automobile use during the depression. It should be noted that these data concern passenger cars only. Had busses and trucks been included, the resulting curves for total car registration and average fuel consumption would have shown almost imperceptible dips. This record of the past leaves no doubt that the American public has a live interest in the future of petroleum.

It is not only motorized transportation, however, that is dependent upon an adequate supply of petroleum. During the recent period of expanded crude oil production, our entire mode of living has become geared to the use of petroleum products. Industry, agriculture, and shipping alike are large consumers of a multitude of hydrocarbon materials derived from petroleum sources. The list includes such varied products as industrial and process oils,

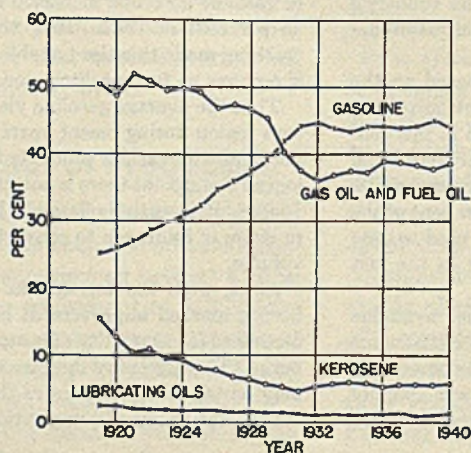


Figure 2. Average Yield of Principal Petroleum Products per Barrel of Crude Oil Produced

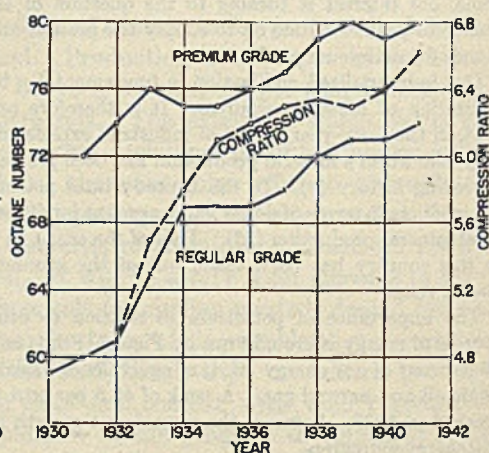


Figure 3. Trends in Octane Ratings of Gasolines and in Compression Ratios of Automobile Engines

greases and extreme pressure lubricants, asphalts and road oils, solvents and insecticides, and an ever-increasing number of chemical raw materials and derivatives. The petroleum chemicals business, which already had contributed a considerable volume of various alcohols and related products, has recently been called upon to increase several fold the country's supply of toluene for explosives and to furnish two thirds of the butadiene for the synthetic rubber program. According to Ickes (7) the production of toluene from petroleum will, by the end of the current

This paper reviews the recent remarkable progress in the petroleum field. Our growing dependence on the products of the oil industry has resulted in considerable concern regarding the ability to supply our future needs for liquid hydrocarbons. The proved reserves of crude oil correspond to some fifteen years' consumption at the prewar rate. However, the excessive wartime requirements for petroleum have led to such a high rate of withdrawal from these underground reservoirs that we may not be able to keep up with the demand for long. In addition to the proved reserves of petroleum known to be present in the earth, large but as yet undiscovered petroleum resources may be expected to exist in various parts of the world. How long we can continue to find this oil and bring it to the surface at the desired rate is a question, but it is certain that eventually a shortage in natural petroleum will occur. When that time comes, it should be possible to supply our needs for gasoline and other hydrocarbon products from such alternate sources as natural gas, shale oil, and coal. It is concluded that there need be no sudden change as far as the supply and consumption of gasoline and other petroleum derivatives are concerned. Future developments in this field will probably be characterized by further technological progress, increased drilling for oil on a world-wide basis, necessary adjustments in supply and demand, and a gradual shift to synthetically produced hydrocarbons.



Figure 4. Passenger Cars in Use in the United States and Their Consumption of Gasoline

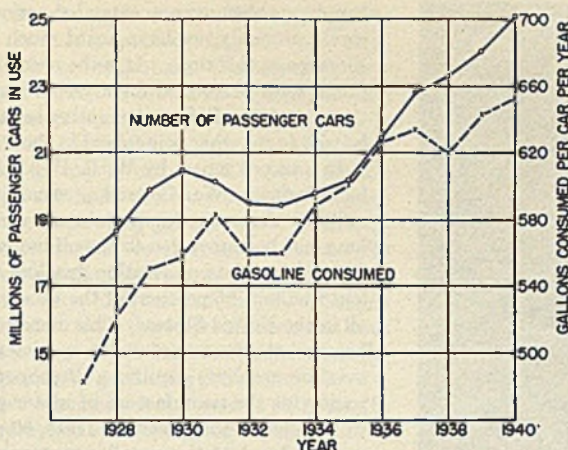


Figure 4

Figure 5. Production of Motor Fuel and Fuel Oil (Includes Diesel and Other Gas Oil and Distillates, and Residual Fuel Oil, but Not Kerosene)

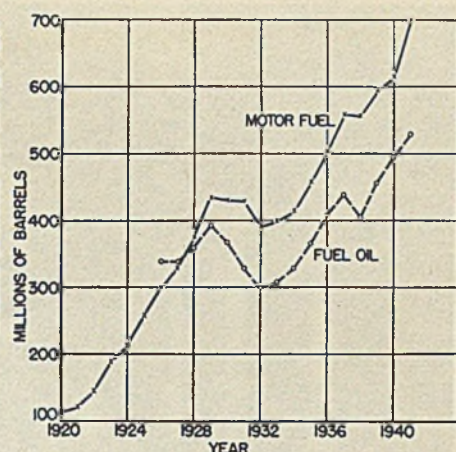


Figure 5

year, be nearly six times that obtained from all by-product operations.

The four main classes of products shown in Figure 2 add up to account for some 90 per cent of the materials derived from crude oil. The group of products included in the classification "fuel oil" rank next to gasoline in volume. The growth in fuel oil production is illustrated in Figure 5. Heating oil accounts for some 25 per cent of the total fuel oil consumption; about two thirds of this is used for homes. How this outlet for petroleum has developed can best be seen from Figure 6 which shows the growth in domestic oil burner installations. Although it may be easier

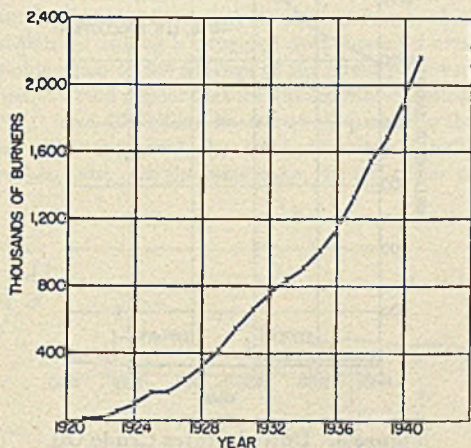


Figure 6. Domestic Oil Burners Installed at Beginning of Each Year

to heat a house than to run an automobile with a substitute fuel, the millions of American families who are dependent upon petroleum for heating can also be counted on to have a genuine interest in the future of our oil supplies.

The position of the United States as a producer of crude oil is shown by Figure 7. The data indicate that prior to the war we supplied some 63 per cent of the world's petroleum requirements. At present the figure is higher. Although considerable crude from other sources is normally worked up in American-owned refineries located outside the United States, our actual import and export of crude are small in comparison with domestic production (Figure 8). The volume of refined products imported has been about equal to that of the crude oil import, while the export of

refined products has been running 20-40 per cent higher than the figures for crude export during the period covered by Figure 8. In other words, the United States production of crude oil has been in rather close balance with domestic requirements of petroleum products.

Figure 9 gives the production and refining of petroleum by states. It is evident that there is considerable flexibility as far as the location of these two branches of the industry is concerned. Due to the ease with which crude oil can be transported by pipe line, tanker, barge, and rail, the refining operations are not tied down to the place of production but can be carried out at points most suitable from the standpoint of distribution and/or consumption of the finished products.

THE rate at which crude oil has been withdrawn from the ground is shown in Figure 10 by the curve labeled "cumulative production". On the "cumulative discovery" curve, the somewhat scattered points indicate the estimates made by various

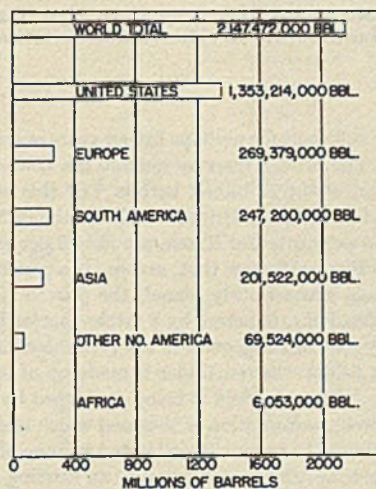
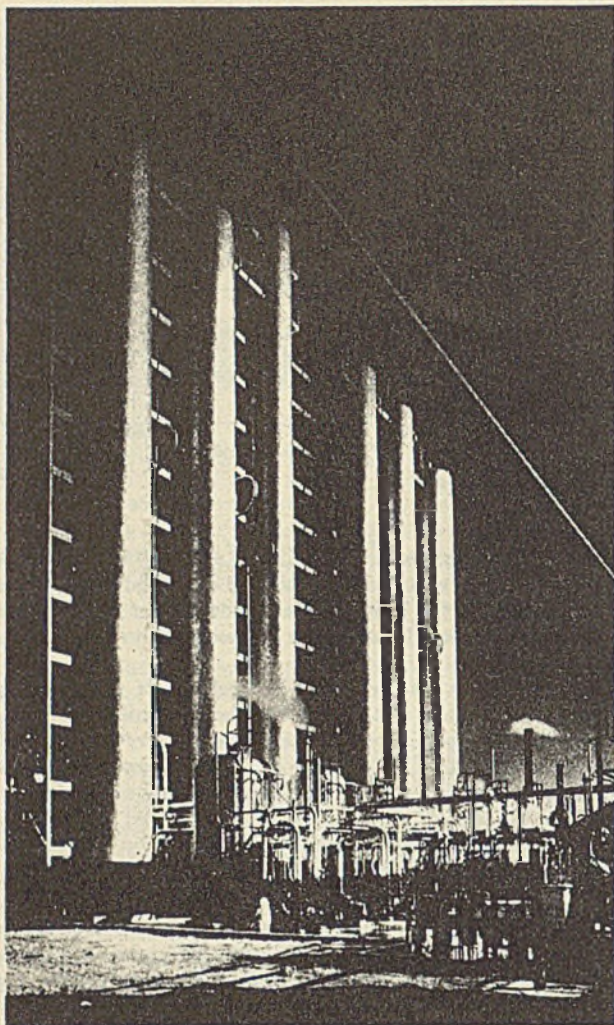


Figure 7. Production of Crude Oil in 1940

authorities at the time indicated. The vertical distance between the two curves represents the "proved reserves" at any one time. These are the oil reserves which, according to best estimates, are known to exist in the ground. As of July 1 of this year, the known and untapped reserves amounted to 20.4 billion





Robert Yarnall Richie Photo

#### Stabilizers Segregate Relatively Pure Hydrocarbons Required in Manufacture of 100-Octane Aviation Gasoline

barrels (6), or sufficient for perhaps fifteen years of our normal requirements. The proved reserves outside the United States are slightly greater, about 22 billion barrels. Of this oil located in other parts of the world, Britain controls about 50 per cent, America 25-30 per cent, and Russia around 20 per cent (15).

The data in Figure 10 show that, except for a period in the 20's when a shortage was seriously feared, the proved reserves have always kept ahead of production by a rather comfortable margin. However, only part of the growth in reserves shown is due to discovery of new fields; the remainder is made up of extensions to existing fields. As a new field is being developed by the drilling of additional wells, information is obtained which may lead to an upward revision of the originally estimated volume of oil present. This is what is meant by an extension to an existing field in contrast to the discovery of an entirely new field. The trend of actual discovery is brought out in Figure 11, which shows the present estimates of the ultimate recoverable oil in the fields discovered each year since 1918. It is apparent that there has been a deficiency in new discoveries as compared with consumption of crude since 1939. It is this lag in the discovery of new petroleum reservoirs which now is the subject of so much discussion.

Normally the fifteen-year backlog of crude reserves would have given the petroleum industry the opportunity to work out its

supply problem over an extended period. Except for the war, we would probably not have heard much about an impending crude shortage at this time. It is the necessity for providing the Allied forces with petroleum for a global war that has aggravated the situation (5). Before attempting to explain why this is so, it may be well to see what is involved in the war requirements.

In a recent report by W. R. Boyd, Jr., chairman of the Petroleum Industry War Council, mention is made of "the tremendous military demands for petroleum, which because of censorship have not been revealed to the oil industry, and already, exclusive of huge amounts of aviation gasoline and lubricants, are equivalent to about 25 per cent of the total current production of crude oil in the United States. This demand has an even greater effect because the manufacture of special war products, particularly aviation gasoline, requires a disproportionate amount of the capacity for the manufacture of motor gasoline" (16). According to Petroleum Administrator Ickes, 60 per cent (or nearly 2 out of every 3 tons) of the supplies sent overseas to our expeditionary forces over distances varying from 3000 to 10,000 miles are oil (7). Using President Roosevelt's figure of 1110 gallons of fuel per bomber, a thousand-plane raid in the European theater of war consumes more than a million gallons of aviation fuel, or the equivalent of about one third of the cargo carried by a modern tanker. The situation is aptly described in Premier Stalin's toast at the time of Prime Minister Churchill's visit to Russia: "This is a war of engines and octanes. I drink to the American auto industry and the American oil industry." Or as Ickes has expressed it, ". . . the side that can throw the most oil into the fray over the longest period of time will win" (7).

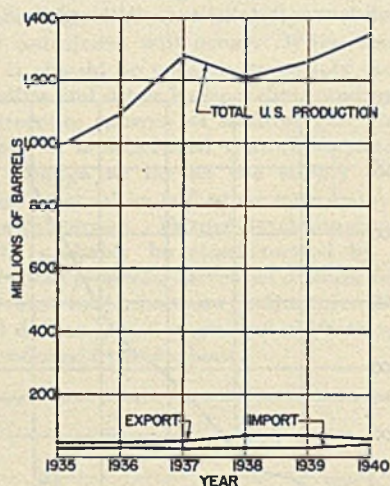


Figure 8. United States Crude Oil Production, Import, and Export

To meet these requirements, the United States is now producing crude oil at the rate of more than 4,200,000 barrels a day. To illustrate what this figure means, we may observe in passing that it represents well over four times the production during the height of the World War in 1918. Only 4-5 days' production at that rate is needed to equal the annual prewar consumption of petroleum and related products in the whole of the Italian Empire with its population of 45,000,000 (11)<sup>1</sup>. Less than 10 days are required to equal the most recently estimated yearly production of crude in Rumania, which is the chief supplier of petroleum to the Axis powers (12).

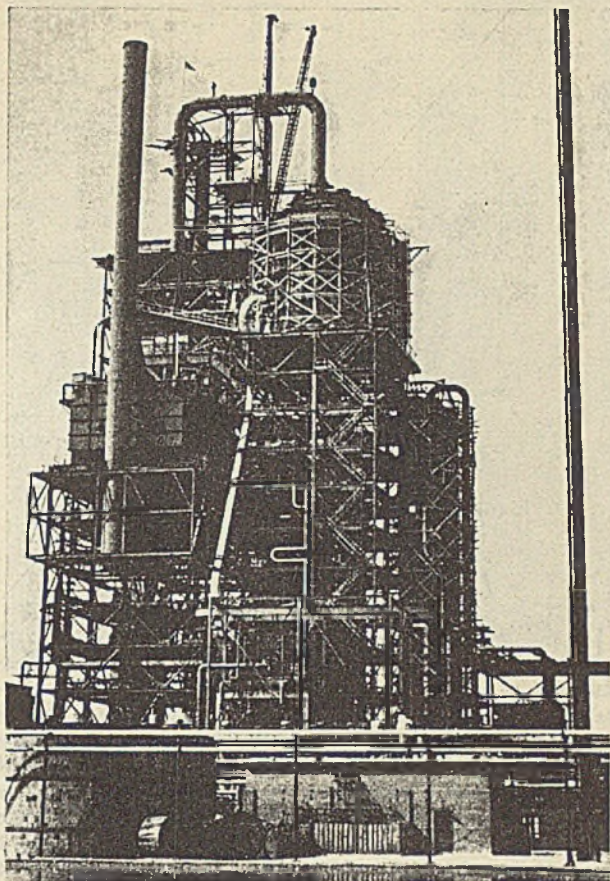
<sup>1</sup> *Oil and Gas Journal* (11) gives the prewar petroleum requirements of Italy as less than 40,000 barrels daily; "Petroleum Facts and Figures" (13, page 18) mentions a somewhat higher figure of 21 million barrels a year as the Italian consumption in 1938 of petroleum and related products (motor benzol, alcohol, and synthetic fuels).



LARGE as current production is, it may at first sight appear strange that there is much of a drain on the reserves of some 20 billion barrels known to be in the ground. The explanation is that a "rate of withdrawal" factor is involved. To understand this problem fully, we must remember that crude oil occurs in the ground in porous rock, the permeability of which governs the physical rate at which the oil can be withdrawn. Also, oil contains no inherent energy, and it must therefore be displaced from the reservoir rock either by expanding gas associated with it or by water. In dealing with such a heterogeneous system, the efficiency with which the oil is displaced improves with reduced rate of withdrawal. Conversely, high rates of withdrawal result in inefficient flushing of the oil from the reservoir rock and consequent reduction in recovery. This imposes certain restrictions on the country's capacity for producing petroleum.

In other words, there is no immediate shortage of oil known to be in the ground. The problem confronting us is rather one of being able to withdraw this oil at the desired rate. In some fields, which are being operated on the best engineering principles, the natural gas is pumped back into the ground to aid in bringing still more oil to the surface; but in many older fields all or most of the gas has been withdrawn, leaving an inordinately high percentage of the original oil to be taken out of the ground by secondary recovery methods.

Next comes the question of oil not yet discovered. It is difficult for anyone to make a reliable estimate of the possible hidden reserves of crude. The viewpoint of the petroleum geologist is presented by Pratt (15), who discusses the prospects of finding oil in terms of the subterranean structures and the efforts to explore these structures for their oil deposits. Of the crude so far discovered and developed world-wide, some 54 per cent is accounted for by the search within the United States (Alaska not included). While this country constitutes only 5 per cent of the land area of the earth, it contains 15 per cent of the structural area most favorable for the occurrence of oil fields. If exploration by drilling is extended over this total area and if per acre yields equal to the average of the already proved areas are assumed, it would appear that the United States ultimately should give up at least 100 billion barrels of oil, including the 46 billion barrels which represent the total discovery (production plus reserves) to date. On the same basis, the rest of the world would



A Catalytic Cracker Being Constructed on the Eastern Seaboard

ultimately produce some 600 billion barrels of oil, including the 38 billion barrels already found. Such considerations lead to the conclusion that "at the present rate of consumption the probable ultimate oil resources of the earth, made available and freely distributed, should meet humanity's needs for 300 years to come".

How to locate these potential oil reserves is a problem with so many technical and economic aspects that an adequate discussion cannot be undertaken as part of this brief review. Not even those best qualified to have an opinion of this subject can predict how long new oil will continue to be brought in at the rate it is needed. This is the situation which has aroused so much recent comment and which logically leads to the question of where we stand with respect to alternate sources for the products now being obtained from petroleum.

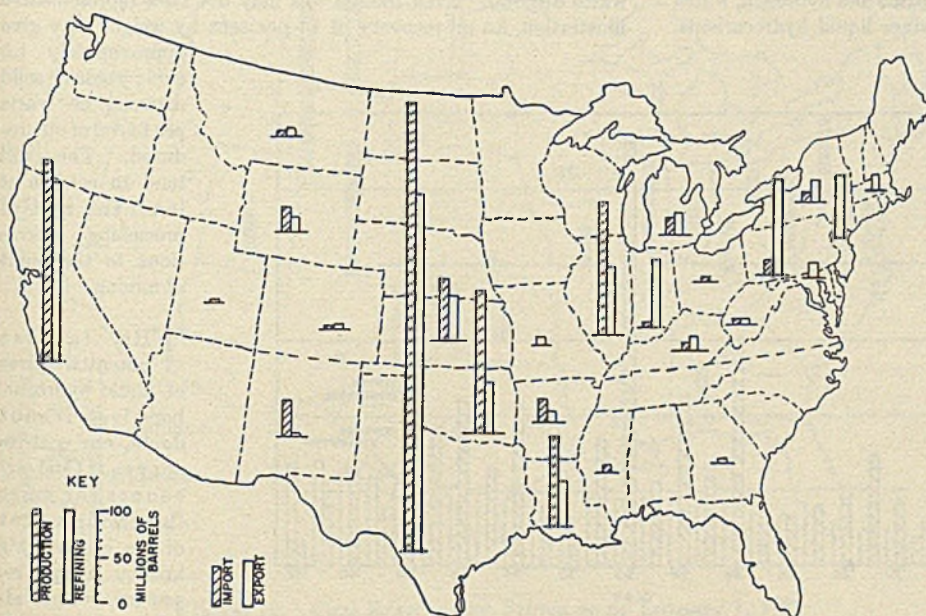


Figure 9. Production and Refining of Petroleum by States



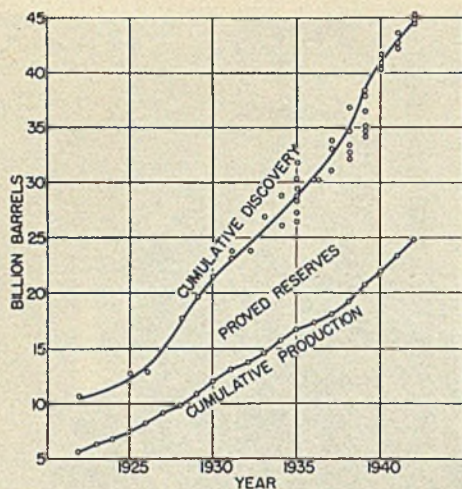


Figure 10. Cumulative Production and Discovery of Petroleum in the United States, Adapted from Levorsen's Data (10)

THE domestically available energy source most closely related to crude oil is natural gas. The production and consumption of natural gas by states, although by no means identical to the distribution shown for crude oil in Figure 9, follows much the same general pattern in that transportation by pipe line makes for a marked flexibility in distribution. To most of us it does not mean much when we are told that the country's proved natural gas reserves amount to some 95 trillion cubic feet (1, 14). A little figuring will show, however, that on a weight basis this is equal to about 75 per cent of the proved reserves of petroleum. At the present rate of consumption the proved gas supply should last about thirty years, or twice as long as the oil supply. Methods are known for converting these natural gas hydrocarbons into liquid petroleum fractions. The heavier constituents can be processed by such direct methods as cracking or dehydrogenation, followed by polymerization and alkylation. Methane, however, which is the major constituent of natural gas, can best be converted into gasoline by the Fischer-Tropsch process. In that case the methane must first be reacted with steam to give a mixture of carbon monoxide and hydrogen, which is then treated with a catalyst to produce liquid hydrocarbons. Technical information is available on this process, but as yet this country has no large-scale operating experience. The process has been used commercially in Germany for some time, and a small pilot-plant unit for carrying out the Fischer-Tropsch synthesis is now in operation at the Bureau of Mines (4). It would be unwise at this time to make any prediction in regard to the amount of gasoline that might be produced in this manner.

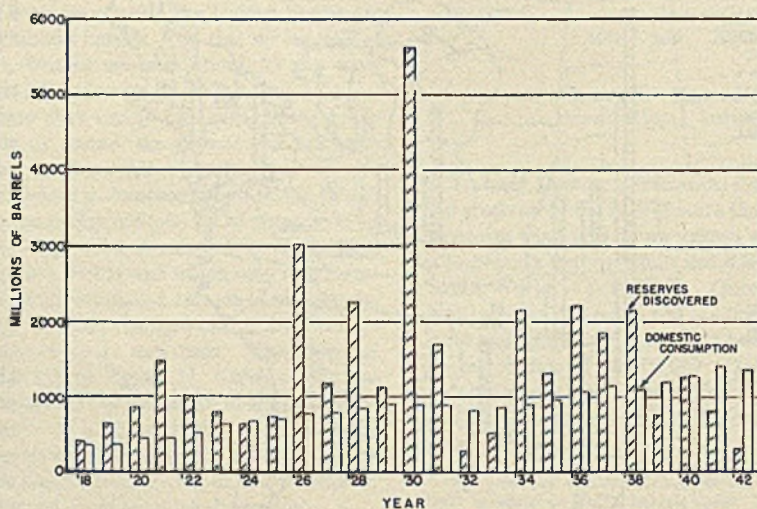


Figure 11. Annual Discoveries and Consumption of Petroleum, According to Heroy (5)

A much larger potential supply of liquid hydrocarbons is obtainable from the oil shales of the United States. Most important are the Tertiary oil shales of the Rocky Mountain region, located chiefly in Colorado and Utah. Other deposits are the Devonian black shales of Indiana and Kentucky and the cannel shales of Pennsylvania and West Virginia. In 1928 these shale deposits were estimated by Dean E. Winchester as capable of producing 92 billion barrels of oil (8). Although this is still considered the most authoritative figure, a great deal of assay work must be done before an accurate estimate of practically available oil from shale can be made. It can definitely be said, however, that the potential supply of liquid hydrocarbons from this source is high compared with known crude oil reserves.

Oil is now being recovered from shales on a limited scale in various parts of the world by retorting under suitable conditions of temperature and pressure. From 1925 to 1929 the Bureau of Mines experimented with the recovery of oil from Colorado shales. Although no commercial scale production was undertaken, sufficient work was done to demonstrate the practicability of producing oil from this source. The oil obtained by retorting shale differs from conventional crude oil in that it has a higher percentage of unsaturated hydrocarbons, a lower percentage of gasoline, a higher wax content, and relatively high content of phenolic compounds and nitrogen bases. Additional work therefore remains to be done on the development of satisfactory refining methods (3, 17).

Beyond the borders of the United States, the Canadian deposits of tar sands can also be included. These deposits spread over thousands of square miles through the central portion of the Williston Basin in the Province of Alberta. They are composed of sands saturated with oil, and figures indicate the reserves of the Athabaska deposits to range from 100 billion barrels up to many times that quantity. Pratt gives an estimate of 100 to 250 billion barrels (15), which places Athabaska tar sand as one of the largest potential sources of petroleum in North America. However, the fact that these sands must be mined to extract their tar oil content presents practical difficulties. Of the total area, variously estimated at 10,000 to 50,000 square miles, not more than 10 square miles, containing perhaps 500 million barrels of oil, can be considered workable by strip mining methods.

Aside from the development work which remains to be done on improved methods of recovery and refining, the production of oil from the tar sands as well as from shale presents a problem in waste disposal. Even though this may not be a representative illustration, an oil recovery of 13 per cent by weight may give approximately 1.5 cubic yards of solid material as waste per barrel of oil produced. This will tend to confine at least the initial processing operations to the point of mining.

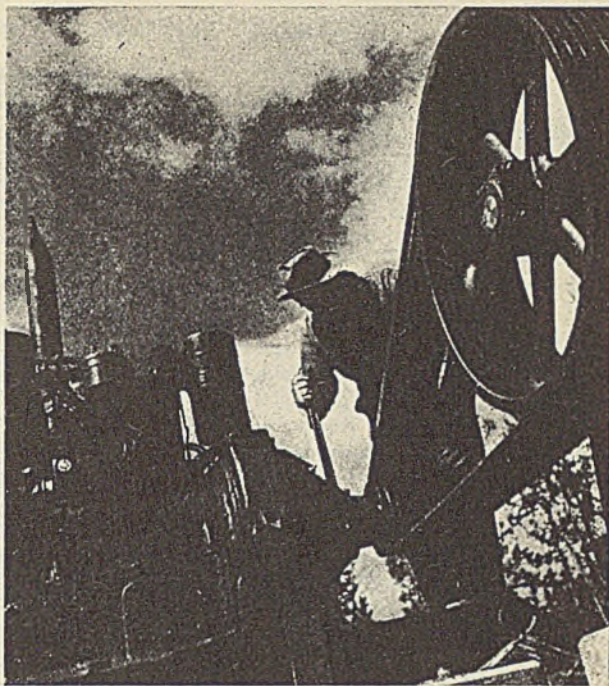
THE largest potential source of liquid hydrocarbons is, without doubt, our coal reserves. Coal accounts for more than 98 per cent of the country's known energy resources, not including water power. (All water power,



developed and suitable for development in the United States, would supply less than 25 per cent of our present total energy requirements.) These coal deposits amount to more than 3 trillion tons. As Figure 12 shows, almost 70 per cent of the total coal reserves lies in the semiarid plains or in the Rocky Mountains, far from present centers of population and industry. About 85 per cent of current production is from the 30 per cent of our reserves east of the Mississippi River. The anthracite deposits are largely confined to Pennsylvania, with lesser quantities located in Virginia and Arkansas, and only smaller amounts in Colorado and Washington (1).

Liquid fuels may be produced from coal by various methods such as low-temperature carbonization, the Fischer-Tropsch synthesis, and high-pressure hydrogenation. The two latter are of most interest from the standpoint of yields obtainable. According to Petroleum Administrator Ickes, it is possible that some 50 million barrels of gasoline may now be made annually in Germany by high-pressure hydrogenation (8). Coal has also been hydrogenated for some time in England on a less extensive scale. In this country the Bureau of Mines has in operation a laboratory-scale pilot plant for direct hydrogenation of coal (4), and has been working on plans for the installation and operation of industrial-scale pilot plants. In recent hearings before a joint committee of Congress, Ickes strongly endorsed a proposal for the Government to build and operate larger-scale demonstration plants for the production of oil from coal. In his words, this "is a proposal to blaze the path now for private capital to do this job when we have no more natural domestic petroleum and it becomes a question of synthetic liquid fuel or the end of the gasoline age". There is no need at this time to go into further discussion of the quality of gasoline that may be produced by these various processes or the yields obtainable from different types of coals. According to Ickes' estimate, the available coal reserves can provide the synthetic fuel we need for a thousand years and still leave enough coal for other present day purposes (8).

This review has been concerned only with the available raw materials which have been handed down by Nature through the ages. By growing vegetable matter it would undoubtedly be



Courtesy, National Film Board of Canada

Trying Out a Lever of the Belt Shift at One of the Pumping Stations on the Pipe Line to Feed Gas and Oil from the Mackenzie Basin to Trucks on the Alcan Highway, Planes Flying a Parallel Route, and Ships Off the Alaska Shore

possible to extend these supplies, but the potentialities of this source of energy cannot readily be estimated. A discussion of some of the technical and economic aspects of this problem is presented by Burke Jacobs in the report on "Energy Resources and National Policy" (1).

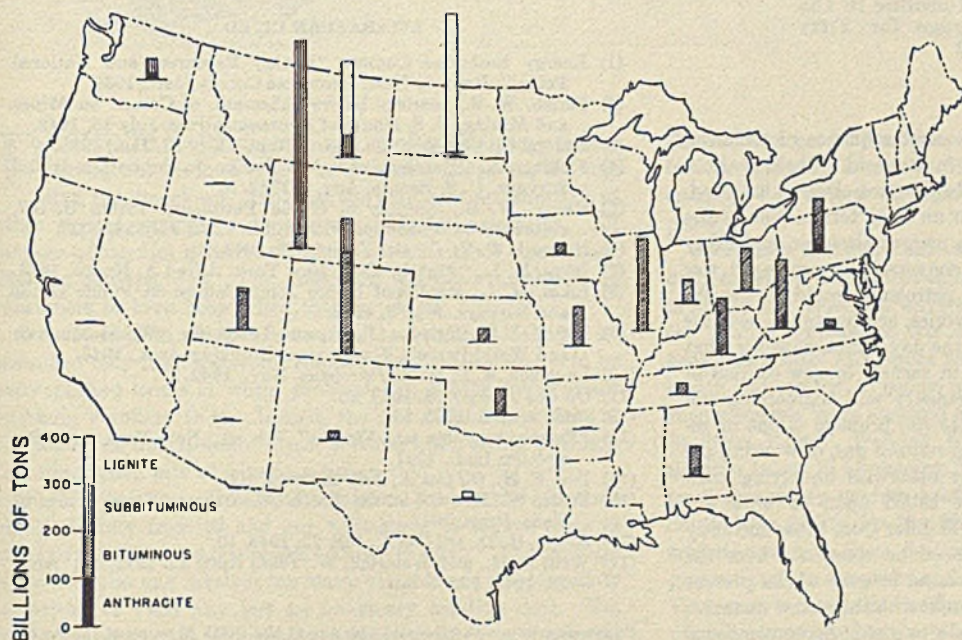


Figure 12. Coal Reserves by States as of January 1, 1937

Anthracite, subbituminous, and lignite reduced to bituminous coal equivalent, according to "Energy Resources and National Policy" (1).

AS TO the question of cost, it may be well to consider the figures in Table I which were submitted by Farish before a House Committee last year (2). These data indicate that gasoline from such alternate raw materials can be produced at a cost sufficiently close to present prices so that with an increasing cost of crude oil we may expect a gradual upward trend rather than any abrupt increase in the cost of gasoline and related products. In this connection, the petroleum industry has not so far benefited by any appreciable increase in price level. Compared to



TABLE I. COMPARISON OF METHODS FOR MOTOR GASOLINE PRODUCTION

Process	Approx. Cost per Bbl. Motor Gasoline per Day <sup>a</sup>	Approx. Tons Steel per Bbl. Motor Gasoline per Day	Approx. Gasoline Cost, Cents	
			Direct cost, including normal overhead but excluding depreciation	Total cost, including normal overhead and 10% depreciation
High-pressure coal hydrogenation	\$12,800	14.1	15.9	22.6
Fischer, European design starting from coal	7,600	8.9	14.7	19.2
Fischer, European design starting from natural gas <sup>b</sup>	4,750	6.5	6.0	8.8
Modern high-pressure hydrogenation of petroleum <sup>c</sup>	1,150	1.4	4.8	5.5
Modern oil refinery, \$1.20/bbl. <sup>d</sup>	700	0.7	5.1	5.3
Modern oil refinery, \$2/bbl. <sup>d</sup>	700	0.7	8.3	8.5

<sup>a</sup> 1942 costs for complete plant including all utility supply and auxiliaries.

<sup>b</sup> Natural gas at 5 cents per 1000 cubic feet.

<sup>c</sup> Crude at \$1.20 per barrel. <sup>d</sup> Crude price at the well.

August, 1939, the start of the present war, all commodities have increased 38.3 per cent, farm products 103.1 per cent, foods 61.2 per cent, and petroleum 19 per cent (11). As Figure 13 shows, the petroleum industry's record is one of decreasing costs brought about by technological improvements. This is particularly evident from the lower curve which represents the average gasoline cost in recent years, excluding the steadily mounting taxes. With a guaranteed supply of basic raw materials we should, in light of the petroleum industry's past achievements, be able to look with confidence toward the future.

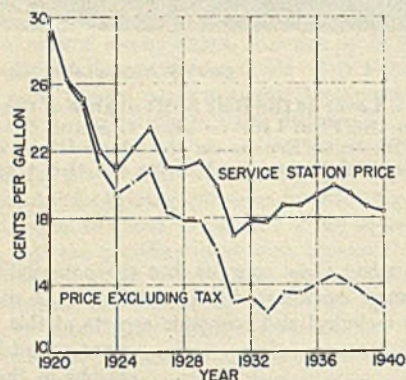


Figure 13. Cost of Gasoline in the United States (Average for Fifty Cities)

It is not possible to predict the exact sequence of technical developments which lie ahead of us in this field. There is also a great deal of uncertainty in regard to the time element involved. New discoveries of crude reserves or an early termination of the war would undoubtedly relieve the present situation and delay the need for synthetic products; conversely, a prolonged war with continued heavy demands for petroleum would, in the absence of any substantial new discoveries, accelerate the need for alternate sources of supply. When the day comes, however, that the petroleum industry must turn in earnest to new sources of liquid fuels, its dependence on chemistry and engineering will become increasingly great. Whether the problem is one of recovering oil from shale, of liquefying natural gas, of working the tar sands, or of hydrogenating or otherwise liquefying coal, chemistry and engineering will be called upon to work out processes which in major respects will differ from those currently in use by industry. We hardly need be concerned over the future of petroleum chemistry in general or even of the present trend toward utilization of petroleum as a chemical raw material, for these new processes will continue to yield the conventional hydrocarbons now obtained from crude oil and natural gas. In addition, such alternate processes are likely to increase the supply of hydrocarbon derivatives containing oxygen, sulfur, and nitro-

gen which are being obtained from petroleum in such dilute concentrations that only in exceptional cases is their recovery a paying proposition.

THIS leads to the following general conclusions: In addition to the petroleum known to be present in the ground, large but as yet undiscovered reserves may be expected to exist in different parts of the world, including the United States. How long we can continue to locate this oil and bring it to the surface at the desired rate is an open question. At some future date, whether it be in the immediate future, in the next generation, or in a much later generation, a shortage in natural petroleum will occur. In the meantime, there is nothing to indicate that this should result in any sudden change as far as our supply and consumption of gasoline and other petroleum derivatives are concerned. Progress will continue in the petroleum industry's efforts to improve the efficiency of its processes and the quality of its products. Advances in engine construction will make for better efficiency in the utilization of fuels and lubricants. Increased drilling on a world-wide basis will bring in more oil. There will be necessary adjustments in supply and demand so that oil will be moved freely from the principal centers of production to the principal centers of consumption. All this will tend to prolong the necessity, at least in time of peace, for turning to alternate sources of supply. As the need arises, synthetic products from the sources indicated will then gradually work their way into the picture.

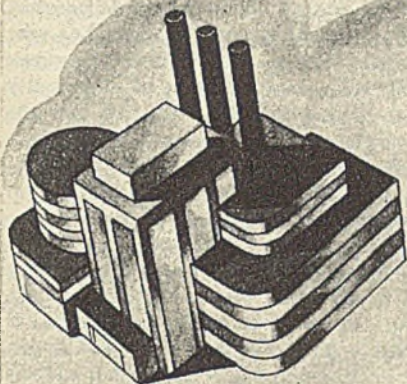
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PRESENTED before the General Meeting at the 106th Meeting of the AMERICAN CHEMICAL SOCIETY, Pittsburgh, Penna. Unless stated otherwise, the charts shown are based on data from the Bureau of Mines and other Government agencies, "Petroleum Facts and Figures" (1941 and previous editions), and on petroleum industry figures.



# Promise and Problems of Peace



## CHEMICAL INDUSTRY'S POSTWAR ROLE

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**P**ROPHETS, both amateur and professional, have arisen throughout the land to give us the form, the shape, the outline, the "mock-up", the map, the plan, and an infinitude of other crystal gazings of tomorrow's peaceful prosperity. All manner of fanciful pictures of things to come whet our desires. That is, perhaps, well. For Americans will need multitudes of consumers to keep busy when the war stops.

Our capacity to produce has soared to heights which can be sustained only if all the world comes to buy. How that is to be accomplished looms as world problem No. 1 with many lesser problems corollary to it. Indeed, the first great compromise of the peace will undoubtedly adjust a rising world living standard to a diminished rate of American production.

Where a balance will be struck between the world's economic ability to buy from us and our willingness to reduce costs in order to sell is beyond our present ability to solve. The problem is too complex and involves too many variable and indeterminate quantities to yield any but an imaginary solution now. Yet many will attempt it and economic panaceas of every shade will be offered. On the one hand, we will be urged to give away our output for the benefit of peoples in the minimum economic levels, and on the other hand, political pressure will attempt to

throttle our production where it competes with others. The basic problems of a new world-wide economy and a medium of exchange available to all must be solved early to ensure lasting peace.

Operations of Lend-Lease and the wide dispersion of great numbers of our troops throughout the world introduce American products and American ways to vast numbers of people outside the former normals of our export trade. Sanitation, public health measures, and insect control suggest new possibilities in health and comfort to people who, lacking previous contact with such measures, have assumed disease and filth to be inescapable. In "One World", Wendell Willkie suggests some of the possibilities latent in awakening backward populations to even the most elementary modern conveniences. Jungle dwellers in the South Seas realize for the first time that insects can be controlled, and with them decimating diseases, when they see the precautions our men take and experience the results that follow. Vast areas in Asia, the Pacific Islands, and Africa are thus being prepared to demand products hitherto unknown to them. Meanwhile, our ties with Latin America are strengthened by the close contacts born of war's necessities. Obviously, then, development of foreign trade forms a vital part of our postwar problems.



### DEVELOPING EXPORT MARKETS

To take advantage of this situation, we must avoid the oft-repeated errors and gaucheries which have heretofore too often characterized American attempts to cultivate export markets. Only careful, intimate studies of the desires and requirements of foreign buyers can ensure their continuing interest in our products. Too often minor clerks without special training, who can be advanced in rank thereby, go into foreign fields to represent American interests in handling major problems. When purchases are to be made abroad, our best men represent us; but sales to foreigners, we seem to think, will make themselves if an order taker is on hand. The fallacy is obvious.

Packaging and labeling must meet customer's requirements. A classic example of American carelessness in this respect is related of a company whose product could be delivered to its destination only by llamas over the high Andes. Now, llamas are small animals capable of carrying loads of a hundred pounds or less. Like union laborers, they have fixed ideas of the loads they will carry and strike when too much is imposed upon them. Thus, when this particular product reached the transshipment point packed in strong cases of 100 pounds *net* weight, the llamas balked and could not be persuaded to move until complete re-packaging had reduced the load on each one to 100 pounds *gross* weight as specified by the original order. The difference seemed negligible to a shipping clerk in Chemical City, U. S. A., but to the customer who knew his llamas and needed the goods, it was quite a different matter.

Vital also to the over-all problem of the postwar period is the mounting deficit of durable goods in our own domestic market. Several recent surveys of this vacuum for goods reveal immediate minimum demands estimated in May to exceed 12 billion dollars and still growing. Major items are minima of a million homes, 2½ million automobiles, and 1¾ million major purchases of household equipment (such as sewing machines, washing machines, vacuum cleaners, stoves, refrigerators, furniture), all to be purchased within six months of peace. This major market for industry's products will depend largely on the faith of people generally in provisions made to ensure their employment and hence their continuing security, and on whether this faith is great enough to persuade them to part with wartime savings.

In the decades following 1918 the sales policies of the chemical industry underwent important changes as each company developed its own sales force to replace the middlemen who had previously handled large volumes of chemical sales. Now a new tendency develops: The industry is broadening its scope still farther by shifting closer and closer to the consumer market. Traditionally, chemicals have been producers' goods, but growth of many items—plastics, alkyds, synthetic textiles are typical—pushes their producers into consumer goods markets whether they wish or not. As each development in these fields follows its normal course, its originator must carry through each step to final market tests. Thus, before it is possible for the maker of a new chemical product to market it, he may be compelled actually to put himself into an industry consuming his product. That having been done, it is not unnatural that he should improve his situation and remain in the consumer goods market permanently. As the number of revolutionary new products of chemical industry increases, this trend is likely to become more and more pronounced. Such a change of outlook represents a distinct departure for most chemical companies, but it is being forced upon them by the nature of their modern development.

### CHEMICAL INDUSTRY'S PROBLEMS

American chemical industry faces problems of its own that will utilize to the utmost all the vision, ingenuity, and foresight it can muster. Upon it rests a grave responsibility to

provide sinews for peace as it has for war, and an equally great opportunity. In preparation for both it will be well to survey the bases on which its future must be built.

Basic to the whole matter is the fundamental difference between chemical and other industry—its freedom from major problems of conversion. The sulfuric acid, soda ash, hydrocarbons, synthetic resins now required for war are identical with those consumed in peaceful pursuits. So it is with most chemical products. The problem of chemical industry generally thus becomes one of adjusting quantity, rather than changing type, of production in converting for peace.

The magnified quantities of many materials now produced will later be the practical equivalents of new products, so great has become their new plentitude and so low their consequent new cost. Such familiar materials as aluminum, magnesium, toluene, ammonia, formaldehyde, and chlorine are thus available in unfamiliar abundance. Developments pushed at frantically accelerated rates to meet war's peculiar urgencies have provided new products of a usefulness as yet only partially explored—butadiene, styrene, acrylonitrile, pentaerythritol among them. Equally important to the future are new techniques for meeting with new assurance and efficiency problems of production which long baffled our industry; the amazing successes of recent years in petroleum chemistry and engineering, in plastics technology, in drying oils, suggest some of these possibilities.

Each of these new phases presents a point of departure from which many roads radiate into tomorrow. Normally they would be mere crossroads quickly passed in an orderly progression, but the curious fact is that orderly progress has ceased to exist for the time being. Despite the apparent swiftness of progress now, industry is actually at a stand for want of opportunity to consider and to plan. Casual observers who view only the surface see today's tremendous industrial turmoil bringing unfamiliar objects into vision with startling rapidity. They mistake turbulence in the stream of events for its forward flow. Only when that turbulence subsides can progress be resumed.

Actually, new departures will be most salutary to ultimate progress. The interlude of war and its destruction of customary landmarks has released us from long cherished habits of both thought and action. Our dependence on orderly progression has been broken. We are free to start again from newly established bases and to go forward unfettered by a past from which we have been completely, if temporarily, divorced. The automotive and rubber industries are striking illustrations. Each year's successive automobile model has embodied conservative changes from its predecessor to minimize obsolescence of tools, dies, and patterns. That has been quite proper, but now automobile builders find their facilities in strange new production and their vision unlimited by last year's tools and dies in approaching the future. Similarly, the industry of rubber fabrication is faced with entirely new raw materials of great, but largely unproved, potentialities. Future developments in both may well strike out in unexpected directions.

### TOMORROW'S CARS AND TIRES

Automobile designers have acquired a wealth of experience with the newly abundant light metals, aluminum and magnesium; with a variety of plastics; with small engines generating huge power by utilizing the extraordinary potentialities of modern aviation gasoline; and with the possibility of tires of unprecedented life and efficiency based on synthetic rubbers of several kinds.

Tire builders are already exploring with considerable success the possibilities of the several varieties of synthetic rubbers now available and of new types of strengthening fabrics. Already their investigations have demonstrated that the accustomed technology of plantation rubber fails to bring out the full potentialities of the synthetic products. Tires made of synthetics



by the accustomed rubber methods reveal surprising shortcomings. The heat produced in the side wall during flexing is, for example, substantially greater than in rubber tires. For the present, little can be done about that since new molds and fabricating equipment are and will remain unobtainable until the war's burden on metals is eased. When rubber fabricators have an opportunity to revise both their methods and their machines, the answers to many present problems will be easily found. Tire builders in the past have developed their methods by degrees. This historical development, coupled with the necessity for frequent removal of damaged tires for repair, has given us our present design. However, when designers are again able to use any materials they fancy without limitation, the possibilities become enormous. For example, the techniques of self-sealing gasoline tanks and bullet-proof tires suggest the building of tires that cannot be punctured. The extraordinary wearing qualities of some of the synthetics and their extreme resistance to air, ozone, sunlight, and other factors in rubber failure through age point directly to future tires that may, not unreasonably, be expected to last as long as the car which they carry. Stronger fabrics of rayon, nylon, steel, and glass fibers provide obvious answers to the problem of blowouts and will permit economies through reducing the thickness of the tire. Already test tires of synthetics are reported to have lives equal to natural rubber tires and some hope is held for lives as great as 100,000 miles. Thus no difficulty is apparent in building the tire as an integral part of the wheel. The air cushion can even be largely enclosed in the wheel itself, reducing the quantity of synthetic required without sacrificing the over-all resilience of the assembly.

Meanwhile the reduction of weight of the car itself through increased efficiency of its engine and redesign of its other parts to use light metals and plastics will give further freedom to designers in lightening the load imposed on tires.

The tire-automobile problem has been discussed at some length to suggest values growing out of our break with history. It is impossible here to do the same in each field of progress but obviously the same kind of analysis can be equally well applied elsewhere.

#### WAR-BORN SHORTAGES

Most important of the problems arising from war are stringent shortages of rubber, tin, silk, quinine, vegetable oils, and a few other natural products formerly imported. We can be confident that imports of these will never be vital in our economy again in any way comparable with the prewar past.

**RUBBER.** Our synthetic rubber program has been realized with incomparable speed and efficiency. Many synthetics have been adapted to rubber's uses and will occupy permanent places in our industry whatever may be the future of rubber itself. Electrical insulation, rainwear, hose for water, oil, steam, air, and various other fluids, waterproof sheeting, and a wide variety of articles formerly fabricated of rubber are being made better of one or more of the newly plentiful synthetics. Rubber appears now to be permanently ousted from every accustomed field with an exception yet necessary for pneumatic tires where its tenure is rapidly weakening.

**TIN.** This metal has been useful in collapsible tubes, in tin plate, in solders, and in bearing metals. In each of these fields new developments suggest its ultimate, but not immediate, obsolescence. Collapsible tubes of plasticized cellulose acetate, ethylcellulose, vinylidene chloride, and other synthetic and semi-synthetic materials are proving unexpectedly economical and useful, and may with improvement permanently displace metal tubes for many purposes. Tin plate for cans has gone through successive improvements which provide continuity of protection with much reduced thickness of coating and hence tin requirement. Various lacquer coatings have been given important

impetus by the tin shortage and are likely to become permanent. Meanwhile many nonmetallic containers of glass and impregnated fiber and fabrics have gained firm footholds where tin cans have been traditional. Tin alloys have given way to other alloys containing less of this metal or none at all and these are proving so satisfactory in solders, bearings, and similar applications that they will be difficult to displace. Furthermore, Bolivian tin ore is now smelted in this country in substantial amounts.

**SILK.** Before war reached us, silk had ceased to be a major problem. That it now causes any disturbance is to be laid solely to extraordinary demands for nylon and rayon for war uses. One can confidently predict that the only silk we need ever import again will be intricate and delicate needlework rather than filament or fabric. Methods of treating other fabrics to give them the qualities of silk for draperies and the perfection of glass fabrics, possessing the additional value of noncombustibility, nullify any urgent need for silk for these purposes, as do rayon and nylon for clothing and hosiery.

**QUININE.** Malaria continues a grave problem. Present views indicate that even exact duplication of quinine by synthesis would leave much to be desired in combating malaria. Because quinine has been the best drug available to us, we have acquired an abiding faith in its power; but when viewed in the light of modern chemotherapy of the sulfonamides, many flaws are apparent in its action, both preventive and curative. Critical analysis of the antimalarial problem thus enlarges the search to include examination of types of compounds beyond those similar to quinine and at the same time suggests a diminished value for a synthetic duplicate of this alkaloid.

Atabrine and Plasmochin, two trade-marked synthetics, are performing invaluable service now and possess important effectiveness against malaria. However, nothing yet discovered meets all requirements, and research is being actively prosecuted in this field by scores of our ablest workers. The vital importance of the ideal synthetic to civilization lies in the prevalence of malaria and similar debilitating diseases throughout most of the habitable portions of the earth. For the emergency, expansion of the growth and collection of cinchona bark in its native Western Hemisphere habitat is supplementing accumulated stocks of the alkaloid and wide use of the synthetics mentioned above. Such measures will have to serve for the time being until normal sources are again available to us, or until present researches bear fruit.

**DRYING OILS.** Shortages are being offset by several important developments. Tung oil originating in China has been critically scarce since the Japanese blockade of the China coast has been effective, and consequently its replacement has been most pressing. The problem is to produce in a more plentiful oil the degree of conjugation of double bonds characteristic of tung oil. Castor oil yields a useful product on dehydration. Distillation of fatty acids of other more plentiful oils produces fractions having enhanced drying qualities, some of them approaching tung when reconstituted either as glyceryl or, better, pentaerythryl, esters. Solvent extraction also has some possibilities as a fractionating process. Isomerization of unsaturated fatty acids by alkali produces increased conjugation. The combined effect of these semisynthetic processes has materially assisted in overcoming the shortage of tung oil. Furthermore, developments of new types of drying alkyd resins have assumed another important share of that burden. In sum, these combine to reduce the stringency of the shortage but they have not yet made tung oil unnecessary.

**PERMANENCE OF SYNTHETICS.** Each of these products, formerly imported, formed the principal economic export of large populations: silk from China and Japan, rubber and tin from Malaya, quinine from Java, tung oil from China. Through sale of these raw products, markets for finished goods made



elsewhere were presumably created in the Far East. However, various factors in the situation, principally exploitation of backward native populations by entrepreneurs, channeled most of the income away from its ultimate creators. Thus the kindly intentioned persons, who already suggest that we forego synthetic rubber production at war's end, would injure us rather than help downtrodden peoples. The salutary effect on the economy of India resulting from the synthesis of indigo half a century ago illustrates the point. Vast tracts of fertile land devoted to the culture of the indigo plant in the nineteenth century removed this land from the production of needed food. When indigo culture became unprofitable with the perfection of synthetic production, the return of the land to the growth of food crops substantially improved the economic condition of the people.

#### HASTENED DEVELOPMENT

Telescoping of the several steps normally taken in putting an idea to work characterizes the war period. Pressure of time forces the shortening of each successive part of the series: research, pilot plant study, and preparation for production. Normal research proceeds to proof of the idea from every point of possible attack so that the results, when reached, possess the utmost validity. Pilot plant study may be long continued for the dual purpose of perfecting the process and of developing the market for product beyond the point where pilot plant output suffices. During the latter part of this period, the production plant is normally designed and built.

These successive steps ordinarily extend over many months, or even years, a period too long to be practicable under the emergency conditions of war. Consequently, the practice has become, for the time being, to shorten each step to its lowest practicable limit as required by surrounding conditions and thus to force earliest possible production. In this sense development and research have been enormously accelerated beyond what would be considered a safe speed normally.

**PENICILLIN.** Also characteristic of war production is its ability to enter new ventures without regard to costs. Penicillin is typical. The value of this product of the mold, *Penicillium notatum*, lies in its cure of infections outside the reach of other agents. Upon that basis alone, industry entered its manufacture. The process of growing the mold is quite undeveloped and is at present conducted in huge numbers of laboratory bottles. One would hesitate to undertake to operate such a process on a production scale under normal circumstances. In our war economy the need for the product is so great that the operation can be financed as a war measure. The tiny output of the drug goes to clinical research and military use for desperate cases, but meanwhile research workers vigorously seek to improve methods of production and to learn the facts upon which synthesis will ultimately be based. These problems are being attacked from every point of view at once in a manner likely to lead to their swiftest solution. At this writing even the structure of penicillin is unknown.

Penicillin's development is the extreme case of acceleration under war's stimulus. Many other operations have been similarly hurried but none to quite the extent of this one. Butadiene, alcohol from wheat, magnesium by ferrosilicon reduction of dolomite and by carbon reduction, are among other telescoped developments.

#### RESULTS OF ENLARGED PRODUCTION

Chemical products that will be available in new abundance suggest the general directions of postwar development. Sulfuric acid production has doubled during the war years so far, as has caustic soda. Ammonia production has reached new heights, partly at the expense of synthetic methanol, and is expected to be substantially cheaper as a result. Chlorine output has

somewhat more than doubled. Toluene produced now in huge quantities from petroleum is some five times as abundant as before, a situation likely to bring it into a new low-price class. Formaldehyde production has soared to high levels that suggest economies in resin production and encourage exploration of possibilities in its derivatives, particularly pentaerythritol. Phenol output, too, is well up.

The light metals—aluminum, magnesium, and their alloys—attain imposing proportions for postwar uses. Output of aluminum is up nearly twelvefold and of magnesium, more than a hundred fold. This increased availability, coupled with widespread experience in fabricating these metals and new methods developed for the purpose, clearly indicate their importance in the future. Mobile equipment of all kinds, air, rail, and highway, gain advantages from light metals that offset their high cost as compared with ferrous alloys. Many enthusiasts are led to predict the gradual replacement of steel as a structural metal by magnesium and aluminum. Perhaps that may come some day. Stiff competition with alloy steels of great strength and a comparable weight-strength ratio must be overcome first. Meanwhile, even the most cursory comparison of production figures shows the light metals so far to be only a little more than one per cent of steel output.

One interesting development stemming from huge magnesium production is a revaluation of compounds of magnesium for purposes now served by sodium salts. Its consequences are still not clear but it has possibilities worth watching.

**DRAIN ON RESOURCES.** Tremendous drains to meet war's demands threaten serious depletion, if not actual extinction, of several vital natural resources. Particular attention has been focused on petroleum. Rates of withdrawal of oil have reached unprecedented proportions, and discovery of new deposits lags far behind. This problem is now the subject of bitter controversy between those who fear early exhaustion of petroleum and others who see continuing expansion of our need for oil. In this, as in all similar controversies, the truth lies somewhere between the extremes. Present known oil reserves in the United States are admitted to have a finite life. Perhaps it is twelve years as some estimates state, but more likely it is some longer period. Furthermore, our natural gas reserves are about equal in tonnage to those of liquid oil, and modern petroleum technology can utilize the hydrocarbons of natural gas in many of its most important processes quite as well as, if not better than, liquid petroleum. Moreover, limitations of a war economy prevent the vigorous prospecting that will undoubtedly discover new oil pools when peace permits. Meanwhile, improved techniques of utilizing oil shale and coal as sources of liquid hydrocarbons promise effective relief from any contemplated shortage of petroleum before it can reach famine proportions. Those taking a gloomy view see in the obvious and imminent necessity for the importation of oil a serious weakening of our national position and a direct threat to our self-sufficiency.

Mineral deposits are undergoing similar, alarming depletion. The new enormous demands for aluminum threaten early exhaustion of our meager bauxite deposits, not yet offset by an economical method of using aluminous clays. Iron ores of the highest quality are being consumed at stupendous rates threatening an early progressive shift to less desirable ores which, fortunately, exist in abundance inversely proportioned to their quality. Copper ores are being similarly depleted with the prospect that copper prices may be forced upward to permanently higher levels as smelting costs inevitably rise. Similar situations exist with respect to lead and zinc.

These threats to the metallic resources of the United States (even of the Western Hemisphere) suggest re-examining the basic structure of our world and steering the course of our future planning to conform. Estimates place the composition of the earth's crust as shown in the table which follows.



Oxygen	46.43%
Silicon	27.77
Aluminum	8.14
Iron	5.12
Calcium	3.63
Sodium	2.85
Potassium	2.60
Magnesium	2.09
Titanium	0.63
Eighty-three elements	0.74
	<hr/> 100.00

Obviously, then, aluminum, iron, and magnesium, the only truly abundant structural metals, may be expected in the long range future to be our principal reliances for metallics. Methods of recovering aluminum from clays and iron from low grade ores must be developed to practical applicability against this need. Magnesium is already extracted practically from sea water, containing 0.13 per cent of the metal, and from plentiful dolomite. Each of these three metals will continue to occupy key positions in our long range economy to the progressive exclusion of others. The interplay among the three is unlikely to have more than temporary consequences since all are necessarily permanently useful.

#### SIGNPOSTS FOR THE FUTURE

**MILITARY DEMANDS.** Already changes in military demands provide a foretaste of the future. Ammonium nitrate, originally produced in huge quantities for inclusion with TNT in aerial bombs has become military surplus through the development of more useful explosives. The excess finds ready outlet in fertilizer. Magnesium production at times has exceeded capacities of fabricating plants and hence is being stored in ingots to meet any possible emergency demands or, failing that, to provide a stock pile for peace use. Production of smokeless powder and of TNT has had to be curtailed to prevent accumulation of stocks, the surplus resulting from both unexpectedly high efficiencies in output above original plans and failure of demand to reach originally projected figures.

**AVIATION.** Complete conquest of the air as the universal highway throughout the world easily tops other accomplishments pushed to fruition by war's necessities. Training of youth in the techniques of flight and incomparably efficient planes for global travel and transport guarantee a secure place for aviation in our future. To make aviation ultimately useful tens of thousands of landing fields must be constructed in this country alone. These will dot the landscape in profusion approaching that of present railroad stations and bus terminals. Their construction will require vast amounts of materials for paving, for buildings and for essential services. Added to these requirements will be further demands for materials of construction for planes themselves in immense numbers. Our demand for aviation fuel, too, is likely to tax facilities available at the war's end, great though these be.

**SYNTHETICS.** Production of butadiene and styrene in the huge quantities required by our synthetic rubber program and lesser amounts of acrylonitrile for the same reason puts these compounds into an entirely new class economically. The effects and meaning of this outside the rubber field can be roughly judged when it is realized that, of the three, only styrene has been used to any considerable extent before. Obviously, substantial reduction in its cost and greater availability will encourage development of polystyrene resins among other derivatives. No such outlets for butadiene and acrylonitrile exist ready made, but their new cheapness will encourage exploration of their possibilities since both possess highly reactive chemical structures.

**FORMALDEHYDE FAMILY.** Somewhat similar conditions exist with respect to formaldehyde and two of its derivatives, pentaerythritol and hexamethylene tetramine. Here, obviously, all three compounds are familiar and have been available to meet

ordinary needs of industry. However, formaldehyde production has soared to new high levels in meeting military requirements. The usual production reaction, oxidation of methanol, has been supplemented by direct oxidation of methane to give a huge combined output. Three principal operations have consumed formaldehyde: resin production (phenolic, urea, and melamine), pentaerythritol, and hexamethylene tetramine. The two last named yield important military explosives as end products, which accounts for their greatly increased production.

Pentaerythritol,  $C(CH_2OH)_4$ , is a reactive tetra-alcohol which readily combines with fatty acids to form esters of remarkable properties. Esters of fatty acids of drying oils possess enhanced drying and polymerizing properties, and the alcohol itself enters an important family of alkyd resins. Undoubtedly other valuable derivatives and uses for this compound will follow its widened availability.

Hexamethylene tetramine, already useful in rubber and plastics technology, has proved valuable as an intermediate in making a new powerful explosive. Details are not available, but this seems reason enough to investigate and revalue this compound as a possible new base for synthesis.

**OTHER SYNTHETICS.** Similar advances put a host of other compounds into new economic classes. Butylene glycols (1,3- and 2,3-) will join ethylene and propylene glycols as available raw materials. Glycerol synthesized from petroleum and recovered from distillery slops will be newly plentiful; so, too, will the growing family of nitroparaffins and their derivatives. The huge demand in condensed army rations for vitamins, both concentrated from natural sources and synthesized, has stimulated active search for new and better syntheses both of finished vitamins and the intermediates required in their synthesis.

Other synthetics whose development war has stimulated include the sulfonamide drugs, surface active agents, exchange resins, and a number of solvents.

**CHLORINE.** The apparent postwar abundance of chlorine suggests naturally the return of chlorinated solvents for broadened general use and wider adoption of this powerful oxidizing agent in the treatment of water supplies and the disposal of sewage. Further enlargement of the production of bleached sulfate pulp is also likely. These developments of prewar applications loom large in comparison with the increasing use of chlorine as a powerful tool in chemical synthesis. In this respect prophecy of the directions of development is extremely hazardous. Already vinyl and vinylidene resins require important quantities of chlorine and the Thiokol and Neoprene families of synthetic rubbers consume other substantial quantities. Beyond these, however, lie many synthetic reactions in which chlorine is useful and these seem likely to become more and more important when supplies of the gas are freely available.

Potassium, remembered as one of the grievous shortages of World War I, causes no concern in this conflict, thanks to the availability of the huge deposits in our own Southwest.

#### AGRICULTURE

**FERTILIZERS.** Vital developments in fertilizers already under way point to revolutionary advances in agriculture. Under pressure of war, concentration of plant food in mixed fertilizers has been forced upward. While this has been accomplished largely by discontinuing the most dilute mixtures, it opens the way for wider use of really concentrated fertilizers. One development now watched with special interest would use water instead of sand or marl as the diluent. Farmers would purchase highly concentrated mixtures of water-soluble salts and apply them to the soil in water solution by spraying rather than by broadcasting powdery solid material as at present. Cheap anhydrous ammonia (some expect a price as low as 2 cents per pound in primary markets) and its immediate deriva-



tives, together with calcium metaphosphate and readily soluble potassium compounds, figure prominently in this prospect. New importance, too, attaches to trace elements essential to plants.

Plant hormones and growth-promoting synthetics appear prominent in the postwar picture. Modification of varieties, production of seedless fruits by artificial pollination, acceleration of growth, and holding of ripening fruit on the tree at will are among the obvious expectations from wider use of these synthetics.

Improved protection of crops from insect pests by less toxic synthetic insecticides seems reasonably sure. The techniques of applying insecticides promoted by war—the aerosols and synergistic additions, for example—suggest greater efficiency in the postwar use of many insecticides and indicate clearly the possibilities of further development.

**ANIMAL PROBLEMS.** Stock raisers, no less than planters, will profit from wartime developments. Huge demands for meat drew special attention of stockmen and veterinarians to diseases causing large losses of animals. Phenothiazine for controlling internal parasites and sulfaguanidine as a remedy for intestinal infections have proved widely valuable. Tetraethylthiuram monosulfide has also proved efficacious as a veterinary remedy in coccidiosis.

The problem of feeding farm animals has undergone important changes with the wider use of proteins from soybeans and other vegetable sources replacing fish meal and tankage in feeds. Defluorinated phosphate rock supplies this essential element lacking in vegetable protein.

Skim milk, always heretofore important as a feed, now is dried for human consumption. This leaves a deficiency of riboflavin, particularly, to be made up in animal feeds by concentrates of this essential vitamin from other sources, especially the slops from fermentation operations.

#### NUTRITION AND HEALTH

Human nutrition has received important impetus under the compulsions of war. Fortification of foods with synthetic vitamins and concentrates of those from natural sources has become the rule rather than the exception. High-vitamin yeasts and others possessing specially valuable proteins will be used in increasing amounts in our future dietary, for the basic reason that yeasts readily consume inorganic nitrogen compounds and convert them to protein much more quickly than crop plants do. A variety of flavors characterize yeasts of different families, and possibilities of introducing them widely into human nutrition are being actively explored. Their present principal function, carrying vitamins, seems likely to be distinctly secondary to their protein content.

The whole field of food and nutrition is undergoing rapid change under the stimulus of war. Dehydration, quick freezing, and canning promise important new economies in food distribution based on improved methods now practiced. Some of these will undoubtedly have permanent effects; others will disappear when personal choice again determines markets.

Nutritional aspects of the food problem dominate prospects for the future. Restoration and fortification of the vitamin and mineral constituent of common foodstuffs have proved their value. Selection of foods to give the most wholesome diversity of amino acids and the addition to normal diets of foodstuffs hitherto considered exotic seem likely to have profound effects on future public health.

Chemotherapy, affecting both man and animals, has risen to spectacular heights in the war years. Sulfonamide drugs, by the miracles they have performed among the wounded, provide a new and powerful stimulus to future research in this field. No one can foresee the ultimate effects of research now in active progress seeking new weapons against disease.

Penicillin promises much that can yet be but dimly seen in the future. When its chemical constitution is unraveled, it will

probably provide clues to other compounds with important potentialities.

Facility in handling human blood plasma to the battlefields promises other useful consequences in handling a variety of delicate biological materials essential in medicine. Blood protein and pectin in shock therapy stem from the dried human plasma technique and have important implications.

#### PROGRESS IN TEXTILES, COATINGS, AND PLASTICS

In textiles, new treatments for fibers and fabrics greatly increase their values. Synthetic resin applications minimize initial shrinkage in cotton goods and give woolen fabrics a dimensional stability to ordinary washing hitherto unattainable. Wool-like fibers made from casein and soybean protein are proving useful additions to our list of textile raw materials. Progress in imparting water repellence, flame resistance, insect repellence, and mildew-proofing to fabrics has been enormous during and immediately preceding the war. Indeed, a leading authority on textiles states that war developments represent "more than had been accomplished in the whole space of time up to the breaking out of the war". Other new developments important in textiles include crease-proofing, improved wetting-out materials and penetrants, and new textile printing techniques using pigments instead of soluble dyes.

Protective coating developments include a number of new alkyds of improved properties, semisynthetic and modified drying oils noted above, and the remarkably useful new water emulsion paints based on quick drying alkyds. These last already serve important purposes in painting porous surfaces and seem likely to enter other fields as the technique of their manufacture is further developed. They are remarkable as requiring a minimum of organic solvent or none at all, yet they yield films in all respects comparable with customary paints.

Synthetic resins and their plastics show enormous expansion and development during war years. Much has been accomplished in applying plastics to a variety of problems, and in this way public attention has been strongly drawn to these useful materials. The comparatively small prewar plastics industry appears as a significant young giant of tomorrow.

Opportunity for this phenomenal growth came from stringent limitations of metals and other customary materials for which the versatility of plastics allowed them to substitute. Other applications utilize special values in certain plastics to do specific jobs. In the first category are molded plastic parts to replace aluminum in washing machines and of molded plastic buttons for military uniforms to conserve brass. In the second are the expanding use of plastic-bonded plywood for construction and boat building, of melamine plastics in electrical applications, and of transparent acrylic resins in the construction of airplanes. Most of the materials and even the techniques employed were already familiar before war came, requiring only adaptation and modification to new needs. Much that has been accomplished is, however, still restricted information not yet available for publication, particularly where novelty is involved.

Among the greatly improved properties now available in resins are heightened impact strength, enhanced resistance to abrasion, lowered power factor, greater resistance to arcing, and negligible water absorption. Molding techniques, particularly in the preparation of the molds themselves, have undergone changes adapting them to quantity production at speeds far greater than any previously required.

Plywood developments require special attention since they appear promising in the prefabrication of dwellings and other units larger than could be reasonably molded before the war. Adoption of waterproof resins to the assembly of thin wood veneer sheets into units of substantial area logically gave new impetus to the plywood industry, previously dependent on less resistant adhesives. The assembly of small pieces of wood into



larger units is also important. The technique of laminating plastics provided a method applying thermosetting resins to this problem, and this art has been much improved, particularly as to speed, by the recent growing use of high-frequency electric heating. Examples of the substantial development of plywood techniques are the PT boats, swift torpedo-carrying motor craft built of plywood, "mosquito" bombers whose principal structure is formed of plywood, and aviation hangars and other structures assembled of plywood sheets. The latter are so designed that they can be disassembled and their parts used for other construction when their present usefulness is over.

#### PETROLEUM PROGRESS

Advances in petroleum technology, already mentioned, promise immense usefulness in peace. This art is moving swiftly even in war and is difficult to summarize on that account. Catalytic methods have developed both in the form, nature, and effect of the catalyst and in the engineering aspects of its application. The so-called Fluid Catalyst technique (employing a finely divided powder carried about in a gas stream as practically a fluid) promises important applications in other field requiring heat transfer.

Equally significant among petroleum developments is the accuracy with which fractionation can separate individual hydrocarbons from mixtures. This technique is based on accumulated knowledge of the properties of hydrocarbons and experience in applying it to practical problems. Time has been required to gain these advantages, and fortunately a secure basis for progress existed when war imposed extraordinary demands on the petroleum industry. The result is the ready availability of new hydrocarbon raw materials in abundance and variety.

Nitration of paraffins, well under way before war came, has grown lustily in importance as the products of the reaction have found useful applications in industry. Rapid expansion in this field suggests the value inherent in further development of hydrocarbon chemistry in other directions, possible now that pure raw materials are abundant.

#### CONCLUSION

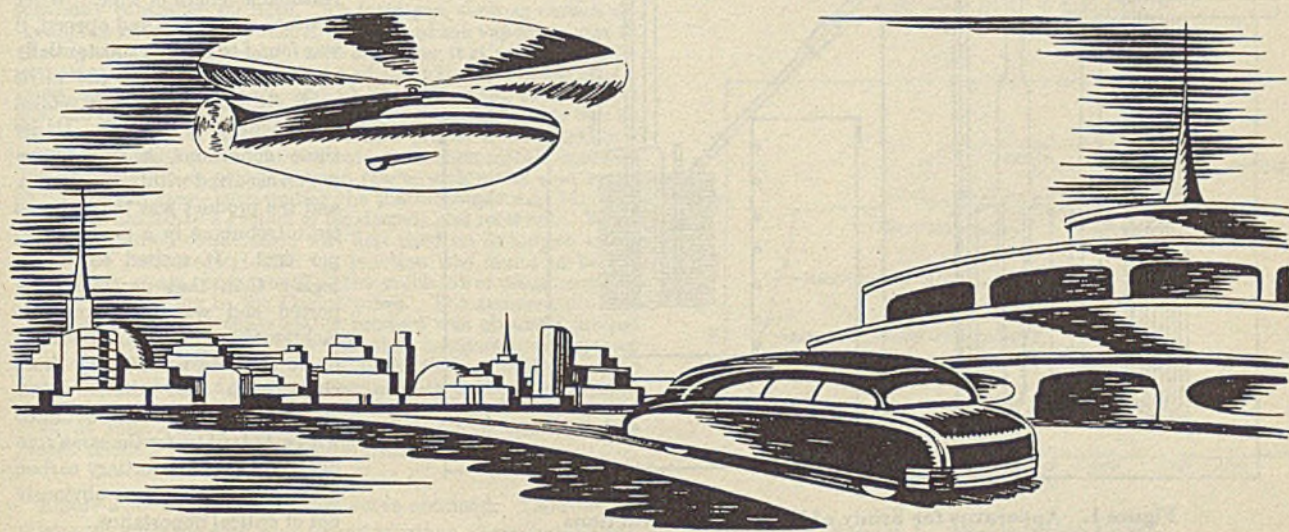
Thus briefly are suggested some of the major developments extending from now forward. The whole is impressive. Indeed, the opportunities for the future become positively overwhelming when to these potentialities which can now be discussed are added countless others still hidden behind censorship. Finally,

it is worth-while to take another quick glance at two of the overall questions whose answers must be found.

For reasons not readily apparent, Senate Bill S702 states in effect that American science and technology need permanent regimentation. This seems strange, even to the point of being nonsense, to anyone familiar in the least degree with recent events. Cooperation between science and the industries based upon it has performed miracles in past months. Yet no czar has forced this. Cooperation has been entirely voluntary and has not lacked the stimulus of competitive rivalry between the several groups involved. How that situation can be improved by legislation creating a bureaucratic director to manage the whole is far from clear. But a serious threat to initiative hangs over both science and industry in this proposal of new and apparently useless bureaucratic control.

Also probable in the days to come is a reopening of the question of protection for certain phases of chemical production against ruinous competition from others. The basic situation on this question is decidedly different from that of a quarter century ago, yet it is made up of precisely the same elements. German commercial strategy is identical with German military methods. Espionage, fifth column, concentration of force on limited objectives, and the use of propaganda are all familiar weapons of German chemical industry. Our industrial system provides no sure defense against attack based on these weapons, and our laws prohibit combinations of effort that could meet them.

Our chemical industry now possesses a roundness and a solidity which is, in general, proof against frontal assault. Its forte is quantity production and in this it has nothing to fear. However, there are in the chemical list numerous products that can be made cheaper by German methods in the small quantities required. The attack can thus be based on essential items which will be provided only if others are also sold with them. By this technique a tiny chink can be widened into a breach of the entire structure. Its success will depend solely on the ability of the Germans to find the initial chink to enlarge. Obviously, the best defense against such selective attack is to provide a complete list of products to all consumers. This will require that some chemicals be made in small quantities and actually sold at a substantial loss. No one company can properly afford to undertake more than a few such losing ventures, but for the good of all, potential cracks must be closed and kept closed. Allocation of these loss items among many producers is easily possible within present legal restrictions and must form part of chemical industry's postwar planning.





# Recent Developments in

THE story of the nitroparaffins began in 1872 when Meyer and Stüber (21) reported that the reaction between isomyl iodide and silver nitrite had yielded a nitro derivative of isopentane. At that time the aromatic nitro derivatives were already of substantial importance, since mauveine had been made by Perkin sixteen years before and the aniline dye industry was in active development. Great interest was therefore aroused by this discovery, and before the end of the year Kolbe (17) had announced the production of nitromethane by reaction between sodium nitrite and sodium chloroacetate. Eight years later Beilstein and Kurbatov (2) found that cycloparaffins could be nitrated in the liquid phase. A petroleum fraction, boiling at 95–100° C., had a density between that of a paraffin and a cycloparaffin of seven carbon atoms, and selective nitration was used in a successful effort to purify it from naphthenic components. The nitro derivative boiled for the most part from 193° to 197° C. and had a composition corresponding to the formula  $C_7H_{14}NO_2$ . On the basis of present knowledge it must have been a mixture of nitroheptanes. The next two decades witnessed many efforts to find a practical way in which the nitration reaction might be carried out, but it was concluded that reactions were slow and accompanied by oxidation; the result was low yields so that between 1900 and 1930 relatively little work was done in this field.

As part of the general research program at Purdue on the chemical utilization of the hydrocarbons of natural gas and petroleum, it was decided to investigate the nitration of isobutane since this

The vapor-phase nitration reaction, starting from the cheapest of all pure organic compounds, the hydrocarbons of petroleum and natural gas, gives rise through relatively simple reaction sequences to the following classes of compounds: mononitroparaffins, dinitroparaffins, amines, diamines, alkyhydroxylamines, oximes, hydroxamic acids, carboxylic acids, aldehydes, ketones, halogenated nitro compounds, nitroalcohols, nitroglycols, nitroalkanetriols, organic esters of the three preceding types, inorganic esters (nitrates, phosphates), aminoalcohols, aminoglycols, aminoalkanetriols, aminoacetals, soaps of the four preceding types, nitro-olefins, and nitroketones. In 1935 an agreement was reached between Purdue Research Foundation and Commercial Solvents Corporation

reaction had not previously been reported. The reasons for this decision were that this hydrocarbon, with its nine primary hydrogen atoms and single tertiary one, was expected to give good yields of mononitro derivative since previous investigators had been almost unanimous in stating that the nitration reaction showed a marked preference for tertiary carbon atoms; also, the boiling point of tertiary nitrobutane is very close to that of butyl

acetate and both Fischer (9) and Hopkins (15, 16) had reported nitroparaffins to be solvents for cellulose nitrate. A recent paper (11) includes an extensive bibliography on previous work in this field.

After a graduate student had been persuaded that this was a promising research problem, isobutane and nitric acid were sealed in a Carius tube and heated to 115° C., a temperature widely recommended for this type of nitration, for what seemed to be a reasonable length of time. When the tube was cooled and opened, it was found to contain substantially nothing but isobutane and nitric acid. It was consequently refilled and brought to 150° C. Under these conditions, a smooth reaction occurred within 15 minutes, and the product was the expected *tert*-nitrobutane in a purity of 99 per cent. It melted somewhat higher than that previously reported and was free from the lachrymatory effects of a sample made by Bevad (4, 5) from chloropierin and dimethylzinc. Equally good results were obtained with *n*-butane under the same conditions so that the tertiary carbon atom of isobutane was obviously not of critical importance.

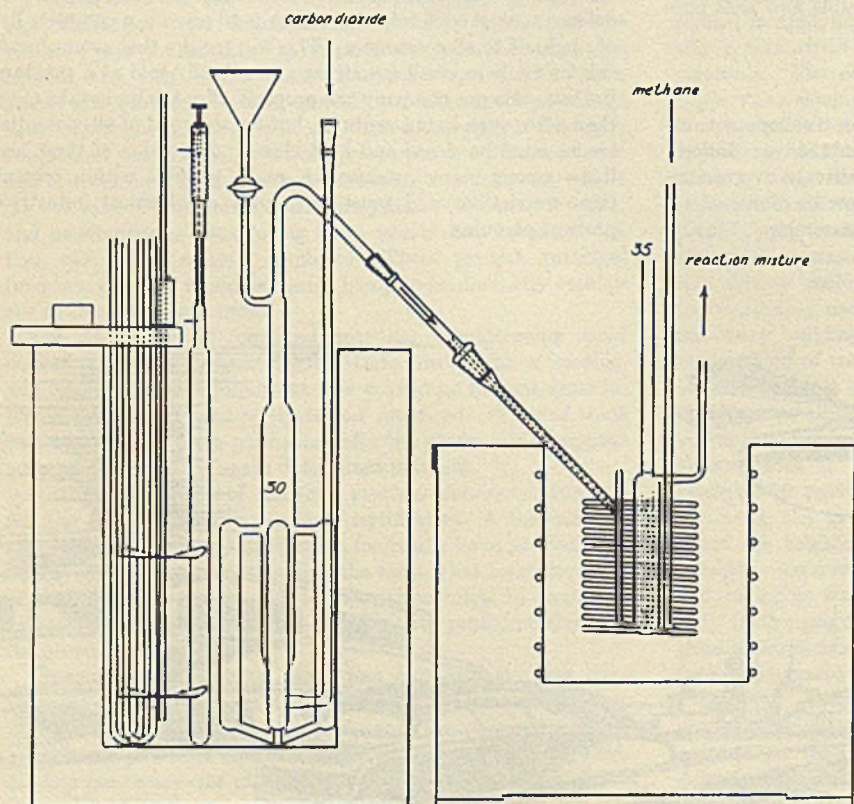


Figure 1. Apparatus for Study of Vapor-Phase Reactions



# NITROPARAFFINS

H. B. Hass

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by which the latter assumed the responsibility for putting these processes into commercial operation. This intelligent gambling on a new and untried process is representative of the free enterprise system at its best. Since vapor-phase nitration represented a wholly new technique, delays inevitably occurred while development problems were being discovered and solved. In May, 1940, the first commercial-scale production of nitroparaffins occurred. Upon termination of hostilities, when the enormously augmented facilities for the production of nitric acid will no longer be required for the manufacture of large quantities of trinitrotoluene, the consumption of nitroparaffins will be limited only by their inherent capabilities and the ingenuity of American chemists.

At this stage of the development the Purdue Research Foundation, which has been established for the purpose of facilitating relations between industry and the university, signed a fellowship agreement with one of the petroleum companies; its purpose was to study the preparation and properties of the nitroparaffins so as to determine whether they appeared to have potential uses. Since the runs in the Carius tubes developed about one gram of nitroparaffin each, it was necessary to find a more rapid means of obtaining materials with which to work. A stainless steel bomb was thereupon ordered which required three months to arrive. Since monthly progress reports are submitted in all work of the foundation, it was necessary to devise some other form of apparatus to be used in the interim. It was suddenly realized that, since the critical temperature of isobutane is 134° C., reaction in the Carius tube at 150° C. had presumably occurred in the vapor phase.

THE flow method has great advantages in the study of the vapor-phase reactions, and an apparatus was constructed similar in principle to that shown in Figure 1:

Azeotropic nitric acid (67 per cent HNO<sub>3</sub>) is contained in vaporizer 30, which is placed in a stirred, electrically heated, thermostatically controlled oil bath. An inert gas, such as carbon dioxide, can be introduced near the bottom of the vaporizer, and in passing up through the nitric acid the latter is stirred. This, together with the large surface area of the vaporizer, maintains a fairly uniform temperature, and by controlling the flow of inert gas, the rate at which nitric acid vapor enters the reactor can be held at any desired figure. The reactor proper is immersed in a salt bath consisting of sodium nitrate-potassium nitrate eutectic. The hydrocarbon is preheated and reacts with nitric acid vapor in the annular space surrounding the thermocouple well 35. The exit gases are led to a system of condensers and receivers. When the flow method of nitration was first used on isobutane at atmospheric pressure and 150° C., reaction was found to be too slow. This was a consequence of the much lower concentrations than those existing in the Carius tubes. The temperature was therefore raised and considerable product was obtained around 300° C. It was ultimately found that temperatures between 400° and 500° C. give best yields under these conditions. The product now obtained bore little resemblance to the pure, crystalline *tert*-nitrobutane. It was a liquid which failed to solidify even at solid carbon dioxide temperature and was therefore placed under a rectifying column for distillation.

Figure 2 shows the rectification curve obtained. The research originated with the idea that *tert*-nitrobutane (2-methyl-2-nitro-

propane) would be virtually the sole reaction product. It constitutes here about 3 per cent. 2-Methyl-1-nitropropane, which, we were certain, would not be formed in any considerable quantity because the reaction producing it involves replacement of a primary hydrogen atom, is now the principal product, and there is a substantial amount of 2-nitropropane and more than a trace of nitromethane. The presence of 2-nitropropane in the reaction products was so incredible that it was confirmed by a quantitative, elementary analysis. The purity of the isobutane was suspected but was checked by rectification. We are evidently dealing here with a reaction causing fission of a carbon-carbon linkage. Much research has established as generalizations, valid in all instances so far, the following three simple rules in high-temperature, vapor-phase nitration at relatively low pressures:

1. Polynitroparaffins are not formed unless paraffins of rather high molecular weight are used.
2. Any hydrogen atom in the hydrocarbon molecule may be replaced by a nitro group.
3. Any alkyl group present in the hydrocarbon may be replaced by a nitro group.

Thus, isopentane yields the following nine nitroparaffins: nitromethane, nitroethane, 2-nitropropane, 2-methyl-1-nitropropane, 2-nitrobutane, 2-methyl-2-nitrobutane, 3-methyl-2-nitrobutane, 2-methyl-1-nitrobutane, 3-methyl-1-nitrobutane. The mechanism by which this occurs is still undecided. Originally it was believed that free radicals were involved, but this fails to explain how ethane can yield a product consisting of 27 per cent nitromethane and 73 per cent nitroethane. The ethyl radical does not decompose into any compound containing only a single carbon atom. Ewell (8) proposed the addition complex mechanism,

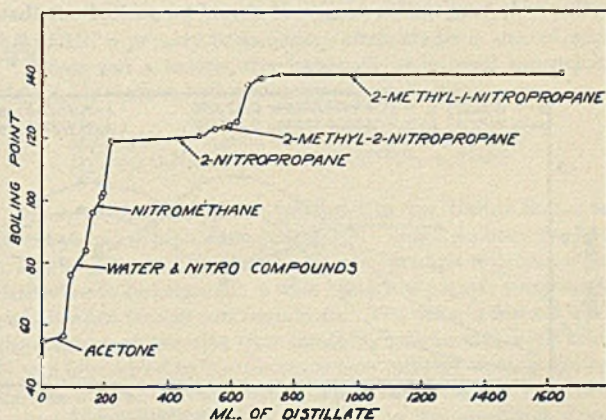
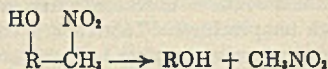
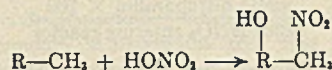


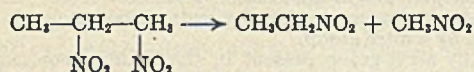
Figure 2. Rectification Curve



TABLE I. PHYSICAL PROPERTIES OF NITROPARAFFINS

	Nitro- methane	Nitro- ethane	1-Nitropro- pane	2-Nitropro- pane
Formula	CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> - CH <sub>2</sub> NO <sub>2</sub>	CH <sub>3</sub> - CHNO <sub>2</sub> CH <sub>3</sub>
Mol. weight	61.04	75.07	89.09	89.09
Sp. gr. at 20/20° C.	1.139	1.052	1.003	0.992
Lb. per U. S. gal. at 20° C.	9.48	8.75	8.35	8.24
Melting point, ° C.	-29	-90	-108	-93
Boiling point, ° C.	101.2	114.0	131.6	120.3
Flash point, ° F. (Tag open cup)	112	106	120	103
Vapor pressure, at 20° C., mm.	27.8	15.6	7.5	12.9
Surface tension at 20° C., dynes/cm.	37.0	31.3	30.0	30.0
Refractive index at 20° C.	1.3818	1.3916	1.4015	1.3941
pH of 0.01 M aqueous soln. at 25° C.	6.4	6.0	6.0	6.2
Rate of evapn., by wt. (n- butyl acetate = 100)	180	145	100	124
Solubility at 20° C.				
Ml. solvent/100 ml. water	9.5	4.5	1.4	1.7
Ml. water/100 ml. solvent	2.2	0.9	0.5	0.6

which would result in the formation of a mole of alcohol for each mole of nitroparaffin containing fewer carbon atoms than the hydrocarbon flowing to the reactor. While this mechanism is not excluded, the quantity of alcohols and their oxidation and decomposition products is less than that which would correspond to the nitroparaffins resulting from fission. Perhaps an addition complex is formed between nitrogen tetroxide and a paraffin, resulting in the formation of two moles of nitroparaffins directly:



This subject is still under active investigation.

FIGURE 3 shows a series of curves obtained in the nitration of methane, using four reactors of different volumes and various reaction temperatures. The upper of each pair of curves represents yield,

$$\frac{\text{moles nitroparaffin} \times 100}{\text{moles HNO}_3 \text{ consumed in reactor}}$$

i. e., it is corrected for unchanged nitric acid in the product. The lower curve represents conversion,

$$\frac{\text{moles nitroparaffin} \times 100}{\text{moles HNO}_3 \text{ entering reactor}}$$

The two curves approach one another as the temperature increases because the amount of unreacted nitric acid approaches zero at these high temperatures. There is a maximum point in each curve which represents a perfect balance between exposure time and temperature. A smooth curve connecting these maxima represents a matching of exposure time and temperature over a rather wide temperature range. It should be pointed out that,

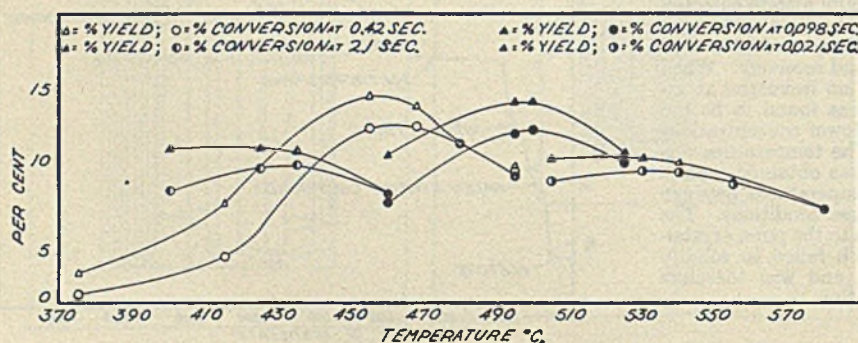


Figure 3. Curves Obtained in Nitration of Methane

even after correcting for unchanged nitric acid, yields are better at fairly high temperatures. This is because the nitration reaction has the rather high activation energy of 51 kg.-cal. It is therefore preferentially accelerated by an increase in temperature. The principal competing reaction is oxidation of the hydrocarbon and of the nitroparaffin by nitric acid. In this reduction the nitric acid forms very little elementary nitrogen but leaves the reactor in the form of nitric oxide. In the commercial plant this material is recycled back to nitric acid so that it is possible to obtain 60-90 moles of nitroparaffin from 100 moles of nitric acid purchased. If the yield of nitroparaffin is plotted against mole ratio of hydrocarbon over nitric acid, a curve is obtained which approaches asymptotically a yield of 40 per cent. The curve does not extrapolate to 100 per cent yield of nitroparaffin at infinite excess of hydrocarbon. This was taken to mean that nitric acid or its decomposition products are attacking the hydrocarbon and not merely oxidizing the nitroparaffin as had been reported to be the case in liquid-phase nitration. This conclusion was confirmed when the operation of the pilot plant provided large quantities of the aqueous layer of the product for detailed analysis. The nitration of propane, in addition to furnishing the first four nitroparaffins, yields minor quantities of such products as 1-propanol and 2-propanol, presumably by oxidation of the hydrocarbon.

Some of the physical properties of the nitroparaffins are shown in Table I. They differ markedly from their aromatic analogs, (a) in being colorless rather than yellow, (b) in having a relatively low toxicity, approximately that of gasoline of similar volatility, and (c) in having a characteristic, mild odor quite unlike that of nitrobenzene.

The idea that *tert*-nitrobutane might be a valuable solvent for cellulose esters developed somewhat unexpectedly. Figure 4 shows that it has a dilution ratio against toluene of only 0.5. There are certain analogies, however, between the nitroparaffins and the ethers. Thus, both of these classes of compounds are capable of furnishing oxygen atoms as donors for hydrogen bridges. The powerful solvent action on cellulose nitrate of mixtures of alcohols and ethers and of compounds containing these functional groups led to a trial of mixtures of alcohols and nitroparaffins. These are likewise powerful solvents for cellulose nitrate and also for cellulose acetate, cellulose triacetate, cellulose acetate-propionate and acetate-butyrate. Mixed solvents containing nitroparaffins are the preferred ones likewise for Vinylite resins. One of the principal outlets of nitroparaffins at the present time is in the fabrication of raincoats for the United States Army, using Vinylite resin.

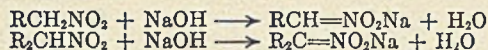
THE interest in the nitroparaffins, however, centers principally, not around their physical properties, but in the multiplicity and variety of reactions to which they lend themselves. When a primary, secondary, or tertiary nitroparaffin is reduced with hydrogen in the presence of Raney nickel, a primary amine is obtained in yields of 90-100 per cent. The temperature used is that of the room although the exothermic reaction carries it somewhat higher. Any convenient tank pressure is suitable; naturally, higher pressures give faster reactions. If an Adkins

even after correcting for unchanged nitric acid, yields are better at fairly high temperatures. This is because the nitration reaction has the rather high activation energy of 51 kg.-cal. It is therefore preferentially accelerated by an increase in temperature. The principal competing reaction is oxidation of the hydrocarbon and of the nitroparaffin by nitric acid. In this reduction the nitric acid forms very little elementary nitrogen but leaves the reactor in the form of nitric oxide. In the commercial plant this material is recycled back to nitric acid so that it is possible to obtain 60-90 moles of nitroparaffin from 100 moles of nitric acid purchased. If the yield of nitroparaffin is plotted against mole ratio of hydrocarbon over nitric acid, a curve is obtained which approaches asymptotically a yield of 40 per cent. The curve does not extrapolate to 100 per cent yield of nitroparaffin at infinite excess of hydrocarbon. This was taken to mean that nitric acid or its decomposition products are attacking the hydrocarbon and not merely oxidizing the nitroparaffin as had been reported to be the case in liquid-phase nitration. This conclusion was confirmed when the operation of the pilot plant provided large quantities of the aqueous layer of the product for detailed analysis. The nitration of propane, in addition to furnishing the first four nitroparaffins, yields minor quantities of such products as 1-propanol and 2-propanol, presumably by oxidation of the hydrocarbon.

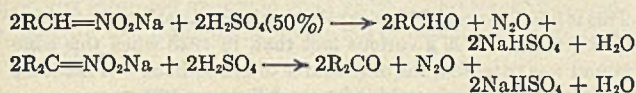


reductor is not available, approximately the same yields can be obtained by following the directions for converting nitrobenzene to aniline—namely, 40-mesh, cast iron turnings, enough water to make the mass stirrable,  $1/10$  mole of hydrochloric acid, and temperature of reflux. About 70 or 80 per cent yields of alkylhydroxylamine,  $RNHOH$ , can be obtained by electrolytic reduction with a lead cathode.

Glacial acetic acid and zinc dust will give a 40 per cent yield of aldoxime from a primary nitroparaffin and ketoxime from a secondary one but better means are available for obtaining oximes from nitroparaffins. When a primary or secondary nitroparaffin is treated with a strong, soluble base, a salt of the nitronic acid or aci-form results:

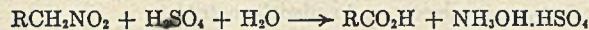


When these salts are acidified, a number of things can happen. If very low temperatures are employed, the nitronic acid is set free and tautomerizes to the nitroparaffin. If reaction is carried out at room temperature by adding the salt to an excess of 50 per cent sulfuric acid with vigorous agitation, an 85 per cent yield of aldehyde is obtained from the primary nitroparaffin and of ketone from the secondary derivative:

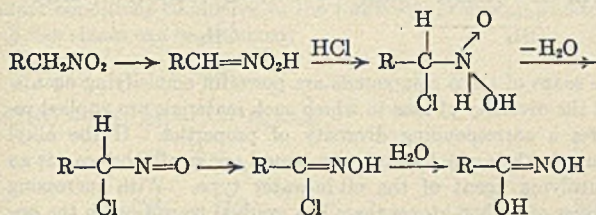


Since these yields are much better than those from the reduction of a nitroparaffin to an oxime, the latter compounds are best made by the foregoing reaction, followed by the conventional treatment with hydroxylamine.

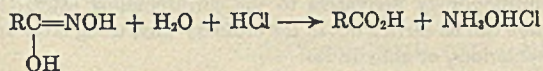
The source of the hydroxylamine is a reaction discovered by Preibisch (23) in 1873:



The following mechanism for this rather astonishing transformation is essentially that given by Nenitzescu and Isăcescu (22):



The assumption that the primary nitroparaffin will tautomerize spontaneously to the nitronic acid in the presence of strong acids is confirmed by the work of Lowry and Magson (19) on nitrocamphor where the reaction can be followed conveniently in the polarimeter. The time required for 99.5 per cent total change to proceed was as long as six years in the absence of acid or base but in the presence of 0.1 *N* trichloroacetic acid it required only 33 minutes. A strong mineral acid would be expected to add to the carbon-nitrogen double bond, the anion going to the relatively electropositive carbon and the proton adding to the nitrogen. The resulting compound would lose water, yielding a nitroso derivative containing an alpha-hydrogen. This would rearrange to the isonitroso structure which, being the acid chloride of a hydroxamic acid, would be readily hydrolyzed to the hydroxamic acid itself. Bamberger and Rust (1) obtained a 3 per cent yield of hydroxamic acid from phenylnitromethane, but Lippincott (18) in the Purdue University laboratory found that this could be increased to about 40 per cent in the case of 1-nitropropane by using 100 per cent sulfuric acid at room temperature for several days. The hydrolysis of the hydroxamic acid,



is strictly analogous to the hydrolysis of an oxime to an aldehyde or ketone and a salt of hydroxylamine. This has been the principal source of hydroxylamine in the United States for several years.

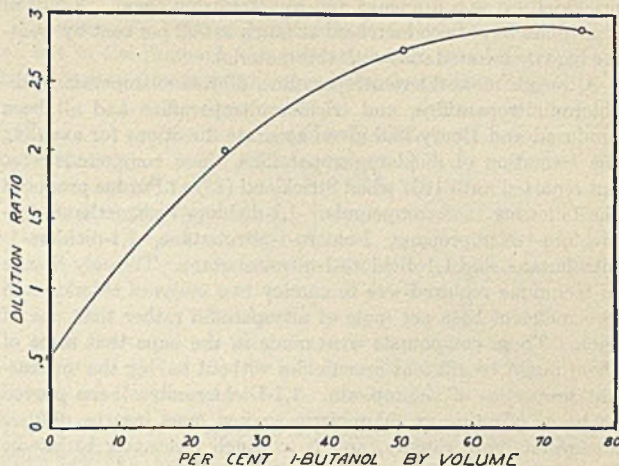
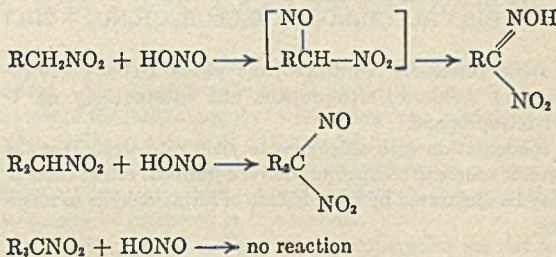


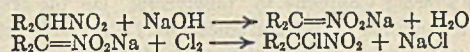
Figure 4. Dilution Ratio of *tert*-Nitrobutane against Toluene

The "red, white, and blue reaction" was discovered by Victor Meyer and his students (20) and consists essentially in treating the salt of a nitroparaffin with nitrous acid in the presence of a mineral acid:



Under these conditions primary nitroparaffins yield red nitronic acid salts, secondary nitroparaffins give blue pseudo-nitroles, while tertiary nitroparaffins fail to react. Meyer proposed that this be used as a means of distinguishing between primary, secondary, and tertiary alcohols which are converted to the iodides and then with silver nitrite to the nitroparaffins. Better methods are now available for characterizing alcohols, but this reaction is still of value in the chemistry of nitroparaffins.

**W**HEN a primary or secondary nitroparaffin is treated with base and a halogen simultaneously or in rapid succession, high yields of alpha halo derivative are produced:



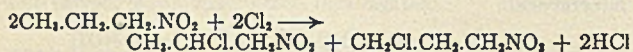
Much of the chloropicrin produced in the United States in recent years has been made in this way. This compound has had a long and interesting history. It was the first aliphatic nitro derivative to be prepared; a wide variety of organic compounds yield it when treated with aqua regia. The name is derived from the common preparation from bleaching powder and picric acid. It was introduced by the Germans as a military weapon during the war of 1914-18. In small concentrations it is a lachrymator and at higher concentrations gives rise to the physiological response which caused the U. S. Army to name it P. S. (puke stuff).



The uncomfortable position of a soldier whose gas mask will not remove chloropicrin can well be imagined. This threat was countered, however, by producing activated carbon which removes chloropicrin effectively from the air breathed by the wearer of a modern respirator. At present chloropicrin finds its principal use as a fumigant and soil-sterilizing agent. Yields of pineapples have been increased as much as 200 per cent by treating heavily infested soils with this material.

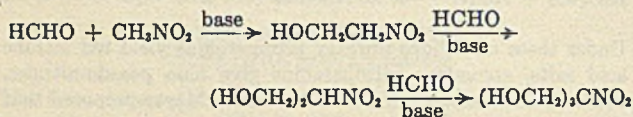
Although monochloronitroparaffins, dibromonitroparaffins, dichloronitroparaffins, and trichloronitroparaffins had all been produced and Henry had given accurate directions for avoiding the formation of dichloronitroparaffins, these compounds were not reported until 1937 when Strickland (23) at Purdue produced the following new compounds: 1,1-dichloro-1-nitroethane, 1,1-dichloro-1-nitropropane, 1-chloro-1-nitrobutane, 1,1-dichloro-1-nitrobutane, and 1,1-dichloro-1-nitroisobutane. The only change in technique required was to employ two moles of chlorine and two moles of base per mole of nitroparaffin rather than one of each. These compounds were made in the hope that some of them might be efficient insecticides without having the unpleasant properties of chloropicrin. 1,1-Dichloronitroethane proved to be as effective as chloropicrin against most insects, diffuses somewhat more rapidly, and is so much pleasanter to handle that the commercial material contains a little chloropicrin to serve as a warning agent. Its trade name is Ethide.

Riley (24), working in this laboratory under the direction of E. T. McBee, discovered conditions for obtaining chlorination of nitroparaffins on carbon atoms other than the one to which the nitro group is attached. This occurs in the absence of a base and moisture, and in the presence of phosphorus pentoxide and intense illumination:

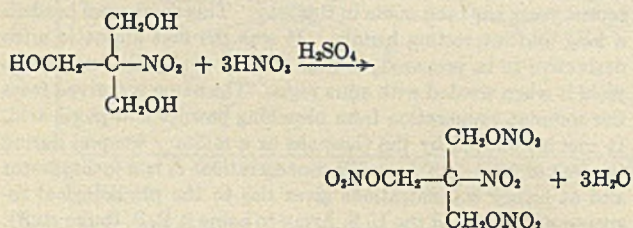


Under these conditions 1-nitropropane yields 2-chloro-1-nitropropane and 3-chloro-1-nitropropane but substantially no 1-chloro-1-nitropropane.

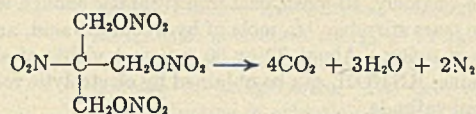
The condensation with aldehydes to yield nitroalcohols is the most prolific source of compounds derived from the nitroparaffins. This may be illustrated by the addition of formaldehyde to nitromethane,



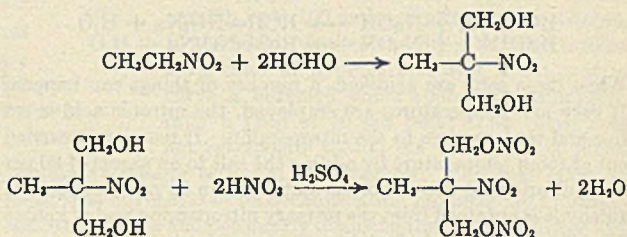
a reaction discovered by Henry (12, 13) in 1895. It is general for all primary and secondary nitroparaffins and practically all aldehydes although, with greater complexity of either reagent, it becomes increasingly difficult to replace all of the alpha hydrogen atoms of the nitroparaffin with hydroxyalkyl or substituted hydroxyalkyl groups. Henry called the end product of the reaction between formaldehyde and nitromethane "nitroisobutylglycerol". This has been abbreviated by the chemists at the Hercules Powder Company to "nibglycerol" but the systematic name is tris-hydroxymethylnitromethane. They were interested in the compound because Hofwimmer (14) in 1912 nitrated it with mixed acid to yield the nitrotrinitrate:



This compound is in perfect oxygen balance and is 7 per cent more powerful than nitroglycerin:

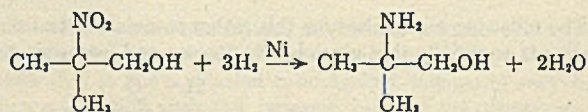


Hofwimmer stated that only the high cost of nitromethane stood in the way of its technological utilization. It is doubtful, however, whether nibglycerol trinitrate can meet modern stability requirements. Bergeim (3) in 1928 disclosed the dinitrate of 2-nitro-2-methyl-1,3-propanediol prepared by the following reactions:



This is also a powerful high explosive which has aroused considerable interest. It is a curious fact that, in 1928 when this compound was patented, the only source of nitroethane was Eastman Kodak Company who sold it for six dollars per 100 grams.

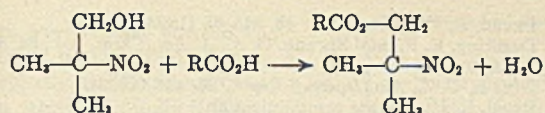
A LARGE number of nitroalcohols, nitroglycols, and nitroalkanetriols have been made in this laboratory, particularly by Vanderbilt (30) and Sprang (6), not with the idea of doing what Father Nieuwland used to call "cluttering up Beilstein", but because they are easily reduced to the corresponding aminoalcohols, aminoglycols, and aminoalkanetriols:



The soaps of these compounds are powerful emulsifying agents, and the diversity of uses to which such materials are applied requires a corresponding diversity of properties. If the alkyl groups in the aminoalcohol compound are small, the soap is an emulsifying agent of the oil-in-water type. With increasing number of carbon atoms there is a gradual transition to the opposite, water-in-oil, emulsifiers. A large variation in volatility can be obtained, depending on the number of hydroxyl groups. In the preparation of self-polishing floor waxes, it is desirable that the amine should evaporate fairly rapidly so that, if water is spilled on the floor, the wax has small tendency to re-emulsify. In the preparation of cosmetics, a volatile amine would give rise to what has sometimes facetiously been called "a mean odor" which would render the product unsalable. The multiplicity of nitroparaffins and aldehydes presents the opportunity of manufacturing a tailor-made surface-active agent for almost every conceivable purpose.

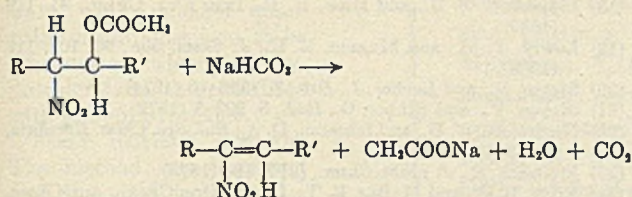
Because a plasticizer is essentially a high-boiling solvent, because mixtures of alcohols and nitroparaffins are powerful solvents for cellulose esters, and because the presence in the same molecule of a nitro and hydroxyl group gives rise to low volatility, it was hoped that the nitroalcohols would be good plasticizers. This might be true if the two functional groups were not on adjacent carbon atoms, but such compounds are somewhat unstable and tend to revert to the aldehyde and nitroparaffin from which they are synthesized. This tendency can be removed by converting the nitrohydroxy derivative to the corresponding ester. This reaction can be carried out in the ordinary way, using fatty acids, acid chlorides, or anhydrides:



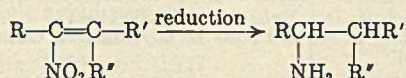


More than one hundred such compounds have been synthesized by Vanderbilt (30) and Tindall (29) and tested as plasticizing agents for cellulose esters.

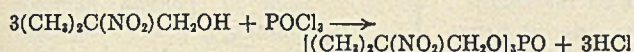
The nitro esters which still contain an active hydrogen atom are so unstable that they can be titrated at room temperature with standard alkali. This reaction was discovered by Schmidt and Rutz (25):



Two years of research were required to find suitable means for reducing the nitro-olefins obtainable by this reaction to the corresponding saturated amines in good yields. This reaction is now a powerful tool for building up amines of definite structure free from isomers:

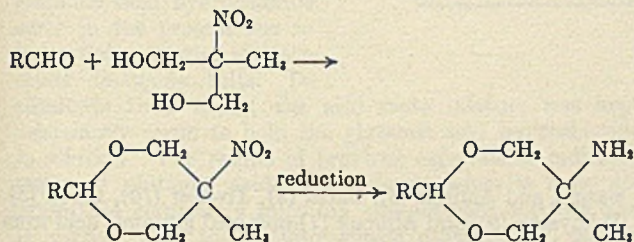


Phosphorus oxychloride yields the nitroalkyl phosphates:



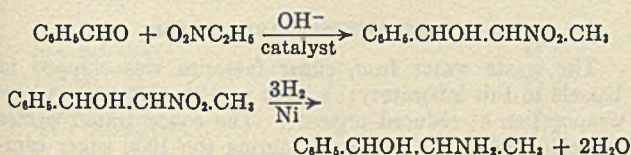
These are also plasticizers.

Senkus (27) and Robinette of the Commercial Solvents laboratory found that, when nitroglycols are treated with aldehydes under conditions conducive to the formation of acetals, 5-nitro-1,3-dioxolanes can be obtained:



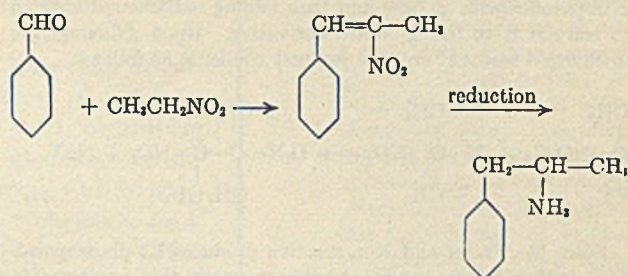
These compounds can be reduced by Raney nickel and hydrogen to the corresponding primary amines which dissolve in such materials as sulfonated castor oil to produce wetting and softening agents for textiles. These are called "instantaneous wetting agents" because in the Draves test (7) no appreciable time is required for wetting the yarn.

The condensation of aldehydes and nitroparaffins is also successful in the aromatic series so that, for example, benzaldehyde and nitroethane in the presence of a base, such as calcium hydroxide or sodium carbonate, will yield 2-nitro-1-phenyl-1-propanol which is reduced by Raney nickel and hydrogen to the corresponding amine:



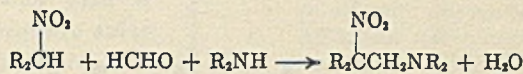
The aminoalcohol has the structural formula of propadrine but contains two asymmetric carbon atoms and differs somewhat in steric configuration. Investigations are now under way to determine the relative pharmacological merits of the two products. Propadrine is closely related to ephedrine which is the *N*-methyl derivative.

If the reaction between benzaldehyde and nitroethane is carried out in the presence of a primary amine, the product is 1-phenyl-2-nitropropene which, upon reduction, yields benzedrine:



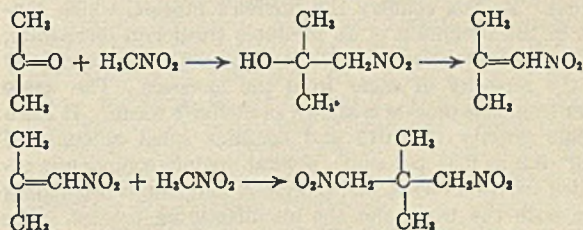
Thus in the aromatic series it is possible to produce the nitro olefins directly.

THE Mannich reaction has proved to be a fruitful source of organic compounds. It requires a compound to furnish what the organic chemist calls an "active hydrogen atom", an aldehyde, and ammonia or an amine. The alpha-hydrogen atoms of the nitroparaffin react as follows:



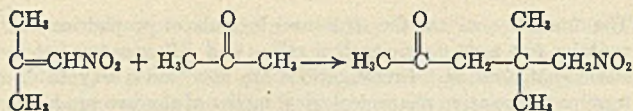
The nitroamines so obtained are capable of being reduced to diamines. These compounds are of particular interest at present in view of the large amount of work being done in various laboratories on the synthesis of antimalarial drugs. Most such compounds consist of a heterocyclic nucleus to which a diamine side chain has been attached. A wide variety of diamines of many classes can be produced in this manner.

It was pointed out earlier that dinitroparaffins are not formed in the vapor-phase reaction under the conditions employed. If these compounds are desired, they must therefore be synthesized by some one of a number of indirect methods. One of these is the addition of nitrogen tetroxide to olefinic double bonds, another is the reaction between nitromethane and ketones reported by Fraser and Kon (10) in 1934. This is believed to occur in the following manner, using acetone and nitromethane as examples:



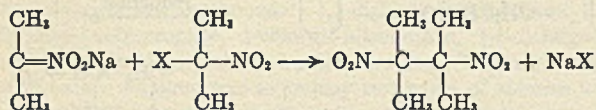
1-Nitro-2-methyl-2-propanol is unknown, the nitration of 2-methyl-2-propanol yielding 1-nitro-2-methylpropene by spontaneous elimination of water. Separate experiments showed (a) that 1-nitro-2-methylpropene is present in the reaction mixtures and (b) that it condenses with nitromethane to yield dinitro-neopentane. An important by-product of this reaction, not reported by Fraser and Kon, is 4,4-dimethyl-5-nitro-2-pentanone formed presumably by the addition of acetone to 1-nitro-2-methylpropene:





By increasing the ratio of acetone to nitromethane, the nitroketone can be made the principal reaction product.

Still another method of obtaining dinitroparaffins, discovered by Seigle (26) in this laboratory, consists in treating a secondary nitroparaffin with a base and then adding half enough halogen to convert it to the halonitro derivative. Upon refluxing, the unchanged reactant and the product condense as follows:



Since the Fraser and Kon reaction produces 1,3-dinitroparaffins, both nitro groups being primary, while this condensation gives two tertiary nitro groups on adjacent carbon atoms, the two methods supplement each other.

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# Glutamic Acid Content of STEFFEN'S WASTE

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IN THE manufacture of beet sugar after the sugar is secured by extraction, concentration, and crystallization, the mother liquor or molasses contains about 50 per cent sucrose. In this country the Steffen's process, which consists in the formation of an insoluble tricalcium saccharate, and its decomposition to sugar (4) has been used successfully for the recovery of sugar from the molasses. The waste water from this process is known as Steffen's waste. It has a specific gravity of 1.015 and contains small amounts of sugar (0.2 to 0.35 per cent), several organic compounds extracted from the beets, and inorganic compounds originating from both the beets and the manufacturing process. The amount of valuable constituents in the waste water is low (12) and a large amount of water must be removed to recover any valuable materials present.

The mineral content of the waste waters from thirteen different plants in the United States was reported by Bartow and Benninghoff (6). Betaine and glutamic acid may be obtained from some of the wastes in relatively large amounts. Alvarado, Olin, and Bartow (2) showed that small amounts of malic, succinic, and citric acids are present in some waste

waters, and Andrlik (3), Barta (4), Tressler (10), Ikeda (8) Takayama (9), and Albrook (1) obtained glutamic acid from either beet molasses or Steffen's waste.

In 1931 Benninghoff (7) found great variations in the amounts of glutamic acid from thirteen Steffen's plants located in different parts of the country. In 1936 Redman (6), using Benninghoff's method with minor revisions, confirmed the latter's results. Eleven of the fourteen samples examined were from the same plants sampled by Benninghoff. Little or no glutamic acid was obtained from the Colorado wastes.

The present investigation was undertaken to study more fully the variations in the amounts of glutamic acid and other constituents present in Steffen's waste from different plants, especially those located in Colorado, and to explain the cause for these variations.

#### TREATMENT OF WASTE WATER

The waste water from sugar factories was shipped in barrels to this laboratory; a large portion was removed by evaporation at reduced pressure. The concentrated wastes (specific gravity 1.4) collected during the 1936 sugar cam-

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paign were treated and found to check by the method used previously by Redman (6).

In the Benninghoff-Redman method sufficient water was used to dissolve completely the crude glutamic acid hydrochloride-salt mixture. Since glutamic acid is sparingly soluble in water (1.5 grams per 100 cc.), the use of excessive amounts of water causes smaller quantities of glutamic acid to be precipitated when the hydrochloride-salt is neutralized with sodium hydroxide.

**FIRST REVISED METHOD.** The method was improved and the yield increased by treating the crude glutamic acid hydrochloride (a mixture of potassium chloride and glutamic acid hydrochloride) with the least amount of water necessary to dissolve the glutamic acid hydrochloride present. Waste obtained during the 1936 and 1937 campaigns, treated according to this revised Benninghoff-Redman method, in most cases gave yields of glutamic acid higher than were obtained by the old method (Table I).

**FURTHER REVISIONS.** Experiments by Wetzstein (11) indicated possible losses of glutamic acid hydrochloride early in the process due to its partial separation with the crude inorganic salts. To eliminate these losses, the acid-waste mixture was kept moderately warm to hold the glutamic acid hydrochloride in solution. The results of previous experiments indicated losses of glutamic acid hydrochloride when it does not crystallize completely from the concentrated mixture and is carried into the filtrate which contains the betaine hydrochloride. To decrease this loss the concentrated mixture containing the glutamic acid hydrochloride and the

Samples of Steffen's waste were obtained during the 1938 campaign from twenty-three Steffen's plants. The Colorado samples yielded glutamic acid differing from the samples collected during previous campaigns which showed no glutamic acid. Samples from the plateau states of Idaho, Montana, Utah, and Wyoming contained more glutamic acid, and the samples from California, Iowa, Michigan, Nebraska, and Ohio contained the most. The differences may be due not only to geographical location, but also to season, to addition of molasses from other plants to the process, to variation in rainfall, or to organic content of the soil. Other factors which might cause variation should be studied later. There was also a variation in the inorganic salts and in the carbon residues obtained after hydrolysis which may have some bearing on the differences in the amount of glutamic acid found.

crude inorganic salts not previously removed by crystallization is cooled to a low temperature ( $-5^{\circ}$  C.) and kept there for 7 to 10 days. This procedure ensures complete crystallization of the glutamic acid hydrochloride.

**SECOND REVISED METHOD.** Five hundred grams of concentrated waste (specific gravity 1.4) were treated with an equal weight of 12 *N* hydrochloric acid. Considerable foaming resulted and the mixture became quite warm. After the foaming subsided, the material was set aside in a moderately warm place ( $27-37^{\circ}$  C.) for 48 hours and then filtered. The filtrate from the inorganic salts which had precipitated was placed in a 3-liter round-bottom flask, covered with an inverted flat-bottomed crystallizing dish which fitted loosely, and heated in a small autoclave at a pressure of 45 pounds per square inch for 3.5 hours. At this pressure hydrolysis is complete. After reduction of the pressure and cooling, the carbon, which had formed during the hydrolysis of the acid-waste mixture, was filtered off and the filtrate concentrated at reduced pressure in a 5-liter balloon flask on a steam bath (distillation temperature  $45^{\circ}$  to  $55^{\circ}$  C.) until the solution

was reduced to a viscous mass. Most of the warm viscous material was poured into a 600-cc. beaker, and the remainder was transferred from the flask to the beaker by rinsing with a sufficient quantity of 12 *N* hydrochloric acid. The thick mixture was kept at  $-5^{\circ}$  C. for 7 to 10 days, when the crude crystallized glutamic acid hydrochloride, mixed with large amounts of inorganic salts, was removed by pressure filtration. The dried mixture of glutamic acid hydrochloride and inorganic salts was extracted with water. The quantity of water used in the extraction process was varied according to the amount of glutamic acid obtained from the samples in previous experiments. Small quantities of glutamic acid required less water (100-150 cc.). If there was no information concerning the content of glutamic acid present, a small portion of water was used in the first extraction. The residue of crude salt was saved for a second extraction.

The aqueous extract was decolorized by activated carbon, and 10 *N* sodium hydroxide was added until the pH of the mixture was 3.28 (the isoelectric point of glutamic acid). In some cases the glutamic acid separated slowly and in others rapidly. The mixture was placed in a refrigerator for 48 hours to allow the glutamic acid to separate completely; then it was filtered off, dried, and weighed. The filtrate was used along with a small amount of water added for the second extraction. If, after standing for some time, an appreciable-

TABLE I. GLUTAMIC ACID BY BENNINGHOFF-REDMAN AND BY REVISED METHODS

Source	Grams per 500 G. Waste (Sp. Gr. 1.14)	
	Benninghoff-Redman method	First revised method
	1936 Campaign	
St. Louis, Mich.	19	23.5
Grand Island, Nebr.	13	18.5
Spreckels, Calif.	11	11.6
Fort Collins, Colo.	0	0.6
	1937 Campaign	
Garland, Utah	10	10.5
Tracy, Calif.	7	9.3
Fremont, Ohio	15	22.2
Worland, Wyo.	0	0.0
Loveland, Colo.	3	8.5
Fort Collins, Colo.	8	7.8



TABLE II. GLUTAMIC ACID IN 500-GRAM SAMPLES OF WASTE (SPECIFIC GRAVITY 1.4) OBTAINED DURING THE 1938 CAMPAIGN

From Colorado		From Plateau States Other than Colorado		From California and Midwestern States	
Source	Glutamic acid, g.	Source	Glutamic acid, g.	Source	Glutamic acid, g.
Delta	16.25	Sugar City, Idaho	16.72	Spreckels, Calif.	16.72
Fort Collins	15.3	Billings, Mont.	15.67	Tracy, Calif.	30.75
Fort Morgan	10.9	Garland, Utah	13.1	Mason City, Iowa	30.7
Longmont	17.15	Spanish Fork, Utah	18.4	St. Louis, Mich.	28.95
Loveland	17.57	Sheridan, Wyo.	16.42	Gering, Nebr.	15.55
Ovid	9.55	Torrington, Wyo.	15.25	Grand Island, Nebr.	21.92
Rocky Ford	12.87	Worland, Wyo.	6.05	Fremont, Ohio	27.05
Sterling	11.7				
Swink	10.65				

amount of crystals had formed in the filtrate containing the betaine hydrochloride, they were removed by filtration and combined with the salt from the first extraction before the second extraction was made. In some cases appreciable amounts of glutamic acid were obtained in the second extraction; in others, all the glutamic acid seemed to have been removed in the first extract.

The revised method differs from the previous revision: (a) changes were made in the temperatures at some stages of the procedure; (b) special precautions were taken to retrieve any appreciable quantities of glutamic acid hydrochloride. The increased efficiency in recovery of glutamic acid by the revised process depends mainly upon the use of the extraction process to remove glutamic acid hydrochloride from the crude inorganic salts without the excessive use of water.

#### GLUTAMIC ACID FROM DIFFERENT AREAS

Samples of waste were obtained during the 1938 campaign from twenty-three Steffen's plants in the United States (Table II). Contrary to the experience of previous years every sample of waste collected during the 1938 campaign yielded glutamic acid. Some of the samples from Colorado during the 1936 campaign had little or no glutamic acid when treated by the revised process. The samples from Colorado during the 1938 campaign (Table II) yielded such unusually large amounts of glutamic acid that the difference in results could not be attributed to a change in procedure alone.

The highest average yield was obtained from the sample from Loveland and the lowest from Ovid. Appreciable amounts of glutamic acid were obtained from the 1937 samples of waste from Loveland and Fort Collins, whereas none had been obtained from samples gathered during preceding years. Yields about twice as large as those in 1937 were obtained from the 1938 samples gathered from these factories and from the factory at Longmont, located in the same area (north central Colorado) just east of the foothills on the eastern slope.

The third highest yield of glutamic acid was obtained from the waste from Delta, a town located on the western slope. The lowest yields for the entire state were from the samples obtained at Fort Morgan, Sterling, and Ovid (the northeastern area along the South Platte Valley). The averages of glutamic acid content from Rocky Ford and Swink, located in the Arkansas River Valley in the southeastern district, were slightly higher than those from the factories located in the northeastern area but definitely lower than those from the plants in the north central area.

Among samples obtained from the plateau states, by far the smallest amount of glutamic acid was from the sample from Worland, Wyo. The 1936 sample (6) from this plant yielded 13 grams of acid and the 1937 sample yielded none. The yield from the 1938 campaign (6.05), strangely enough, is about an average of the other two results.

Among this entire group, the highest yield of acid was from the sample from Spanish Fork, Utah. This is interesting since only traces of glutamic acid (7) were found in the sample obtained from this factory in 1931. Although samples in this group came from widely scattered areas, the variation in yields of glutamic acid was smaller than expected. Considering this group alone, it appears that seasonal variations in wastes obtained from the same factory are sometimes greater than geographical variations. The results from the samples obtained

from Worland, Wyo., and Spanish Fork, Utah, seem to emphasize this point (Table III).

The amount of glutamic acid from Torrington, Wyo. (average 15.25 grams) checks closely with the amount obtained from Gering, Nebr. (average 15.55 grams). These two factories, located in different states, are on the North Platte River and not separated by a great distance.

The samples from California and the midwestern states (Table II) come from widely separated localities. Gering, Nebr., is so near Torrington, Wyo., that the sample from that factory might have been classed with those of the plateau states (Table II). However, Grand Island, Nebr., is over 200 miles east of Gering and much too far east to be classed with that group. Spreckels and Tracy, Calif., are within 100 miles of each other. Most of the miscellaneous samples (Gering, Nebr., excluded) give relatively high yields of glutamic acid.

The samples from Mason City, Iowa, St. Louis, Mich., and Fremont, Ohio, give large amounts of the acid without great seasonal fluctuations (Table III).

It is hard to explain why the sample from Tracy, Calif., during the 1937 campaign (Table III) gave 9.3 grams of the acid, whereas the samples from this same source during the 1936 and 1938 campaigns yielded 32.5 and 30.75 grams, respectively. The glutamic acid content of the waste from Mason City, Iowa, is consistently high.

The wastes obtained from Spreckels, Calif., and Grand Island, Nebr., during previous seasons yielded amounts of glutamic acid varying from 8 to 18 grams. The yields of the

TABLE III. GLUTAMIC ACID FROM STEFFEN'S WASTE FROM VARIOUS SUGAR FACTORIES OBTAINED DURING DIFFERENT CAMPAIGNS\*

Source	Grams/500 G. Waste (Sp. Gr. 1.4)			
	1931	1936	1937	1938
Spreckels, Calif.	18	11.6	8	16.72
Tracy, Calif.	..	32.5	9.3	30.75
Delta, Colo.	0	7.5	..	16.25
Fort Collins, Colo.	0	0.6	8	15.3
Fort Morgan, Colo.	..	..	..	10.9
Longmont, Colo.	..	..	..	17.15
Loveland, Colo.	0	0	8.5	17.57
Ovid, Colo.	..	..	..	9.55
Rocky Ford, Colo.	..	0	..	12.87
Sterling, Colo.	..	..	..	11.7
Swink, Colo.	0	4.5	..	10.65
Sugar City, Idaho	..	..	..	16.72
Mason City, Iowa	23	34	18	30.7
Blissfield, Mich.	18	37	..	..
St. Louis, Mich.	19	23.5	..	28.95
Billings, Mont.	..	..	..	15.67
Fremont, Ohio	..	..	22.5	27.05
Gering, Nebr.	..	..	..	15.55
Grand Island, Nebr.	0	16.5	..	21.92
Garland, Utah	..	16.0	10.5	13.1
Lewiston, Utah	8	..	..	..
Spanish Fork, Utah	Trace	..	..	18.4
Sheridan, Wyo.	..	..	..	16.42
Torrington, Wyo.	..	9	..	15.25
Worland, Wyo.	2	0	13	6.05

\* No samples were obtained from the sources for which no figures are given.



TABLE IV. SOURCES OF MOLASSES SHIPPED TO STEFFEN PLANTS FURNISHING WASTE DURING 1938 CAMPAIGN

Steffen Plants	Factories Supplying Molasses
Spreckels, Calif.	Manteca, Calif.
Tracy, Calif.	Hamilton City, Calif.
Delta, Colo.	Hardin and Sidney, Mont.
Ft. Collins, Colo.	Windsor, Greeley, Ft. Lupton, Colo.; Lovell and Wheatland, Wyo.
Ft. Morgan, Colo.	Brush, Colo.
Longmont, Colo.	Ft. Lupton and Brighton, Colo.
Loveland, Colo.	Eaton and Windsor, Colo.
Ovid, Colo.	Greeley, Colo.
Rocky Ford, Colo.	Greeley, Ft. Lupton, Sugar City, Colo.; E. Grand Forks, Minn.; Missoula, Mont.
Sterling, Colo.	Brush and Greeley, Colo.; Bayard and Mitchell, Nebr.
Swink, Colo.	Sugar City, Colo.
Sugar City, Idaho	Belle Fourche, S. Dak.; Chinook, Mont.; Shelley and Blackfoot, Idaho
Mason City, Iowa	Chaaska and E. Grand Forks, Minn.
St. Louis, Mich.	None
Billings, Mont.	Hardin and Sidney, Mont.
Gering, Nebr.	Bayard and Lyman, Nebr.
Grand Island, Nebr.	Missoula, Mont.; E. Grand Forks, Minn.
Fremont, Ohio	Findlay, Ohio
Garland, Utah	West Jordan, Ogden, Layton, Utah; Belle Fourche, S. Dak.; Teppenish, Wash.
Spanish Fork, Utah	West Jordan and Gunnison, Utah
Sheridan, Wyo.	Hardin, Mont.
Torrington, Wyo.	Lyman, Nebr.; Hardin and Sidney, Mont.
Worland, Wyo.	Lovell, Wyo.

acid from the samples obtained during the 1938 campaign from these two sources were comparatively high.

#### INORGANIC SALTS AND CARBON RESIDUES

**INORGANIC SALTS.** The amounts of crude inorganic salts precipitated upon the addition of 12 *N* hydrochloric acid to the concentrated waste vary greatly, 55.7 to 124.6 grams. The amounts obtained do not represent all of the salts present in the mixture. In many cases a quantity as large or even larger is precipitated with the glutamic acid hydrochloride after concentration of the hydrolyzed mixture. The concentrated waste from all sources contains a high percentage of potassium and could be used to supply potassium salts in cases of emergency.

**CARBON RESIDUES.** The amount of carbon obtained by acid hydrolysis of the concentrated waste varied from 4.2 to 58.1 grams. Most of the samples gave between 15 and 35 grams. With the exception of the sample of waste from Mason City, Iowa, all of the samples with high glutamic acid content yielded large amounts of carbon. Benninghoff (?) found the same relation and also a relation between the amount of carbon formed and the amount of volatile matter in the residue upon evaporation.

Not all samples yielding large amounts of carbon have a high glutamic acid content. The 1938 sample from Worland, Wyo., gave more carbon than the average but yielded the smallest amount of glutamic acid. The amounts of carbon obtained from the Ovid and Swink, Colo., samples were about average, yet the yields of glutamic acid were comparatively low.

#### FACTORS IN VARIATION OF GLUTAMIC ACID CONTENT

Many factors may cause variations in the glutamic acid content of Steffen's waste. Three have been studied: (a) the effect of varying amounts of molasses from non-Steffen factories on the glutamic acid obtained from Steffen houses (Table IV); (b) the effect of irrigation water and rainfall

upon the constituents of the beets; (c) the effect of soils upon the constituents of the beets.

The following conclusions were drawn after a complete and thorough study of these factors: (a) The addition of molasses from other plants may have altered the glutamic acid content of the waste water from some Steffen houses. (b) The unusual amounts of rainfall in most beet producing areas during 1938 may account for the unusually high yields of glutamic acid from the waste water collected during that year. (c) There is a possibility that beets grown in highly organic soils may contain a larger amount of nitrogenous precursors of glutamic acid than beets grown in soils with smaller amounts of organic matter present.

Other factors which might cause variations in the glutamic acid content of the waste water are the state of maturity of the beets when harvested, the number of times the molasses has been reworked in the factory before being discarded, the length of time during which the beets have been stored, the difference in the methods used to process the beets, and temperature changes during the growing season of the beets.

No information has been gathered concerning the latter factors except that there are no great differences in the processing of the beets at different factories. It seems highly probable that the variations in the waste water are due mainly to variations in the beet composition.

Over a period of years the sugar content of the beets processed at the Mason City, Iowa, plant has been somewhat lower than that at many plants in the Rocky Mountain region. In general, the sugar content of the beets processed in the Colorado plants during the 1938 sugar campaign was below normal. These facts lead to the conclusion that waste water from the processing of beets low in sugar content might be abnormally high in glutamic acid content. Such a relation could not be definitely established without more evidence.

#### SUMMARY

1. The method used by Benninghoff and Redman for the preparation of glutamic acid from the concentrated waste has been improved and higher yields of glutamic acid have been obtained.

2. No glutamic acid or only small amounts were obtained from the Colorado wastes examined in 1931, 1936, and 1937, but all of the 1938 samples yielded glutamic acid in appreciable amounts.

3. The highest yields of glutamic acid were from samples procured from factories located in the midwestern states and in California.

4. The glutamic acid content of Steffen's waste from some areas is high and varies a little from season to season. The content in wastes from some other areas varies greatly from season to season.

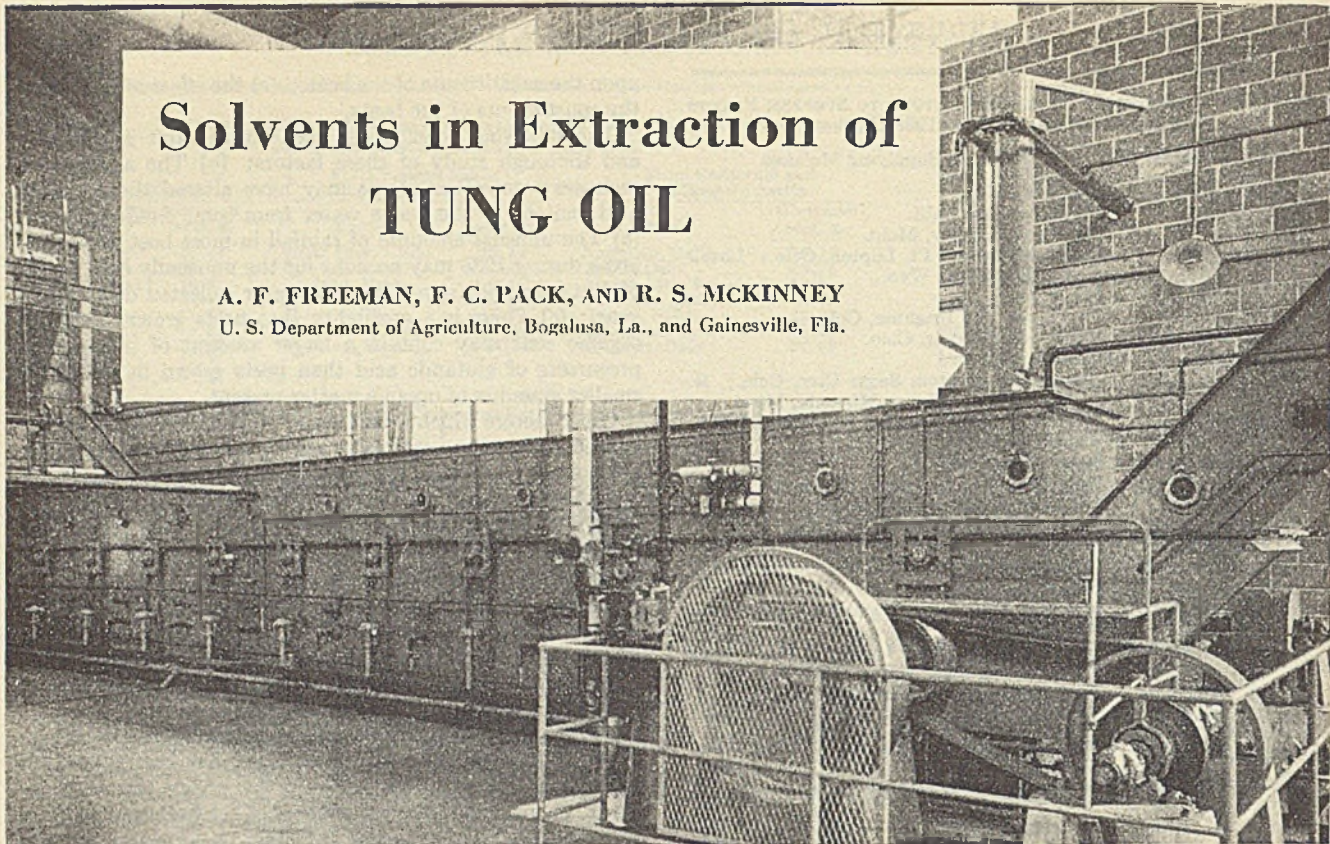
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# Solvents in Extraction of TUNG OIL

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THE possibility of extracting tung oil by a solvent process was studied during 1938-1942 (1, 8). The drying oil industry has shown interest in the progress of these investigations, in view of the possibility of increased yields of tung oil, at a time when tung oil imports have practically ceased and the price has risen to more than double its normal value. It is estimated that the expected yield of tung oil to be expressed from the 1942 domestic crop of tung fruits could be increased by at least another million pounds if a satisfactory solvent process was available.

In the laboratory an effort has been made to evaluate a wide variety of commercially available solvents for the extraction of tung oil by a solvent extraction process. Solvents having either relatively low or high boiling temperatures have been considered impractical for commercial purposes due to the unusually high losses of solvent vapors in the case of the former, and to the difficulty of completely separating the solvent from the oil and to the production of inferior grades of tung oil as a result of the excess heat required in the case of the latter. Many organic solvents can be eliminated because of the limited solubility of tung oil in them, while others are not suitable because they dissolve appreciable quantities of substances besides tung oil from the tung meal. Still other solvents may be unstable under the conditions of the process, and their decomposition products may react with tung oil and impair its value as a drying oil. One halogenated hydrocarbon, trichloroethylene, has been reported to decompose during the solvent extraction of soybean oil and in early experiments was held to be unsatisfactory. Recent developments, however, indicate that trichloroethylene has been used successfully in the solvent extraction of soybean oil, and that the use of an inhibitor, such as aniline, diminishes this decomposition to an extent where it is no longer a problem. This class of compounds

is of considerable interest, and merits further study, particularly since many of these solvents have relatively high flash and fire points, and consequently are considered nonhazardous.

By a proper adjustment of conditions during distillation, it may be possible to use higher-boiling solvents for the extraction of tung oil, but generally solvents of less extreme boiling ranges will be selected because of ease of operation and better quality of recovered oil. Limited production and supplies and high cost of some solvents will probably eliminate them from use, notwithstanding the fact that they have been shown to be satisfactory otherwise. A number of such solvents were included in this study despite present limitations, and a brief description of the results obtained is given in Table I.

The application of solvent extraction to tung oil has been retarded by the fact that solvent-extracted tung oil is solid at ordinary temperatures. On the other hand, expressed tung oil is liquid even at ice box temperatures. The solidifying of the solvent-extracted tung oil is due to the presence of the eleostearic acid glyceride, the principal constituent of tung oil (2, 4) in the beta form.  $\beta$ -Eleostearic acid triglyceride melting at 65° C. is formed from its lower-melting geometric isomer (alpha form) by the action of light or suitable catalysts, particularly sulfur and iodine. The experiments by Morrell and Samuels (7) indicate that the difference between the alpha and beta acids consists in different configurations of the unsaturated groups—e. g., *cis-cis-trans* and *trans-cis-cis*. The drying oil industry prefers the liquid form of tung oil to which it has become accustomed, since the solid form introduces difficulties in handling, both in shipping and in industrial processing. Therefore it seemed desirable to select, if possible, a solvent which does not favor the conversion of tung oil to the solid form. A heating process (5) was developed whereby the solid oil, which may result from a solvent-extraction process, is rendered permanently liquid. This undoubtedly removes the objections to the use of a solvent-extraction process in which there is the possibility of producing a solid or partly solidified oil. However if this could be accomplished merely by the selection of another solvent, it would be of interest.

●

Photograph above shows a Kennedy Continuous Countercurrent Solvent Extractor and is reproduced through the courtesy of The Wolf Company.



## EXTRACTION METHODS

After consideration of various methods, it was decided to limit the extractions to two types: (a) an analytical procedure (3) in which the extraction of oil is carried out under reflux at an elevated temperature, at or somewhat below the boiling point of the solvent, and (b) an extraction process in which the ground tung meal and the solvent are shaken by mechanical agitation at room temperature, followed by filtration under vacuum. In the first procedure the miscella was concentrated at atmospheric pressure and then freed as completely as possible of solvent by heating at 105° C. under a vacuum of 28.5 inches of mercury. In the second procedure the removal of solvent from the miscella was carried out under reduced pressure at the requisite temperature, as shown in Table II.

**METHOD 1.** Five grams of tung kernels ground twice in a No. 1 Russwin food grinder were rolled in filter paper and extracted (3) in a Butt tube over a 150-ml. boiling flask for 4 hours. The sample was then ground vigorously in a mortar with one gram of analytical-grade sea sand, and extraction was continued for 2 more hours. Concentration was performed by distillation of the bulk of the solvent at ordinary pressure, followed by heating at 105° C. in a vacuum oven at 28.5 inches of mercury. Data obtained on extraction by this method are given in Table I.

**Метод 2.** Ten grams of tung kernels ground twice in a No. 1 Russwin food grinder were placed in a 250-ml. glass-stoppered bottle with 100 ml. of solvent and agitated vigorously on a mechanical shaker for one hour. The miscella was filtered with suction and concentrated under reduced pressure, heat being supplied to the boiling flask by an oil bath over an electric heater. Data obtained by this method are given in Table II.

In the first method an effort was made to determine the quantity and quality of the oil extracted by the solvent by comparison with the oil extracted from a similar meal sample by a standard pentane-hexane petroleum fraction. The standard petroleum ether, Skellysolve F, was selected by the American Oil Chemists' Society for analytical extraction of vegetable oils, since it is an excellent solvent for glyceride oils and extracts negligible quantities of other lipids.

In the second method no effort was made to continue the extraction until the oil was completely extracted from the meal. With this exception the latter method probably approximates, on a small scale, the type of extraction which in commercial practice would result from allowing solvents at ordinary temperature to flow through the ground meal.

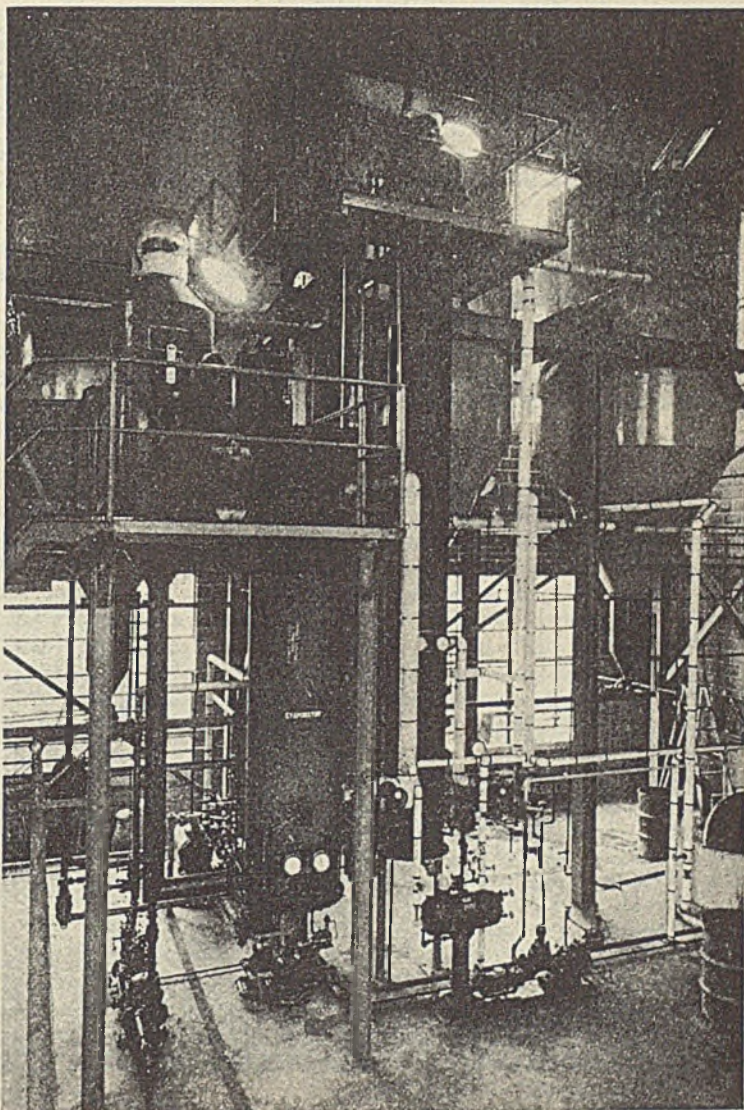
Indices of refraction and iodine numbers were determined on the oils extracted by various solvents by methods 1 and 2 (Tables I and II). The Wijs method (5) was used with the oils obtained by both methods and the Woburn method (6) on the oils extracted by method 2. The latter, indicating the total unsaturation of the oil, is probably a better indication of the quality of tung oil.

## DISCUSSION OF RESULTS

In the first method there was evidence, especially in the case of the higher boiling solvents, that the quality of the oil was ad-

versely affected during extraction in the 6-hour period when it was heated together with the solvent at the elevated temperature necessary to maintain the refluxing operation, and that some of the solvent was retained by the oil. Solvent retention was also indicated in a number of instances in the second method. Increasing values of refractive index were obtained on the extracts when the refractometer prisms were opened for brief intervals between successive readings, indicating evaporation of retained solvent. The first and last indices obtained are shown in Table II. However, iodine values were determined only on the concentrates resulting from the procedures described. The quality of oils extracted by any one solvent can be adversely affected by variation of the extraction and evaporation conditions. For example, during evaporation a lower quality of oil, due to polymerization and oxidation, may be produced by heating for a long period at a moderate temperature than by heating for a shorter period at a higher temperature.

The last column in Table II contains brief comments on the value of each solvent in the extraction of tung oil as determined by the conditions of the experiment or as indicated by present commercial solvent-extraction practice with solvents of extreme boiling range. These tables undoubtedly include some solvents which might be considered too costly for commercial use, but future production methods may make their use economically



Kennedy Vacuum Distilling Unit for Continuous Countercurrent Solvent Extraction Process

Courtesy, The Wolf Company



TABLE I. RESULTS OF EXTRACTING TUNG OIL FROM PREPARED KERNELS BY METHOD I WITH VARIOUS SOLVENTS\*

Solvent	Extraction Data			Check Extn. with Skellysolve F			Characteristics of Oil
	% oil	Iodine No., Wijs	$n_D^{20}$ , <sup>b</sup>	% oil	Iodine No., Wijs	$n_D^{20}$ , <sup>b</sup>	
1. Isopentane, <i>P</i>	60.85	166.8	1.5178	63.25	167.0	1.5175	A, G
2. <i>n</i> -Pentane, <i>P</i>	62.03	166.7	1.5175	63.25	167.0	1.5175	A, G
3. Petroleum naphtha (pentanes-hexanes fraction), <i>N</i>	60.37	163.4	1.5162	59.57	165.1	1.5162	A, G
4. Petroleum naphtha (pentanes-hexanes fraction), <i>N</i>	...	...	....	...	...	....	(From Skellysolve F. used as standard)
5. Petroleum naphtha (mixed hexanes), <i>P</i>	62.15	166.6	1.5173	63.25	167.0	1.5175	A, G
6. Petroleum naphtha (essentially <i>n</i> -hexane), <i>N</i>	61.65	159.3	1.5145	59.57	165.1	1.5162	B, G
7. Petroleum naphtha (essentially <i>n</i> -hexane fraction), <i>N</i>	63.81	163.8	1.5181	61.97	164.9	1.5166	B, G
8. Cyclohexane, <i>P</i>	64.24	162.6	1.5180	61.69	166.7	1.5172	A, H
9. Benzene, <i>M</i>	62.18	160.2	1.5181	59.57	164.0	1.5162	B, G
10. Benzene, <i>P</i>	64.74	161.8	1.5163	61.97	164.9	1.5166	B, G
11. Petroleum naphtha (essentially <i>n</i> -heptane fraction), <i>N</i>	64.04	162.6	1.5169	61.97	164.9	1.5166	C, J
12. Petroleum naphtha (essentially an octanes fraction), <i>N</i>	64.75	118.7	...	62.98	163.4	...	B, K
13. Petroleum naphtha (essentially an octanes fraction), <i>N</i>	71.33	159.6	1.5150	69.41	163.8	1.5170	B, R
14. Methylcyclohexane, <i>P</i>	62.81	156.0	1.5134	59.57	165.1	1.5162	C, J
15. Methylcyclohexane, <i>N</i>	64.79	162.6	1.5150	61.69	166.7	1.5172	A, I
16. Toluene, <i>M</i>	65.46	161.8	1.5163	61.69	166.7	1.5172	(See Table II) C, H
17. Petroleum naphtha (essentially high-boiling octanes fraction), <i>N</i>	63.73	149.6	1.5159	59.57	165.1	1.5162	B, G
18. Xylene, <i>M</i>	68.98	150.4	1.5128	61.69	166.7	1.5172	C, H
19. Methylene chloride, <i>P</i>	64.45	162.1	1.5169	63.25	167.0	1.5175	A, G
20. <i>sym-trans</i> -Dichloroethylene, <i>P</i>	65.80	161.6	1.5154	64.03	162.2	1.5152	A, G
21. Chloroform, <i>M</i>	68.08	164.3	1.5171	61.69	166.7	1.5172	B, G
22. 1,2-Dichloropropane, <i>P</i>	...	...	...	...	...	...	(See Table II)
23. Carbon tetrachloride, <i>M</i>	60.69	156.9	1.5154	61.69	166.7	1.5172	A, G
24. <i>n</i> -Butyl chloride, <i>P</i>	65.01	155.1	1.5150	63.25	167.0	1.5172	A, G
25. Ethylene dichloride, <i>P</i>	68.06	155.3	1.5140	64.03	162.2	1.5152	E, L, G
26. Trichloroethylene, <i>P</i>	...	...	...	...	...	...	(See Table II)
27. Trichloroethylene, <i>P</i>	63.41	152.5	1.5145	64.03	162.2	1.5152	F, I
28. 1,1,2-Trichloroethane, <i>P</i>	...	...	...	...	...	...	(See Table II)
29. Perchloroethylene, <i>P</i>	71.70	145.3	1.5144	64.03	162.2	1.5152	F, L
30. Ethylene dibromide, <i>P</i>	...	...	...	...	...	...	(See Table II)
31. Acetone, <i>P</i>	62.37	164.2	1.5162	60.19	164.0	1.5162	D, I
32. Isopropyl ether, <i>P</i>	62.72	165.9	1.5172	63.25	167.0	1.5175	A, G
33. Ethyl acetate, <i>M</i>	...	...	....	...	...	....	(See Table II)

\* Key to letters used in table:

- A. Equal in color to oil extracted with Skellysolve F.  
 B. Oil slightly darker than that extracted with Skellysolve F.  
 C. Oil darker than that extracted with Skellysolve F.  
 D. Oil considerably darker than that extracted with Skellysolve F.  
 E. Oil had pale green color.  
 F. Oil had slight green color, more pronounced than E.  
 G. Oil contained no solid particles before or after vacuum stripping.  
 H. Oil contained slight amount of suspended white solid particles before vacuum stripping.

- I. Oil contained considerable amount of suspended white solid particles before vacuum stripping.  
 J. Oil was white solid before vacuum stripping.  
 K. High solvent retention, no index of refraction taken.  
 L. Oil considerably more viscous than that extracted with Skellysolve F.  
 M. A. C. S. grade or equal.  
 N. Commercial grade.  
 P. Technical grade.  
 R. Oil was white solid on storage at 5° C. for 24 hours, liquid at room temperature.

feasible. Conclusions as to the value of these thirty-three solvents for use in the extraction of tung oil are based upon the quality and quantity of the oils extracted by the solvents under the conditions employed in this study and are not necessarily applicable to commercial extraction processes under other conditions. However, it is believed that this study will be of value to those interested in the extraction of tung oil by a solvent process.

### CONCLUSIONS

Solvents 1 to 4 (petroleum naphthas) and solvent 19 (methylene chloride) were considered of doubtful value for tung oil extraction, because of probable solvent losses due to the low boiling ranges of these solvents. The ranges are from a low of 26.7° to a high of 60° C., but practically all of the materials comprising these solvents boil at something less than 50° C. The oils extracted with solvents 1 to 4 were high in quality. Solvent 19 yielded an oil of somewhat less than average quality. Solvent 20 (*sym-trans*-dichloroethylene) and 31 (acetone) yielded oils of borderline quality, but in view of their boiling ranges would probably be classified with solvents 1 to 4.

Solvents 5 to 7 (petroleum naphthas in the hexane class), 8 (cyclohexane), 10 (benzene), 11 (a petroleum naphtha essentially *n*-heptane), 14 and 15 (different grades of methylcyclohexane), 21 (chloroform), 32 (isopropyl ether), and 33 (ethyl acetate) were all found to be satisfactory solvents under the conditions described for the extraction of tung oil, judged, of course, from the grades of oil obtained with each solvent and the general properties of each solvent. Solvent 9, different grade of benzene from solvent 10, produced an oil of borderline quality. With this exception this group probably represents the most promising of the solvents examined. Isopropyl ether (solvent 32) has been reported to be unusually hazardous in nature through the production of explosive peroxides during storage.

Solvents 12 and 13 (relatively high-boiling petroleum naphtha octanes fractions) and 16 (toluene) produced oils of borderline quality. It is possible, however, that these solvents may find use in commercial extraction, if improved grades of oil can be obtained by use of better facilities for solvent stripping. Solvent 17 (a high-boiling petroleum naphtha octanes fraction) and solvent 18 (xylene) gave oils of poor quality under the conditions of the experiment. It is considered likely that grades of oil obtained with these two solvents could be improved with better facilities for solvent stripping.

Solvents 22 to 30 are halogenated compounds and, with the exception of one, are compounds of chlorine. These solvents yielded oils of borderline quality, and they should be studied further. It is possible here, also, that these solvents may find use in commercial extraction, when their properties have been examined more fully. Some difficulties have been experienced in the solvent extraction of drying oils with halogenated solvents, particularly in the decomposition of the solvent and consequent halogenation of the drying oils which impairs their commercial value. Recent developments, however, have indicated that one of these compounds, trichloroethylene, has been used successfully in the solvent extraction of soybean oil, and that by using an inhibitor such as aniline, this decomposition was diminished to an extent where it was no longer a problem. This class of compounds is of considerable interest, however, and merits further study, particularly since many of these solvents have relatively high flash and fire points, and consequently are considered nonhazardous.

### ACKNOWLEDGMENT

The authors acknowledge their indebtedness to H. S. Paine of the Bureau of Agricultural and Industrial Chemistry, who suggested this investigation.



TABLE II. RESULTS OF EXTRACTING TUNG OIL FROM PREPARED KERNELS BY METHOD 2 WITH VARIOUS SOLVENTS<sup>a</sup>

Solvent No.	Boiling Range, C.	Temp. Range of Bath, ° C.	Heating Period, Minutes	Pressure Range, Mm.	Iodine No., Wijs	Iodine No., Woburn	n <sub>D</sub> <sup>20</sup> , °		Characteristics of Oil	Value of Solvent
							Initial <sup>b</sup>	Final <sup>b</sup>		
1	26.7-30.0	58-88	20	86-95	165.9	237.78	1.5183	1.5183	A, H-4, L	U
2	34.4-37.8	55-80	28	72-85	165.6	238.44	1.5176	1.5177	A, J-4, L	U
3	35.0-58.9	90-108	12	83-160	162.4	230.51	1.5168	1.5175	A, H-2, M	U
4	35.0-60.0	71-103	18	78-120	163.6	231.84	1.5169	1.5175	A, J-2, L	U
5	54.0-71.0	84-104	15	84-102	163.9	231.86	1.5178	1.5178	A, H-4, L	S
6	60.0-82.2	80-98	17	80-88	161.7	225.57	1.5158	1.5173	A, H-2, L	S
7	63.3-70.0	79-111	22	83-118	162.1	232.60	1.5170	1.5174	A, H-4, L	S
8	79.0-82.0	77-100	14	85-90	162.4	231.84	1.5160	1.5175	A, H-4, L	S
9	79.5-81.0	84-116	15	81-89	158.5	221.28	1.5169	1.5176	B, F, H-2, L	M
10	79.0-83.0	90-115	26	83-120	161.4	225.90	1.5170	1.5176	D, H-2, L	S
11	87.8-97.8	71-95	22	85-110	159.4	222.27	1.5147	1.5176	A, H-4, L	S
12	84.4-112.0	60-120	10	70-80	163.8	....	1.5170	1.5170	B, H	M
13	85.5-114.4	79-109	20	80-86	158.4	....	1.5155	1.5173	B, H-2, L	M
14	100.0-103.0	83-116	17	78-95	157.3	231.84	1.5143	1.5175	B, H-2, L	S
15	95.0-102.8	116-132	15	81-98	165.6	225.23	1.5157	1.5177	B, H-2, L	S
16	110.0-111.0	92-115	20	76-160	159.9	220.62	1.5168	1.5174	B, F, H-2, L	M
17	115.5-138.9	92-118	20	82-85	153.9	219.29	1.5136	1.5173	B, H-2, L	V
18	137.0-140.0	83-117	25	76-90	143.9	220.61	1.5159	1.5173	D, H-2, L	V
19	40.0-41.0	50-70	15	80-100	156.6	....	1.5137	1.5149	D, I, L	U
20	48.4	35-120	10	80-100	161.9	224.56	1.5158	1.5157	D, I-2, L	M
21	48.4	107-145	15	80-130	163.2	226.25	1.5162	1.5162	D, I-2, L	M
22	96.8	83-98	20	84-89	157.1	....	1.5168	1.5175	D, H-2, L	S
23	96.8	105-128	9	80-130	156.8	....	1.5146	1.5173	B, H-2, L	M
24	96.8	80-110	10	80-130	164.8	....	1.5142	1.5142	B, H-2, L	M
25	78.0-78.0	87-108	18	81-103	158.7	225.20	1.5171	1.5175	B, H-2, L	M
26	77.9	75-110	27	85-95	163.1	225.90	1.5164	1.5175	C, H-4, L	M
27	83.6	55-105	22	89-95	155.7	223.25	1.5157	1.5176	B, J-2, L	M
28	83.6	100-120	10	80-130	159.5	....	1.5185	1.5176	C, H-2, L	M
29	83.6	90-110	10	80-130	163.4	....	1.5171	1.5175	C, H-2, L	M
30	88.0-87.5	77-91	18	73-80	149.2	211.20	1.5159	1.5177	C, H-2, L	M
31	88.0-87.5	35-120	10	80-130	162.2	225.50	1.5162	1.5162	C, H-2, L	M
32	87.2	65-103	20	89-95	142.9	199.50	1.5139	1.5176	C, P-4	M
33	87.2	90-140	10	80-130	161.2	....	1.5155	1.5155	C, P-4	M
34	87.2	85-120	13	80-130	161.2	....	1.5169	1.5172	C, P-4	M
35	113.5	70-133	32	85-89	155.0	213.30	1.5155	1.5173	C, G-4	M
36	113.5	100-130	10	80-130	158.6	....	1.5182	1.5182	C, G-4	M
37	113.5	100-135	15	80-130	161.8	....	1.5167	1.5171	C, G-4	M
38	113.5	100-135	15	80-130	144.9	....	1.5152	1.5172	C, G-4	M
39	121.0	89-115	27	73-75	157.1	192.23	1.5169	1.5170	C, H-4, L	M
40	121.0	135-149	10	80-130	164.7	....	1.5173	1.5174	C, H-4, L	M
41	121.0	135-150	12	80-130	164.7	....	1.5172	1.5174	C, H-4, L	M
42	131.7	92-125	30	85-90	139.2	204.80	1.5180	1.5180	E, K-4, R	M
43	131.7	145-170	15	80-130	158.0	....	1.5170	1.5171	E	M
44	56.1-56.5	77-128	18	79-115	164.2	225.90	1.5169	1.5175	A, H-2, N	M
45	56.1-56.5	35-130	10	80-130	....	....	1.5161	1.5162	A, H-2, N	M
46	63.0-69.0	72-95	17	87-100	161.6	223.95	1.5152	1.5175	C, P-4	T, S
47	63.0-69.0	35-120	10	80-130	169.7	221.90	1.5154	1.5154	C, P-4	T, S
48	77.1	102-132	17	77-120	163.1	230.85	1.5158	1.5175	A, P-2	S
49	77.1	35-130	10	80-130	....	....	1.5161	1.5161	A, P-2	S

<sup>a</sup> Key to letters and numbers used in table:

- A. Almost colorless oil.  
 B. Faint yellow oil.  
 C. Light yellow or lemon-colored oil.  
 D. Yellow oil.  
 E. Light brown oil.  
 F. Oil slightly cloudy.  
 G. Oil slightly cloudy after storage.  
 H. Small quantity of white precipitate after storage.  
 I. Faint trace of dark precipitate after storage.  
 J. Considerable quantity of white precipitate on storage.  
 K. White solid after storage.  
 L. Precipitate insoluble on standing at room temperature.

- M. Questionable under conditions of experiment, based upon borderline quality of oil obtained.  
 N. Precipitate dissolved on standing at room temperature.  
 P. Oil entirely clear after storage.  
 R. Oil permanently liquid after heating short interval over Bunsen flame.  
 S. Oil of satisfactory quality under conditions of experiment.  
 T. Solvent considered unusually hazardous in storage.  
 U. Solvent of doubtful value for commercial tung oil extraction because of probable solvent losses due to low boiling range.  
 V. Solvent unsatisfactory under conditions of experiment, based upon poor quality of oil obtained.

1. After storage at approximately 5° C. for 2 months.  
 2. After storage at approximately 5° C. for 4 months.

<sup>b</sup> Differences due to evaporation of retained solvent.

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Tung Tree Orchard

Photo by Bureau of Plant Industry, U. S. D. A.



# Catalytic Desulfurization of Gasolines

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## BY COBALT MOLYBDATE PROCESS

An efficient process has been developed through the semipilot plant stage for catalytic desulfurization of gasoline fractions containing as high as 3-4 per cent by weight of sulfur in the form of organic sulfur compounds. The process is equally applicable to straight-run or to cracked stocks. Thiophenes, as well as thiophanes, thioethers, and mercaptans, are decomposed to hydrogen sulfide and hydrocarbons. Products containing less than 0.01 per cent sulfur may be obtained. The catalyst employed consists of cobalt molybdate, either as such or deposited on a carrier. In excess of 1500 liquid volumes of feed have been desulfurized by 1 volume of catalyst without regeneration and without detectable loss in activity. The catalyst can be regenerated repeatedly in the conventional manner to its original activity.

ALMOST from the inception of the petroleum industry the refiner has been faced with the problem of treating distillates either to remove sulfur compounds or to convert them into a more desirable form. For many years the latter procedure was followed wherever possible and gave rise to such well-known processes as doctor treatment (8), lead sulfide treatment (8), copper sweetening (2, 3), etc., which convert mercaptans into the less objectionable disulfides. Where stocks of moderately high sulfur content have been encountered, conventional treatment with sulfuric acid has been tried in order to obtain products of 0.10 to 0.25 per cent sulfur content. Recently, however, data have been published (7) indicating that, as the sulfur content of a gasoline is progressively decreased to a value of about 0.05 per cent, depending upon the character of the particular stock, there is a more or less gradual increase in lead susceptibility. As the sulfur content is decreased still further, there is a relatively rapid increase in lead susceptibility which becomes marked in the region of 0.01 per cent sulfur. This information, which has been confirmed in the present investigation, suggests that, at least in the case of gasolines to be blended with tetraethyllead, it is desirable to reduce the sulfur content to 0.01 per cent or less; the added

cost of such treatment is partially offset by the decreased amount of tetraethyllead required to obtain any given octane rating.

A cursory review of literature, including published patents, reveals that, in spite of the rather large amount of prior art disclosed on desulfurization, few actual data are available to indicate what may be expected with various types of relatively high sulfur content stocks under different operating conditions. In general, previous methods for removing organically combined sulfur from hydrocarbon fractions may be roughly divided into three groups: The first comprises those processes which depend upon the selective action of sulfuric acid or of a solvent to remove the undesirable sulfur compounds. In the case of stocks of relatively low sulfur content, sulfuric acid treatment can be and is employed. However, with many distillates of relatively high sulfur content, desulfurization with sulfuric acid is accompanied by such high losses of desirable products that treatment is not ordinarily commercially feasible. Recently, a number of processes designed primarily for the removal of mercaptans from gasoline distillates and employing a solvent have been developed and are exemplified by the well-known Shell Solutizer (10) and Atlantic Unisol (6) processes. The second group of processes includes those in which the sulfur compounds are decomposed in the presence of a metal or metal oxide and in the absence of hydrogen, to form either hydrogen sulfide or a metallic sulfide and, presumably, hydrocarbons. Probably the best known is the Phillips high-temperature bauxite treatment (1) which has been used for the decomposition of mercaptans and alkyl sulfides and disulfides in gasoline distillates. The third group comprises those processes which are more truly catalytic in nature and involve the treatment of hydrocarbon fractions at elevated temperatures and pressures with hydrogen in the presence of a catalyst; the sulfur compounds are thereby decomposed into hydrogen sulfide and hydrocarbons. According to patent literature, these processes are capable of decomposing all types of sulfur compounds and the catalysts most frequently mentioned are thiomolybdates and thiotungstates. Usually, however, desulfurization has been only incidental to more profound changes such as are encountered in cracking hydrogenation and dehydrogenation. The so-called Hydroforming process (9), which was recently put into operation in a number of refineries in the United States, is probably the best example of this type.

Since no method appeared to be available for the selective decomposition of all types of sulfur compounds without at the same time causing rather profound changes in the hydrocarbons present, this investigation was undertaken with the principal object of developing such a process.

### EFFECT OF HYDROGEN

Several initial experiments were conducted in which vaporized Santa Maria Valley viscosity-reduction pressure distillate, containing 3.0 per cent by weight sulfur, was passed over various

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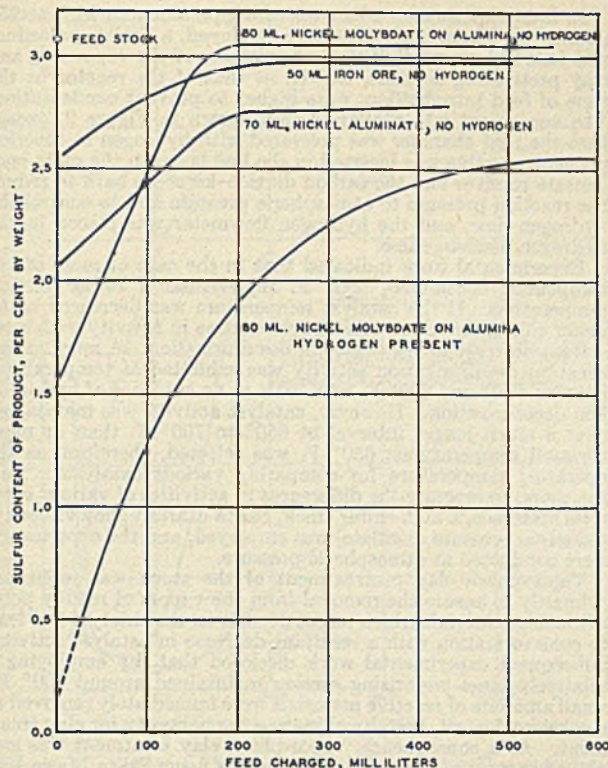


Figure 1. Desulfurization of Santa Maria Valley Viscosity-Reduction Pressure Distillate at 800° F. and Atmospheric Pressure in the Presence and Absence of Hydrogen

metals and metal oxides in the absence of hydrogen. These experiments, conducted at approximately 800° F. and atmospheric pressure, were primarily for the purpose of ascertaining what sulfur reduction could be expected by processes of the type belonging to group 2, mentioned above. The data presented in Figure 1 show the sulfur content of the material being produced after the indicated amount of feed had passed through the reaction zone and are typical of the results obtained. Even when the nickel catalysts, many of which are known to have a marked affinity for sulfur, were employed, the sulfur reduction during the period of greatest catalytic activity was only nominal and the thiophene compounds were apparently unaffected. Furthermore, the activity of the catalysts rapidly declined to a point where little or no sulfur was being removed. The results of these experiments confirmed the conclusions drawn from published data.

As previously mentioned, a more promising line of investigation seemed to be the possibility of selectively decomposing sulfur compounds in the presence of hydrogen and an appropriate catalyst. To demonstrate this contention, two runs were conducted at 800° F. and atmospheric pressure, using as a catalyst a nickel molybdate supported on alumina, with all factors maintained constant except that hydrogen was introduced along with the feed stock at a rate of 1260 cubic feet per barrel

of liquid feed in one run, whereas no hydrogen was employed in the other. Comparison of the data in Figure 1 indicates the marked effect of hydrogen; a sulfur reduction from 3.0 to 0.54 per cent was obtained in the presence of hydrogen, whereas reduction in the absence of hydrogen was only to 1.99 per cent, the comparison being made over the periods of greatest catalytic activity.

It is of particular interest to note that in the run where the vaporized feed was admixed with hydrogen and then passed through the catalyst bed, there was an initial period in which no hydrogen sulfide was present in the exit gases, the catalyst presumably undergoing partial conversion to sulfide. Subsequent to this period there was a copious evolution of hydrogen sulfide and a more or less constant degree of sulfur reduction. On the other hand, in the run where no hydrogen was employed, no hydrogen sulfide was evolved and the sulfur content of the product rapidly approached that of the feed stock as the catalyst lost activity. In both runs the volume of product recovered amounted to 99 per cent of that introduced as feed. These experiments indicated definitely that, in the presence of hydrogen, organic sulfur compounds (including thiophenes) can be catalytically decomposed more or less selectively.

#### EQUIPMENT AND PROCEDURE

On the basis of the foregoing experiments and a consideration of the various aspects of catalytic processes as described in published articles, it was concluded that continuous vapor-phase treatment in the presence of hydrogen would be the most feasible commercial process for the catalytic desulfurization of gasoline fractions. Figure 2 is a diagram of the equipment used in the further study of this problem.

The following typical procedure was employed for atmospheric pressure operation:

Approximately 100 ml. of catalyst were introduced into the catalyst chamber; the latter was brought to reaction temperature, usually 650° F. or higher, over an interval of approximately 3 hours, hydrogen being passed through the catalyst bed during the entire period. When the catalyst section reached a temperature of approximately 400° F., feed stock admixed with hydrogen was introduced into the vaporizing section, maintained at approximately 400° F.; the vaporized material was passed through the clay pretreating section, likewise maintained at about 400° F.,

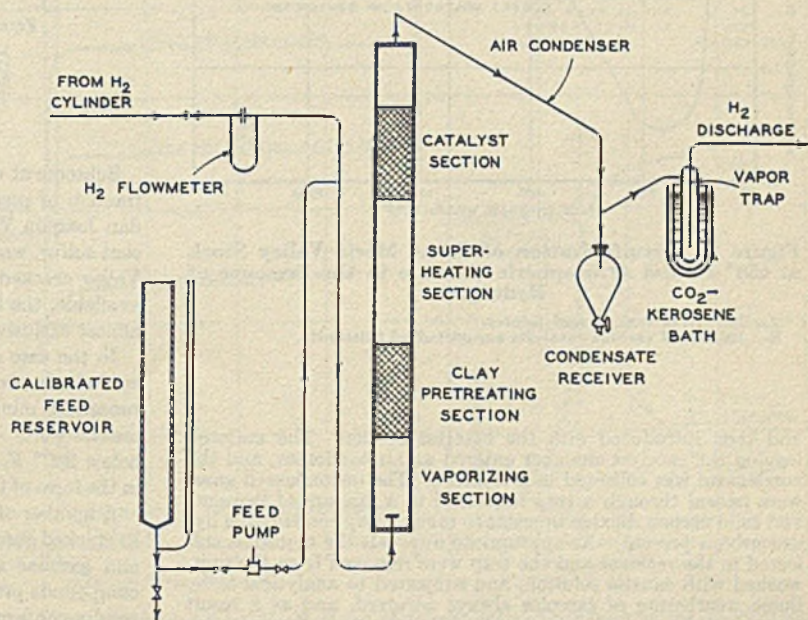


Figure 2. Catalytic Desulfurization Unit



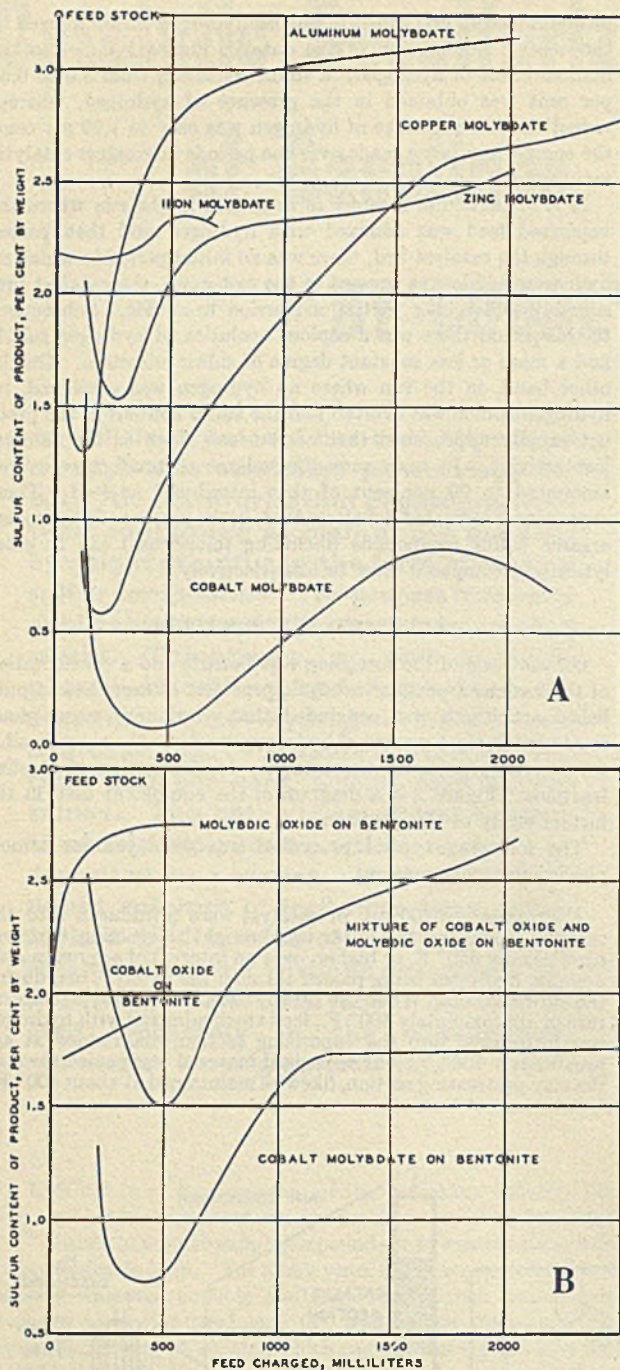


Figure 3. Desulfurization of Santa Maria Valley Stock at 650° F. and Atmospheric Pressure in the Presence of Hydrogen

- A. 100 ml. of various molybdates.  
 B. 100 ml. of various catalysts supported on bentonite.

and then introduced into the catalyst section. The material leaving the catalyst chamber entered an air condenser, and the condensate was collected in a receiver. The uncondensed gases were passed through a trap immersed in a mixture of kerosene and solid carbon dioxide in order to remove any condensable hydrocarbons present. At appropriate intervals the materials collected in the receiver and the trap were removed from the unit, washed with caustic solution, and subjected to analytical tests. Some weathering of samples always occurred, and as a result any small amounts of lower-boiling hydrocarbons formed were largely lost prior to testing of the products.

In later experiments where operating pressures as high as 250 pounds per square inch gage were employed, a similar procedure was followed except that the temperatures of the vaporizing and clay pretreating sections, as well as that of the reactor at the time of feed introduction, were higher to prevent condensation. The equipment was similar to that shown in Figure 2, except that the feed chamber was pressured with hydrogen at reaction pressure, a valve was inserted in the line between the main condensate receiver and the carbon dioxide-kerosene bath to reduce the reaction pressure to atmospheric pressure and to control the hydrogen flow, and the hydrogen flowmeter was placed in the hydrogen discharge line.

Experimental work indicated that in the case of most of the compounds considered, 650° F. represented a rather critical temperature. If the catalyst temperature was decreased much below this figure, there was a rapid decline in activity with a resultant decrease in the degree of desulfurization. A more or less constant desulfurization activity was exhibited at temperatures between 650° and 800° F. with little or no evidence of hydrocarbon decomposition. However, catalyst activity was maintained over a much longer interval at 650° to 700° F. than at more elevated temperatures; 650° F. was selected, therefore, as the operating temperature for comparing various catalysts. Furthermore, to magnify the differences in activities of various catalytic materials, a high-sulfur stock, Santa Maria Valley viscosity-reduction pressure distillate, was employed, and the experiments were conducted at atmospheric pressure.

Vapor-phase clay pretreatment of the stock was instituted primarily to ensure the removal from the vapors of readily polymerizable materials which might deposit on the catalyst and lead to coke formation with a resultant decrease in catalyst activity. Subsequent experimental work disclosed that, by employing a relatively large vaporizing section maintained around 600° F., small amounts of reactive materials were immediately removed as a cokelike deposit, thereby obviating the necessity for clay treatment. As a consequence, vapor-phase clay treatment was employed in most of the earlier experiments using Santa Maria Valley distillates and was eliminated in favor of an enlarged vaporizing section during later work with San Joaquin Valley pressure distillate as feed stock.

#### FEED STOCKS

Initially the feed stock chosen for study was pressure distillate derived from the viscosity reduction of Santa Maria Valley residuum. This material was believed to present a particularly difficult treating problem because the major portion of the sulfur is present in the form of difficultly removable thiophene-type compounds. The following data indicate the distribution of sulfur among the various types of sulfur compounds present in a 200–300° F. fraction of the above-mentioned distillate:

Form of S Present	Actual S Present, % by Wt.
Mercaptans	0.208
Disulfides	0.004
Sulfides	0.6
Thiophenes	2.19
Total	3.00

Subsequent experimental work disclosed that the 200–400° F. fraction of pressure distillate, derived from thermal cracking of San Joaquin Valley naphthenic crude oil and containing 0.7 per cent sulfur, was equally as difficult to desulfurize as Santa Maria Valley cracked distillate. Since this material was more readily available, the latter part of the investigation utilized this stock almost exclusively.

In the case of both stocks, the fraction boiling below 200° F. was eliminated from consideration, primarily because such a procedure minimized vaporization losses and facilitated experimental work. Furthermore, an analysis of the material boiling below 200° F. disclosed that the sulfur present was principally in the form of the more readily removable mercaptans.

A number of other gasoline feed stocks were investigated, such as cracked gasolines of wider boiling range, straight-run gasolines, and gasoline extracts in which substantially all of the sulfur compounds present in the parent stock were concentrated. The results confirmed the expectation that the thiophenes would be the most difficult sulfur compounds to decompose. The products



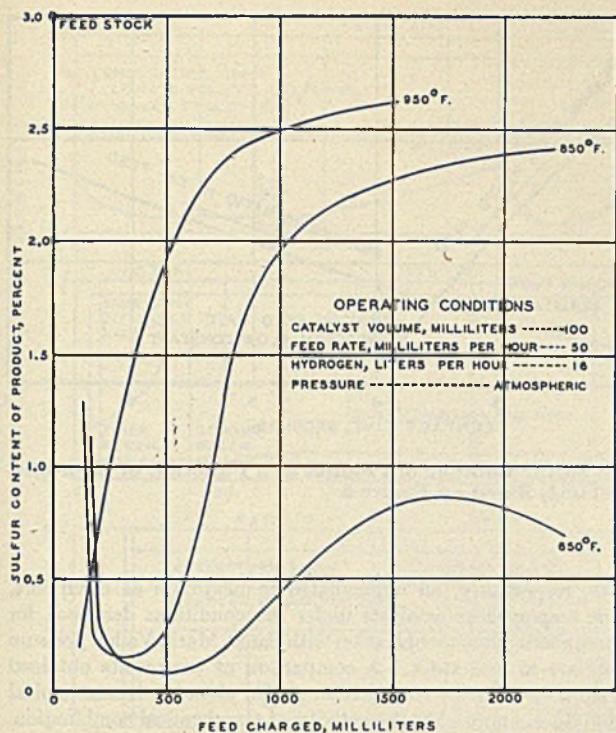


Figure 4. Effect of Variations in Operating Temperature on Desulfurization of Santa Maria Valley Stock with Cobalt Molybdate

were invariably sweet to the doctor test, showing quantitative conversion of mercaptans. Furthermore, under conditions resulting in substantial desulfurization of the above two stocks, all other gasoline stocks tested were desulfurized to an equal or greater degree. The discussion will therefore be confined largely to the desulfurization of these two stocks.

Early in the investigation it was observed that the feed pump introducing Santa Maria Valley stock into the vaporizing section was operating more and more erratically with each successive run. This trouble was not encountered when freshly distilled pressure distillate was employed but only when using stock which had stood for several days after fractionation. The difficulty was traced to the presence in

the aged distillate of an excessive amount of gum which was separating as a solid precipitate and coating the pump check valves. To determine the effect on sulfur reduction of various types of stock pretreatment to remove gums, a series of experiments was conducted with the following feed stocks: aged pressure distillate; liquid-phase, zinc chloride treated, aged pressure distillate; freshly distilled pressure distillate; and liquid-phase, zinc chloride treated, freshly distilled pressure distillate.

Although not of sufficient duration to determine the effect on catalyst life, these experiments indicated that stock pretreatment of the type used had little or no effect on the degree of sulfur reduction. Therefore, in order to minimize experimental difficulties, most of the runs employing Santa Maria Valley stock were conducted with a 200–300° F. fraction which had been zinc chloride treated and freshly distilled prior to introduction into the treating system. In later work with San Joaquin Valley cracked distillate, zinc chloride treatment was dispensed with as it was possible to maintain a supply of reasonably fresh stock.

#### ACTIVE DESULFURIZATION CATALYSTS

Since various molybdenum compounds had been reported in the literature as cracking-hydrogenation catalysts, the initial investigational work was centered on a study of such compounds as possible selective desulfurization catalysts. A number of materials exhibited definite catalytic activity of the desired type, and the data obtained in testing the more active substances are presented graphically in Figure 3A.

Of the various materials considered, cobalt molybdate is by far the most active, both as regards the initial period of high activity and the subsequent period of relatively constant desulfurization. This compound was therefore selected for further study. Cobalt molybdate may be considered a chemical union

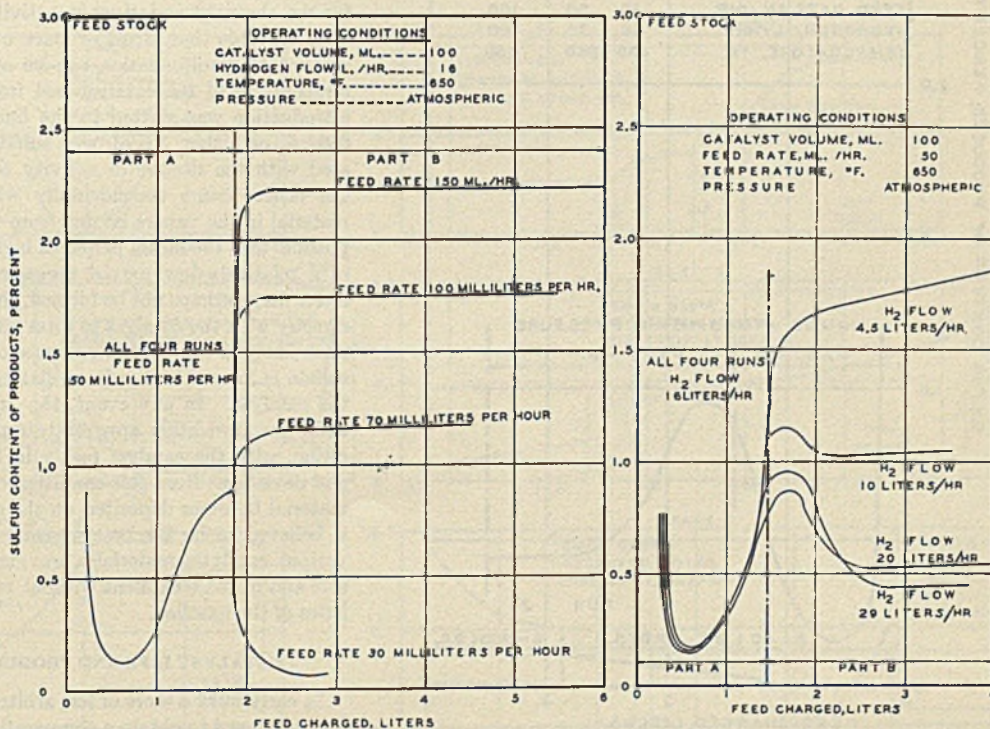


Figure 5. Effect of Variations in Feed Rate (left) and in Hydrogen Flow (right) on Desulfurization of Santa Maria Stock with Cobalt Molybdate



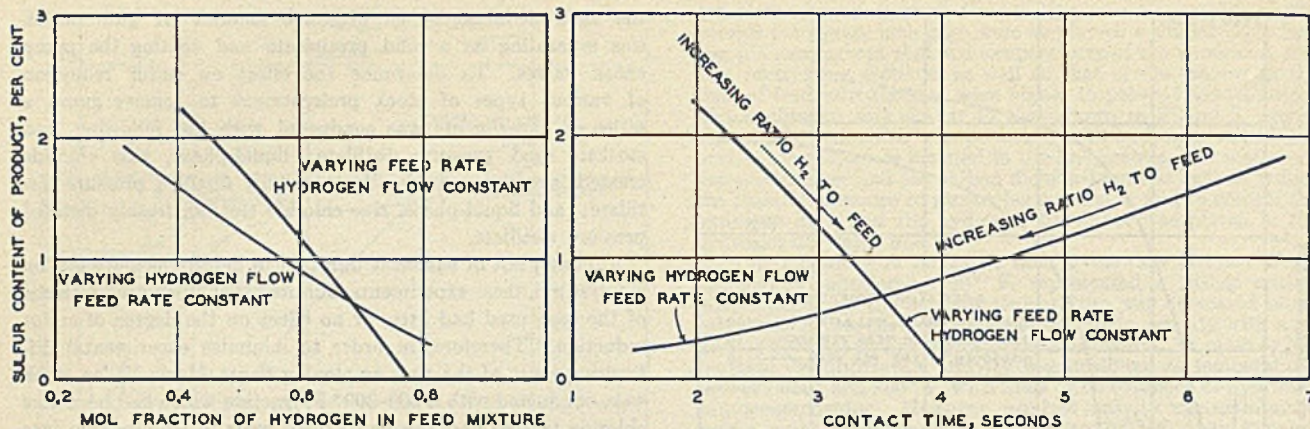


Figure 6. Effect of Variations in Feed Rate and Hydrogen Flow on Sulfur Content of Product as a Function of Hydrogen Partial Pressure and of Contact Time, Based on Figure 5

of cobalt oxide and molybdic oxide,  $\text{CoO} \cdot \text{MoO}_3$ . To demonstrate that the high activity of this compound is due to an actual chemical combination of these oxides with a resultant alteration of the spacing of the various atoms in the crystal lattice, four experiments were conducted; cobalt oxide, molybdenum trioxide, a mechanical mixture of these two oxides, and cobalt molyb-

date, respectively, all impregnated in bentonite as a support, were employed as catalysts under the conditions described for atmospheric pressure operation with Santa Maria Valley pressure distillate as feed stock. A comparison of the results obtained (Figure 3B) reveals that neither oxide, alone or in mechanical admixture, approaches the activity of the chemical combination.

#### CHARACTER OF GRAPHS

Particular attention should be called to the graphs, which show the sulfur content of the product at any instant expressed as a function of the total volume of feed passed over the catalyst up to the particular point under consideration. In most instances there was an initial rapid increase in activity to a point at which maximum desulfurization was obtained, followed subsequently by a more or less rapid decrease in activity to a point of relatively constant desulfurization. At present the causes for the observed variations in activity are not definitely known. It is probable that a major part of the initial increase in the amount of desulfurization can be attributed to the increase in temperature of the catalyst bed from the point at which feed introduction was started to the final operating temperature of 650° F. or higher. Hydrogen sulfide may be intimately associated with the decline in activity to the "steady state", since the latter occurs coincidentally with the appearance of this material in the vapors issuing from the catalyst chamber. It is possible that the initial period of high activity is realized because of a relatively low partial pressure of hydrogen sulfide. The latter may perhaps not be formed, the sulfur compounds reacting directly with the catalyst to form a metallic sulfide; but what is more likely in view of the influence of hydrogen is that hydrogen sulfide is formed and is immediately removed by reaction with the catalyst. In any event, the final period of relatively constant desulfurization apparently represents an equilibrium condition, with the catalyst partly in the form of metallic sulfide, and deviations from this condition occur only slowly as cokelike material becomes deposited on the catalyst. This latter period is believed to be the best measure of the relative activities of various catalytic materials, provided the desulfurization is the sole aim of the treatment without regard to the other characteristics of the gasoline.

#### CATALYST LIFE AND PRODUCT SULFUR CONTENT

In early work a more or less arbitrary set of reaction conditions was employed to obtain a comparative measure of the efficiencies of various catalysts. The subsequent work was concerned with a determination of the important operating variables and their

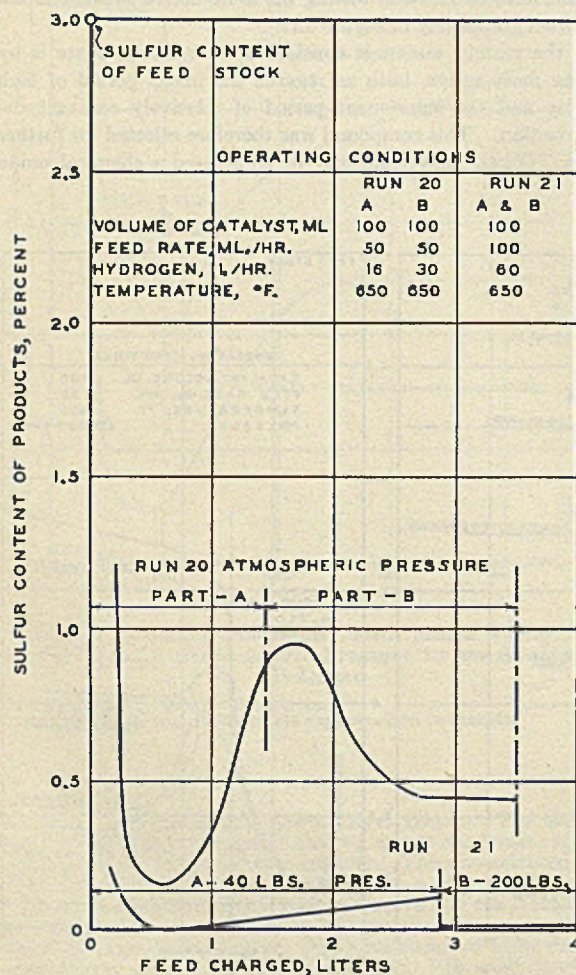


Figure 7. Effect of Variations in Operating Pressure on Desulfurization of Santa Maria Valley Stock



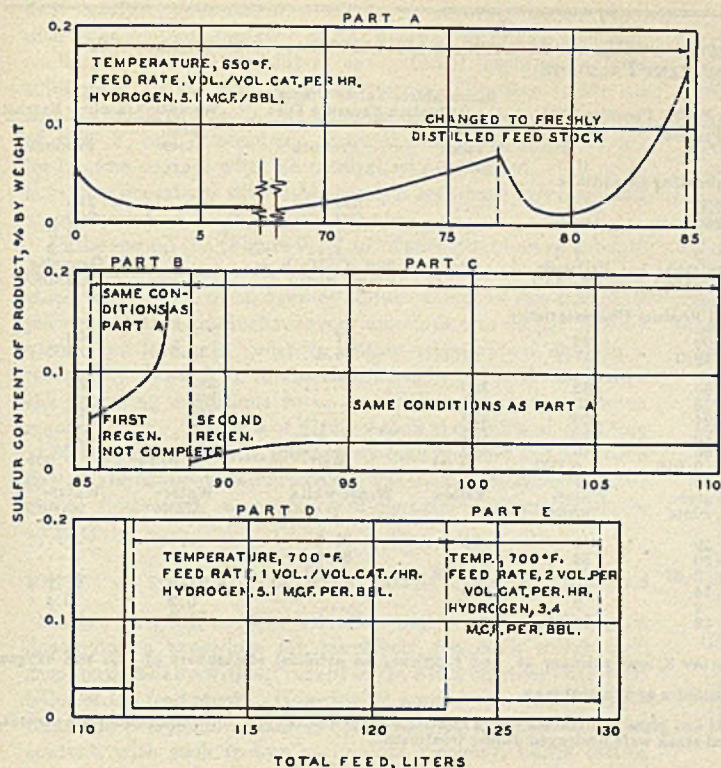


Figure 8. Exhaustion Test of 100 ml. of Cobalt Molybdate-Alumina Catalyst

effect on catalyst life and desulfurization. It appeared reasonable to suppose that approximately the same results would be obtained with various catalysts of similar activity; therefore,

of catalyst per hour, a greater amount of desulfurization was obtained than in run 20 conducted at atmospheric pressure and a feed rate of only 0.5 volume of feed per volume of catalyst per hour.

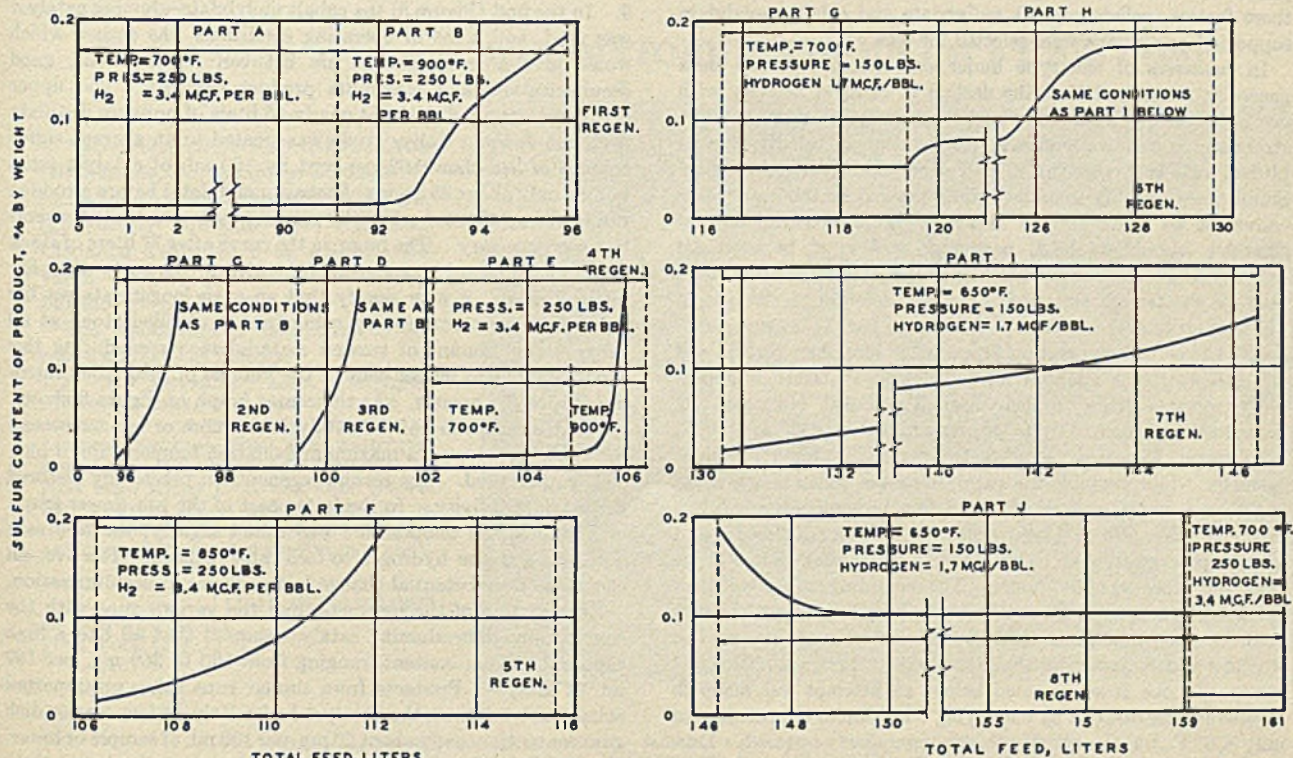


Figure 9. Exhaustion Test of 50 ml. of Cobalt Molybdate Catalyst

pelleted cobalt molybdate was selected since it could be readily prepared.

**EFFECT OF TEMPERATURE.** A series of experiments was conducted in which reaction temperatures of 650°, 850°, and 950° F. were employed, all other factors being maintained constant. The results in Figure 4 show that at atmospheric pressure catalyst activity declines rapidly when operating at temperatures in the neighborhood of 850° F. and higher.

Two other series of runs were conducted at atmospheric pressure; in one the feed rate was varied and in the other, the hydrogen rate, other factors being maintained constant (Figure 5). Figure 6 shows graphically the sulfur content of the various steady-state products from these two series of experiments expressed as a function of the mole fraction of hydrogen in the reaction chamber vapors and of the calculated time of contact. The information in Figure 6 shows readily that, when desulfurization is the sole aim without regard to other characteristics, the partial hydrogen pressure in the reaction zone more or less directly controls the sulfur content of the product while the time of contact is of secondary importance.

These results suggest that operation at hydrogen pressures above atmospheric would increase the amount of desulfurization obtained with a given weight of catalyst, and this conclusion is confirmed by the results of runs 20 and 21 (Figure 7). In run 21, conducted at pressures of 40 and 200 pounds per square inch gage and a feed rate equivalent to one volume of liquid stock per volume



TABLE I. CHARACTERISTICS OF FEED STOCKS TREATED BY COBALT MOLYBDATE DESULFURIZATION PROCESS AND OF RESULTANT PRODUCTS

	San Joaquin Valley Pressure Dist.		Santa Maria Valley Viscosity-Reduction Pressure Dist.		Aromatic Gasoline Extract		
	Feed stock	Product A	Product B	Feed stock	Product	Feed stock	Product
Operating Conditions							
Catalyst temperature, ° F.	...	750	850	....	800	....	725
Reactor pressure, lb./sq. in. gage	...	250	150	....	200	....	100
H <sub>2</sub> flow rate, M cu. ft./bbl. feed <sup>a</sup>	...	5.1	5.1	....	3.4	....	3.0
Feed rate, vol./vol. of catalyst/hr.	...	2	1.3	....	1.1	....	1.0
Catalyst	...	Pelleted CoMoO <sub>4</sub>	Pelleted CoMoO <sub>4</sub>	....	30% CoMoO <sub>4</sub> + 70% Al <sub>2</sub> O <sub>3</sub>	....	Granular CoMoO <sub>4</sub>
Feed and Product Characteristics							
Product recovery, % of feed vol.	...	100	98	....	97	....	98
Gravity, ° A. F. I. at 60° F.	46.2	49.2	47.7	49.1	56.4	35.5	35.6
Engler distillation temperature, ° F.							
Initial	192	180	185	190	....	284	280
10% over	243	230	242	232	....	294	293
50% over	303	294	303	275	....	305	305
90% over	377	375	383	325	....	337	336
Maximum	403	408	446	352	....	389	365
Sulfur content, % by wt. <sup>b</sup>	0.63 <sup>c</sup>	0.018	0.000	3.0 <sup>e</sup>	0.01	0.018 <sup>d</sup>	0.001
Copper-dish gum content, mg./100 ml.	915	20	7	....	....	....	....
Color	Brown	Water-white	Water-white	Yellow	Water-white	Water-white	Water-white
Knock rating, C. F. R. Motor Method							
Clear	73	59	62	70	60.5	....	....
3.0 ml. tetraethyllead/gal.	79	80	84	75	80.0	....	....
Lead susceptibility slope	0.55	2.05	2.40	0.49	1.90	....	....
Solubility in 99% H <sub>2</sub> SO <sub>4</sub> , % by vol.	35	14	21	33	10	71.2	71.7
Olefins by bromide-bromate, % by vol.	49 <sup>f</sup>	2	7	....	....	0.2	0.4
Aromatics (acid acyl.-olefins), % by vol.	...	12	14	....	....	71.0	71.3/

<sup>a</sup> Measured at atmospheric pressure.

<sup>b</sup> Determined by Ethyl lamp method (4, 5), using burner 2b, absorber 3, and chimney 4b, and supplying an artificial atmosphere of CO<sub>2</sub> and oxygen instead of air.

<sup>c</sup> The sulfur compounds present were about 2/3 thiophenes and 1/3 sulfides and mercaptans.

<sup>d</sup> The sulfur compounds present were substantially all sulfides.

<sup>e</sup> This test is reliable only in the case of low sulfur content products and gives high values where relatively large amounts of sulfur compounds are present.

<sup>f</sup> Approximately 85% of the phenolic compounds present in the feed stock were destroyed during treatment.

#### REGENERATION AND PROLONGED USAGE OF CATALYSTS

Aside from initial activity, the value of any catalyst is primarily determined by two factors—namely, the ease with which the initial activity can be restored after it has declined during use, and the number of times such regeneration can be accomplished before it is necessary to discard the catalyst. To evaluate these factors, pelleted cobalt molybdate and cobalt molybdate supported on alumina were selected for test.

In processes of the type under consideration it has been generally recognized that the decline in catalyst activity with use is due to the deposition of cokelike materials in the catalyst structure. As a consequence, regeneration is usually accomplished readily by controlled oxidation to remove the carbon. Simultaneously, any metallic sulfide present in the catalyst is converted to oxide. Since these reactions generate a considerable amount of heat, particular care must be exercised in order to avoid local overheating of the catalyst which would lead to shattering, sintering, or other deleterious changes in physical structure.

A number of regeneration procedures were then tested, and the following was adopted for both catalysts, since it apparently restored them to their original activity: Nitrogen was passed through the catalyst bed, maintained at 650° to 700° F. This served to remove any volatile materials present. Subsequently, while keeping the catalyst in the same temperature range, the major portion of the carbon present in the catalyst chamber was oxidized by treatment with a mixture of nitrogen and air, the proportion of air being increased from about 5 to 100 per cent over a period of 6-7 hours. The remaining carbon was then removed by passing air alone through the catalyst bed while increasing the temperature from 700° to 950° F. over a period of 2 hours and maintaining that temperature for an additional 2 hours. In one case, as noted below, an attempt was made to regenerate the catalyst by employing a maximum temperature of only 850° F., but the activity was not completely restored. During all of the regenerations some sulfur dioxide was evolved,

indicating the reconversion of the cobalt molybdate from a partial sulfide to an oxide.

The approximate useful life between regenerations which can be expected under various operating conditions with cobalt molybdate catalysts, and the effect of repeated regenerations on this life are illustrated by the runs presented in Figures 8 and 9. In the first (Figure 8) the cobalt molybdate-alumina catalyst was used, and a set of operating conditions was chosen which would give a long catalyst life between regenerations, good desulfurization, and maximum product recovery. The upper graph of Figure 8 shows that nearly 85 liters of pressure distillate from San Joaquin Valley crude was treated to an average sulfur content of less than 0.02 per cent by 100 ml. of catalyst (containing only about 25 grams of cobalt molybdate) before a sudden rise in the sulfur content of the product indicated that regeneration was necessary. The hump in the curve after 77 liters of stock had been processed was coincidental with a change to a freshly distilled stock; it may signify that an even longer catalyst life could have been realized by using freshly distilled stock at all times. The amount of treated material recovered during this run amounted to 99 per cent of the volume of feed stock introduced into the reactor. As the center graph of Figure 8 shows, the first regeneration of the catalyst was more or less unsuccessful, probably because a maximum oxidation temperature of only 850° F. was used. The second regeneration practically restored the catalyst activity. In the latter part of the run (lower graph of Figure 8) the temperature was raised slightly, the feed rate doubled, and the hydrogen to feed ratio reduced. The over-all effect was no substantial change in the degree of desulfurization.

Examination of the products from the various runs with the cobalt molybdate-alumina catalyst showed that all had a high copper-dish gum content, ranging from 160 to 360 mg. per 100 ml. of sample. Products from similar runs using unsupported cobalt molybdate as the catalyst had relatively low copper-dish gum contents, usually about 20 mg. per 100 ml. of sample or lower. Tests revealed that, in general, the use of supported cobalt molyb-



date catalysts gave rise to products of relatively high copper-dish gum content, but that it was possible to reduce this gum content by a small amount of conventional inhibitor or by a subsequent vapor-phase clay treatment. The clay treatment was particularly effective at temperatures in the neighborhood of 400° F. and atmospheric pressure. Clay treatment of the feed before contact with the catalyst was ineffective. All products from operations with either catalyst contained only negligible amounts of A. S. T. M. preformed gum.

In the second run (Figure 9) 50 ml. of pelleted cobalt molybdate catalyst (78 grams) were used. At 700° F. over 91 liters of stock was treated to an average sulfur content of less than 0.02 per cent, with a product recovery amounting to 99 per cent by volume of feed. In order to obtain regeneration data in a reasonably short time, it was then thought advisable to change the operating conditions so as to shorten the cycles between regenerations. The data of Figure 9 show the results of operating at 850° and 900° F. with moderately high pressure and hydrogen flow. The catalyst used in this run was subsequently regenerated eleven times with no evidence of permanent deterioration in activity.

#### EFFECT OF DESULFURIZATION ON OTHER CHARACTERISTICS

In the foregoing sections attention was focused principally on developing a procedure for selectively removing sulfur from gasoline distillates without regard to the effect on other characteristics of the feed stock. However, in normal commercial operations the petroleum refiner is concerned, in addition to sulfur content, with such factors as product recovery, knock rating, olefin content, aromatic content, changes in Engler distillation temperature, etc. Table I, therefore, presents detailed information on the properties of a number of different feed stocks and of the products derived therefrom under conditions of treatment which would be employed for maximum desulfurization efficiency and product recovery.

Under the conditions of operation selected, the olefinic, diolefinic, and phenolic compounds appear to be largely hydrogenated while the aromatic hydrocarbons are substantially unaffected. Owing to the hydrogenation of the olefinic hydrocarbons, treatment of thermally cracked distillates lowers the clear knock rating. However, as a result of increase in lead susceptibility accompanying the reduction in sulfur content, the knock rating of the treated material containing 3.0 ml. of tetraethyllead per gallon is ordinarily higher than that of the original stock containing the same proportion of tetraethyllead. In the case of straight-run and catalytically cracked distillates, which normally contain relatively small proportions of olefinic hydrocarbons, the desulfurization treatment is accompanied by only negligible changes in clear octane rating. Products of good color and stability can be readily obtained, and as previously indicated, the yield of treated material usually amounts to about 99 per cent by volume of the feed stock.

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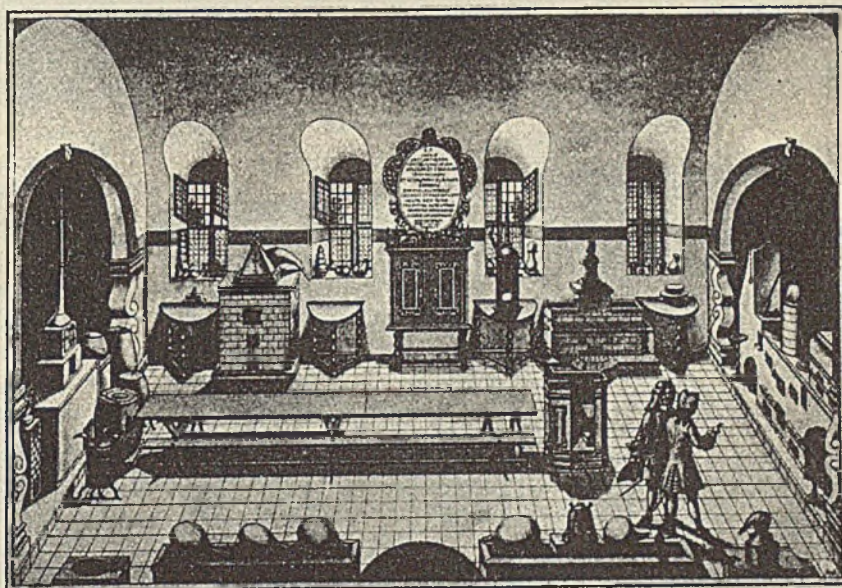
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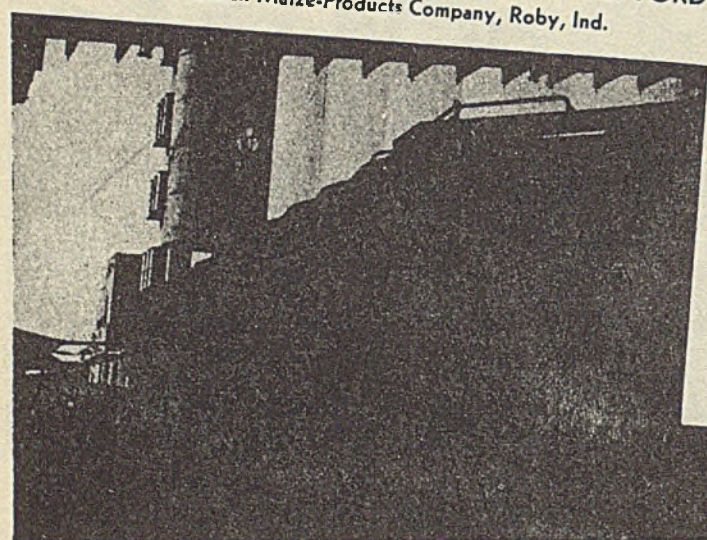




# WAXY CORNSTARCH

*As a Replacement for Tapioca*

H. H. SCHOPMEYER, G. E. FELTON, AND C. L. FORD  
American Maize-Products Company, Roby, Ind.



Waxy corn which had been developed to a high-yielding hybrid was grown on a commercial scale and wet-processed with only minor changes in operating procedure. The waxy starch has a clear, soft, nongelling paste and has been found to replace high-grade tapioca satisfactorily in dextrans, adhesives, paper coatings and sizes, textile sizes and finishes, print gums, and food products. It is chemically different from other starches in that it is substantially pure amylopectin or branched-chain portion of starch. It is to be expected that such a starch will find special uses where it is more suitable than the present commercial starches.



OVER the six-year period prior to the war, the United States imported annually about 350 million pounds of duty-free starch (14). This was chiefly tapioca, of which about 93 to 97 per cent came from the Netherlands Indies and most of the remainder from Brazil and the Dominican Republic. The tapioca imported was of two principal grades: (a) medium-grade flours which are less clean and uniform and generally sell at a price under that of cornstarch; (b) high-grade tapioca which is a clean, pure, uniform product selling at a price generally somewhat above cornstarch.

Because of its price the medium grade has been the chief competitor of cornstarch and before the war, when it was available in quantity, supplanted cornstarch in many instances. The high-grade tapioca starch was imported for special uses for which corn is not well suited, such as envelope gums, remoistening glues, and certain food products such as minute tapioca. The analysis by Hosking (6) of tapioca and sago importations as a function of price indicates that these starches supplied a market of approximately 100 million pounds annually in the period 1926 to 1932 when their price was about equal to cornstarch. This quantity of tapioca is sold because of special properties which ordinary cornstarch does not have. The starch from waxy corn has been found (16) to possess properties which should allow it to replace tapioca in many of these special uses.

Attention was first called to the peculiar properties of waxy corn in 1908 by a missionary who found it growing in China and sent samples of the seed to G. N. Collins of the U. S. Department of Agriculture (9). It was found that the new corn had a different type of endosperm and that its cut surface resembled a hard wax; hence the term "waxy" was used to identify this type of corn. The name "waxy maize" thus originated because of the appearance of the corn and not because it contained wax. It was found later that the starch from this corn stained red with iodine (16) instead of blue as does ordinary starch. Little further work was done on waxy corn except to study it genetically and show that it is recessive when crossed with ordinary American varieties (7).

When viewed under a microscope, waxy and common cornstarch are similar in size and general granule shape (Figure 1). A typical sample of waxy starch has an average size of 11.83 microns and a range of 3.7 to 23 microns.

Examination of the curves given by Morgan (11), where transparency is plotted against temperature of the paste, indicates that waxy cornstarch gelatinizes rather sharply, starting at 70° C.

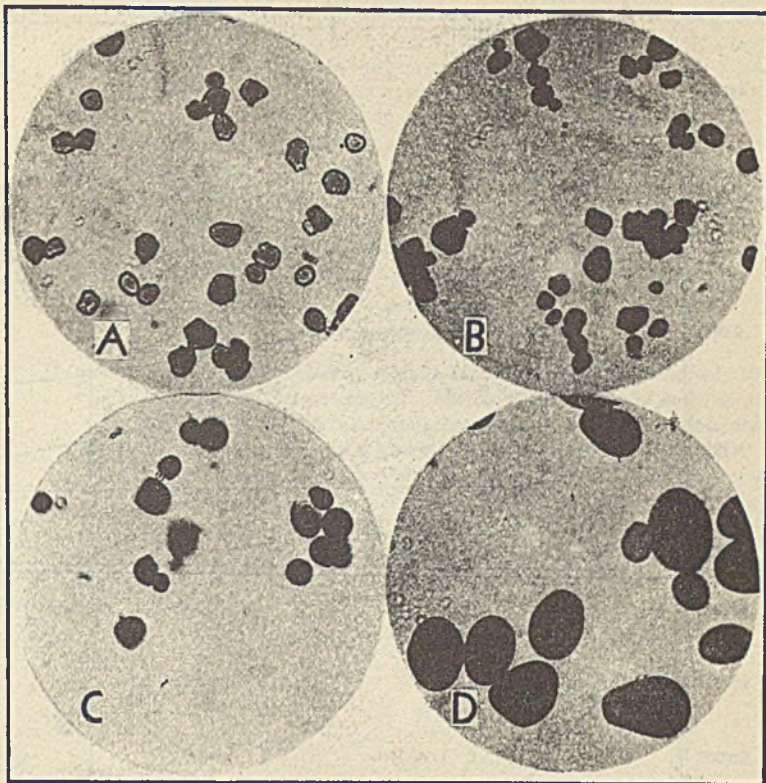


Figure 1. Photomicrographs of Waxy Corn (A), Common Corn (B), Tapioca (C), and Potato (D), Starches ( $\times 450$ )

and proceeding uniformly and completely over a range of only 8° while the gelatinization of ordinary cornstarch starts at 64° C. and continues regularly over a range of 30°. The shape of the gelatinization curve for waxy starch resembles that of tapioca rather than cornstarch although it starts about 9° higher.

The hot viscosity of dilute waxy cornstarch pastes was reported (5) to be greater than that of tapioca at 75° to 90° C. However, they are less resistant to breakdown on continued cooking than are tapioca pastes; Figure 2 shows comparative hot viscosities of potato, tapioca, waxy, and common cornstarch in concentrations of one part of starch to ten parts and to twenty parts of water.

#### CHEMICAL PROPERTIES

The properties of waxy cornstarch acquire added significance when viewed in connection with the modern concepts of starch chemistry. Potato, corn, and tapioca starches have been shown to consist of two fractions. One is a straight-chain glucose polymer which comprises about 22 per cent of the material in common cornstarch and about the same or slightly less in potato and

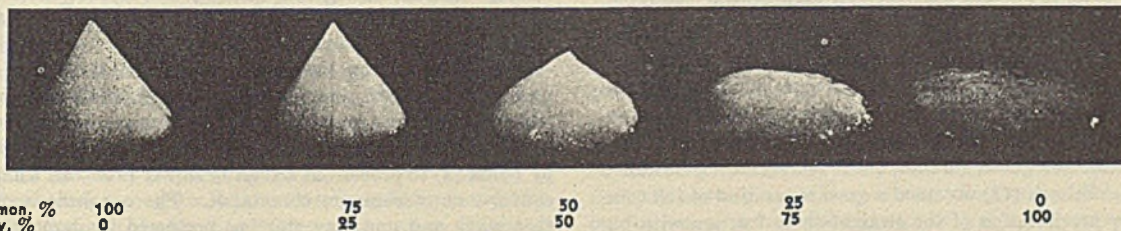


Figure 3. Gels of Common and Waxy Cornstarch at a Concentration of One Part Starch to Ten Parts Water



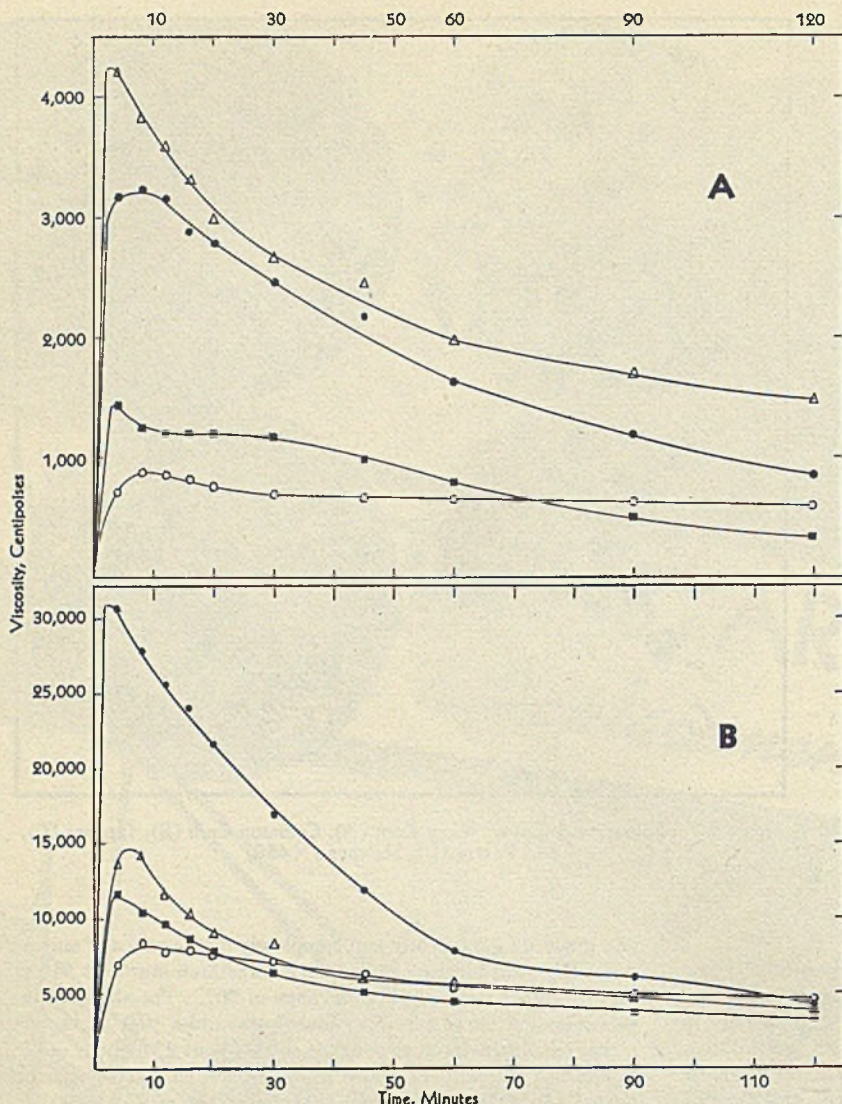


Figure 2. Hot Viscosities of Waxy Corn, Common Corn, Tapioca, and Potato Starches Cooked in a Boiling Water Bath

A. 1 part of starch in 20 parts of water  
 B. 1 part of starch in 10 parts of water  
 Δ waxy corn, ● potato, ■ tapioca, ○ common corn

tapioca. The other component is a branched-chain glucose polymer of much greater molecular weight and remarkably different properties. These fractions of starch have been separated by three methods. Meyer (10) extracted starch with warm water and, despite the fact that this method is by no means quantitative, established that the main constituent in the extract was a straight-chain glucose polymer whereas the other fraction had a branched-chain configuration. The straight-chain component was named "amylose" and the branched-chain portion, "amylopectin". Thus the terms amylose and amylopectin, originally used by Maquenne and Roux (9), have been given a definite chemical meaning which should eliminate much of the confusion in the starch literature resulting from indiscriminate use of these terms. A second method for the separation of the two components of starch was described by Pacsu and Mullen (12) who found that the straight-chain component was selectively adsorbed by cotton. Schoch (13) obtained a good separation of the components by precipitation of the straight-chain fraction with butanol.

The amyloses from corn, potato, and tapioca have distinctly different properties, as do also the various amylopectin fractions. Thus the properties of corn, tapioca, and potato starch differ because their components are different although they are present in about the same amounts. It has been suggested that potato amylose is of greater molecular size than is corn amylose (1). A complete explanation of the differences between these similar fractions of the different starches should result from future investigations.

The iodine color of the amylose is deep blue and of the amylopectin fraction, reddish purple. The red-violet color given by waxy starch with iodine indicates the similarity of this starch to the amylopectin of other starches. This conclusion is substantiated by the report of Schoch (13) that waxy cornstarch gave no precipitate with butanol. It is also confirmed by a quantitative test developed by Bates, French, and Rundle (1) which measures the amylose content of starches by a method based on their formation of iodine complexes. This method also shows that waxy cornstarch contains no straight-chain component and is therefore pure amylopectin. As a result of osmotic pressure measurements on the acetates of waxy starch and the amylopectin fraction of ordinary cornstarch, Hixon and Foster (4) concluded that the two materials are identical. This conclusion was supported by measurement of the viscosities of waxy starch and of ordinary corn amylopectin, dispersed in ethylene diamine solution.

Concentrated waxy cornstarch pastes remain fluid even after standing for several days (Figure 3). This result is due to the absence of the gel-forming constituent which is the straight-chain portion. The fluid character of waxy cornstarch pastes is found not only in the starch as prepared but also in the usual modifications such as thin boiling starches and dextrans which may be made from it. It has also been pointed out that waxy pastes are difficult to retrograde.

Waxy cornstarch has an alkali number of 4.1, according to Schoch (13), who also lists an average value of 5.6 for the amylopectin of common cornstarch and 25.0 for the amylose fraction. Thus, alkali numbers, butanol precipitation tests, iodine adsorption, gel characteristics, and viscosity in ethylene diamine solutions all give confirmatory evidence to the completely branched nature of waxy cornstarch molecules.

Waxy and ordinary cornstarch also differ in the clarity of their pastes. The waxy pastes are quite clear, both hot and cold, whereas ordinary cornstarch quickly becomes opaque on cooling.

The conversion of waxy cornstarch by malt amylase was shown by Brink (2) to proceed at a slightly slower rate than comparable conversions of common cornstarch. The conclusions of Brink that waxy and nonwaxy starches possessed fundamental structural differences has now been confirmed since the amylose frac-



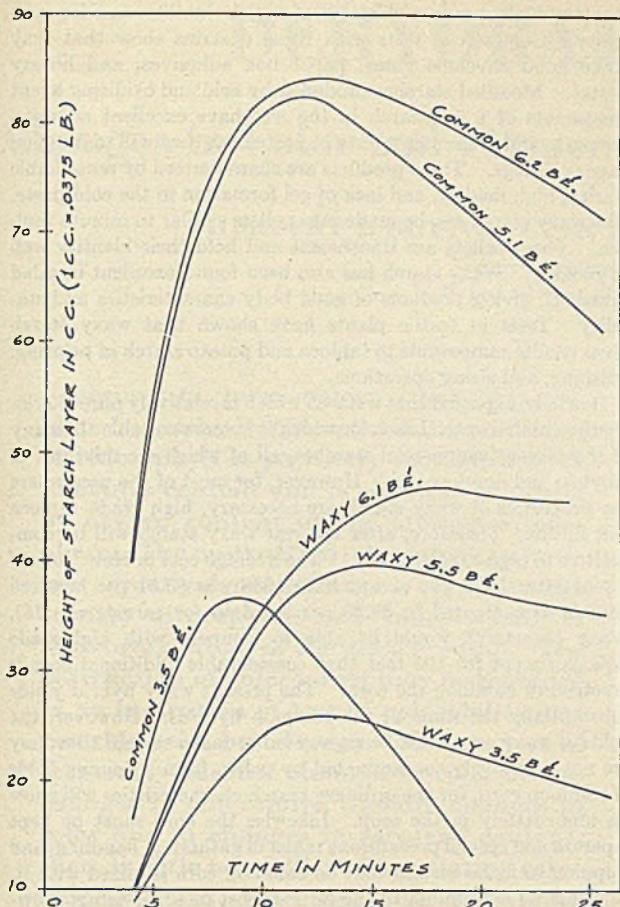


Figure 4. Comparison of Starch Settling Rate of Common with Waxy Corn from Starch-Gluten Slurry in 250-Cc. Graduated Cylinders

tion of starch is readily converted in 90–100 per cent yields (8) of maltose whereas only 57 per cent of amylopectin is converted to maltose by saccharifying enzymes.

The conversion of waxy starch by liquefying enzymes ( $\alpha$ -amylases) can be readily carried out. This result is in accord with the report (7) that amylopectin is much more readily attacked by this type of enzyme than is amylose.

#### SOURCES OF WAXY STARCH

Waxy starch is found not only in corn but also in some varieties of barley, rice, millet, and grain sorghum (5). It has been estimated that at least 50,000 acres of waxy sorghum are being grown in the United States. Most of this waxy sorghum is of the forage type and is primarily used for seed or feed. Grain from the waxy sorghums is somewhat difficult to store and possesses undesirable milling characteristics due to pigment which, during wet milling operations, stains the starch and is difficult to wash out. If varieties of waxy sorghum suitable for grain production and having desirable milling characteristics were developed, they might offer a practical source of waxy starch. At present the new hybrid waxy corn varieties seem to be the more promising source.

The original Chinese waxy corn was extremely low yielding and could not be considered a commercial source of waxy cornstarch. Considerable work on improved varieties has been carried out at the University of Wisconsin, University of Nebraska, Iowa State College, and the U. S. Department of Agriculture. Through a cooperative breeding program between the Iowa Agricultural Experiment Station and the Division of Cereal Crops and Diseases, Bureau of Plant Industry, a hybrid waxy Iowa 939 was developed.

Sufficient seed was available from yield test plots in 1941 to plant a considerable acreage in 1942. This, however, was not true hybrid seed but hybrid, one generation removed, or F-2 seed. Part was planted in Iowa and part in Indiana. The yield of corn was somewhat lower than from common corn hybrids under the same conditions but within the range expected from second generation hybrid seed. A quantity of open pollinated waxy corn obtained from the University of Nebraska was planted in Nebraska for the National Starch Products Company. The crop harvested from all these lots amounted to 17,000 bushels, and was combined and processed by American Maize-Products Company.

#### PROCESSING OPERATIONS

The plant processing of waxy corn was carried out similarly to regular wet corn processing. This is briefly outlined as follows: The corn is steeped in a countercurrent system for approximately 48 hours in process water containing sulfur dioxide at about 128° F. After steeping, the corn is screened and run through a Foos mill to crack it and free the germ. The germ is removed from the cracked corn by flotation, and the slurry, after germ separation consisting of fiber, starch, and protein, is further ground on a Buhr

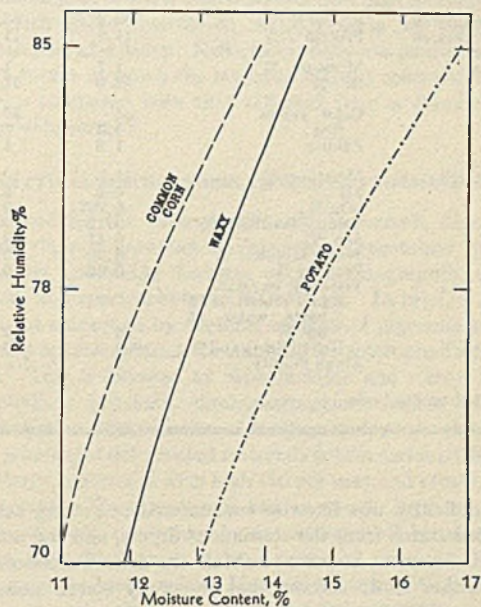


Figure 5. Moisture Absorption of Cornstarches at 85° F. and Various Relative Humidities

mill to permit good separation of the gluten and starch from the fiber by silk reels and shakers. The gluten and starch portion is run over tables and the starch allowed to settle out. The gluten tailing over the tables contains some starch which is further removed by settling this slurry to a higher concentration and then centrifuging.

The log of the processing operations for waxy starch as compared to ordinary corn is given in Table I; there is substantially no difference in the control analytical data obtained from the two operations. As for the operations in the plant which are controlled to a considerable extent by the experience of the operator as well as chemical analysis, it was found necessary to feed the tables the starch and gluten mixture a little more slowly than regular corn because the waxy starch seemed to separate more slowly from the gluten than ordinary cornstarch. This is shown by the comparative settling rates of waxy and common cornstarch and gluten as given in Figure 4.



TABLE I. COMPARATIVE ANALYSIS OF PRODUCTS IN THE WET MILLING OF WAXY AND COMMON CORN

Product		Common Corn	Waxy Corn
Corn	Moisture, %	18.44	20.8
	Protein <sup>a</sup> , %	9.68	10.55
	Starch <sup>a</sup> , %	70.50	67.34
	Water solubles <sup>a</sup> , %	4.98	7.67
	Ash <sup>a</sup> , %	1.23	1.49
	Oil <sup>a</sup> , %	3.90	4.59
Steeping	Time, hours	48	48
	Temperature, ° F.	128	128
	Moisture of steeped corn, %	46.0	46.8
	Steep water, ° Bé.	4.5	4.5
Fiber analysis			
	Coarse		
Fine	Starch <sup>a</sup> , %	10.0	10.6
	Moisture, %	66.3	65.3
Table feed liquor	Starch <sup>a</sup> , %	37.5	33.9
	Moisture, %	68.0	68.3
Sol. protein <sup>a</sup> , in raw starch, %	° Baumé	6.3	6.1
	Total protein <sup>a</sup> , %	7.67	9.69
	Soluble protein <sup>a</sup> , %	0.82	0.37
	Total solids, %	12.50	12.14
	Soluble solids, %	1.10	0.74
Gluten to settlers	From tables	0.580	0.48
	1st wash	0.110	0.107
	2nd wash	0.055	0.041
	3rd wash	0.032	0.030
Centrifuged gluten	Protein <sup>a</sup> , %	43.6	34.3
	Starch <sup>a</sup> , %	46.6	56.0
Centrifuged starch	Protein <sup>a</sup> , %	63.9	63.4
	Protein <sup>a</sup> , %	11.1	11.7
Dried germ	Moisture, %	1.7	1.75
	Oil, %	52.0	52.8
Crude oil	Color, yellow	35	37
	Red	5.5	7.5
	Acidity	1.8	1.5
Finished starch	Moisture, %	11.5	12.9
	pH	5.5	5.7
	SO <sub>2</sub> , %	0.007	0.007
	Acidity (as HCl), %	0.12	0.13
	Ash, %	0.11	0.12
	Water solubles, %	0.20	0.20
	Protein, %	0.30	0.30
	Viscosity, cc./min. 1 part starch to 17 parts water at 66° F.	90	23
	No. 10 Scott at 3%	200	30
	Alkali fluidity, cc.	2	No flow

<sup>a</sup> Reported on dry basis.

Some difficulty was likewise encountered in getting satisfactorily dried starch from the continuous dryers, and the rate was decreased somewhat in order to obtain the desired moisture content. Further study showed that the waxy starch seemed to come to equilibrium with a little higher moisture content than ordinary corn, as brought out by Figure 5. This graph shows that the waxy starch has somewhat higher moisture equilibrium than ordinary cornstarch but not quite so high as potato. For example, at 85° F. and a relative humidity of 78 per cent, the waxy starch had a moisture content of 13.2 as compared to 12.2 for common corn and 14.75 for potato starch. The same general relation held at other temperatures and humidities. The yield of starch was lower from the waxy than from common corn, although as indicated in Table I the starch content of the gluten and the fine and coarse fiber was sufficiently low to indicate satisfactory separation. This was due apparently in part to the waxy starch having a slightly lower starch content than common corn. This difficulty with the corn will no doubt be corrected by improved hybrids in future years.

#### USES

Laboratory investigations and experimental commercial runs with waxy corn indicate that it will have many uses and, in some instances at least, be definitely superior to tapioca starch. The starch dextrinizes readily, in fact considerably faster than ordinary

cornstarch, to produce dextrans of high solubility and low viscosity. Commercial tests with these dextrans show that they make good envelope gums, paper box adhesives, and library pastes. Modified starches produced by acid and oxidizing agent treatments of waxy starch in the wet have excellent adhesive strength, and preliminary tests indicate that they will make good paper coatings. These products are characterized by remarkable clarity, high fluidity, and lack of gel formation in the cold paste. The waxy starch can be made into pellets similar to minute tapioca. These pellets are translucent and hold their identity well in cooking. Waxy starch has also been found excellent in salad dressings, giving products of good body characteristics and stability. Tests in textile plants have shown that waxy starch gives results comparable to tapioca and potato starch in printing, finishing, and sizing operations.

It is to be expected that a starch which is relatively pure amylopectin will find special uses for which it is more suitable than any of the present commercial starches, all of which are mixtures of amylose and amylopectin. However, for most of the uses where the properties of waxy starch are necessary, high grade tapioca will suffice. Therefore, after the waxy starch will be competitive to high-grade tapioca. The average cost in New York of tapioca starch for the period 1929-1938 was \$3.51 per hundred pounds as compared to \$3.25 per hundred for cornstarch (16). Waxy cornstarch would be able to compete with high-grade tapioca except for the fact that considerable additional cost is involved in handling the corn. The present waxy hybrid yields substantially the same as the common hybrids. However, the fields of waxy corn must be segregated to make certain that they are not excessively contaminated by pollen from adjoining fields of common corn, for the ordinary starch characteristics will show up immediately in the crop. Likewise the corn must be kept separate and special precautions taken in gathering, handling, and shipping to make certain that no common corn is mixed with it. Considering a premium to the farmer, cost of supervising, growing, and harvesting as well as supplying hybrid seed, it is estimated that the cost per bushel of waxy corn compared to common corn will be in the neighborhood of 15-25 cents per bushel extra. When the waxy corn is available for processing in commercial quantity, this added premium will increase the cost of the starch by 45 to 75 cents per hundred pounds over common starch.

This year approximately 3000 acres of waxy corn were planted, largely in North Central Iowa and Nebraska. This should produce about 4,500,000 pounds of finished starch. At the same time a crop of waxy hybrid seed has been grown which can be used to plant a large acreage in 1944 if the demand warrants it.

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# DEHYDRATED SPINACH

## Changes in Color and Pigments during Processing and Storage

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Experiments have shown that, in unblanched dehydrated spinach, destruction of chlorophyll is positively correlated with moisture content and is affected very little by oxygen content of the storage atmosphere. The destruction of carotene is, however, greatly dependent upon oxygen in the storage atmosphere and independent of moisture content of the dried product. The destruction of chlorophyll may be regarded as an indication of loss of palatability and ascorbic acid, but does not indicate loss of carotene. Because changes in color due to changes in chlorophyll obscure changes in color due to changes in carotene content, there is little possibility of correlating carotene content with spectral reflectance measurements.



APPEARANCE, including color, is an important criterion in determining the acceptability of food products. In addition, there is the possibility that color may serve to indicate the degree of retention of certain nutritional values of the product. The relation of color to carotene (provitamin A) content is readily apparent in certain vegetables in which carotene is the predominant pigment; for example, sweet potatoes having 20 p. p. m. of carotene are light yellow in color, while carrots with 130 p. p. m. of carotene are deep orange (dry basis). In green vegetables visual estimation of the carotene is complicated by the presence of chlorophyll pigments that mask the yellow color of the carotene. However, in general, carotene is synthesized by green plants in a rather constant ratio to the chlorophyll (13). Hence the intensity of green may serve to indicate the carotene content—for example, the dark green of spinach and beet tops (40 p. p. m. of carotene) as compared to the pale green of lettuce and celery (6 p. p. m. of carotene).

In the processing and storage of green vegetables, the principal color change is a dulling and browning of the green. This change in color is due to the conversion of chlorophyll to its degradation product pheophytin (3, 4, 7, 11).

In the present paper, changes in color and pigment content that occur during blanching, dehydration, and storage of spinach are reported, and correlations between color, pigment content, nutritive value, and palatability, etc., are discussed. Essentially, there are two methods for the study of color changes of vegetable materials: (a) the physical analysis of the color of the light reflected from the material (for example, spectral reflectance data), and (b) the analysis of extracts of the material for concentrations

and light-absorbing properties of the pigments that contribute to color. Both methods were employed in the present study.

### DETERMINATION OF SPECTRAL REFLECTANCE

Dehydrated vegetables are prepared for reflectance measurements by being ground and then formed into a pad in a Carver press. The apparatus required for the study of light reflected from dehydrated materials has been met by a modification of the optical system of either a Cenco (5) or a Beckman spectrophotometer. With either instrument measurements are made upon three samples at a time. Reflectance data are presented in the form of curves in which the intensity of light reflected from the sample is compared with that reflected from a standard magnesium oxide surface.

### ANALYTICAL METHODS FOR PIGMENT DETERMINATIONS

A method for the determination of chlorophyll, pheophytin, xanthophyll, and carotene in dehydrated vegetables has been evolved by combining features of chromatographic, solvents partition, and spectrophotometric methods. In brief, it consists of pigment extraction by acetone, transfer of pigments to ether, and direct spectrophotometric analysis for chlorophyll and pheophytin. This is followed by saponification and removal of the chlorophyllous pigments, chromatographic isolation, and spectrophotometric determination of carotene and xanthophylls.

The grinding of dehydrated materials entails certain difficulties, particularly in material with high (10 per cent and greater) moisture content. These materials have a tough, leathery texture and are not easily subdivided by any of the available mechanical grinders. In these cases a hand-operated meat grinder, fed slowly, gave the best results. Materials of low moisture content (5 per cent and less) can be ground satisfactorily in a Waring Blender or in a Wiley mill.

Dehydrated materials require rehydration before pigments can be extracted quantitatively. Rehydration results in imbibition and swelling of the cell walls and cell constituents. This treatment facilitates the entry of water-miscible solvents and the extraction of pigments otherwise "sealed off" or too firmly adsorbed to be released.

Extraction of rehydrated materials, particularly those of high carbohydrate content, is also facilitated by washing with hot water (50° C.) prior to extraction. Hot-water washing removes from the plant certain constituents which probably act as barriers in the unwashed material to the entry of the extraction solvents. Carotene and chlorophyll have been found to be stable under these conditions of washing. Extraction is subsequently performed with acetone containing 10 per cent of water. The rehydration and washing are accomplished in a single step as described in the following procedure:

Five grams of finely divided material are weighed, placed upon a Büchner funnel (5.5 cm.), and washed with hot water (50° C.) under gravity flow (about 200 ml. total). The filter paper and the rehydrated washed sample are transferred quantitatively to



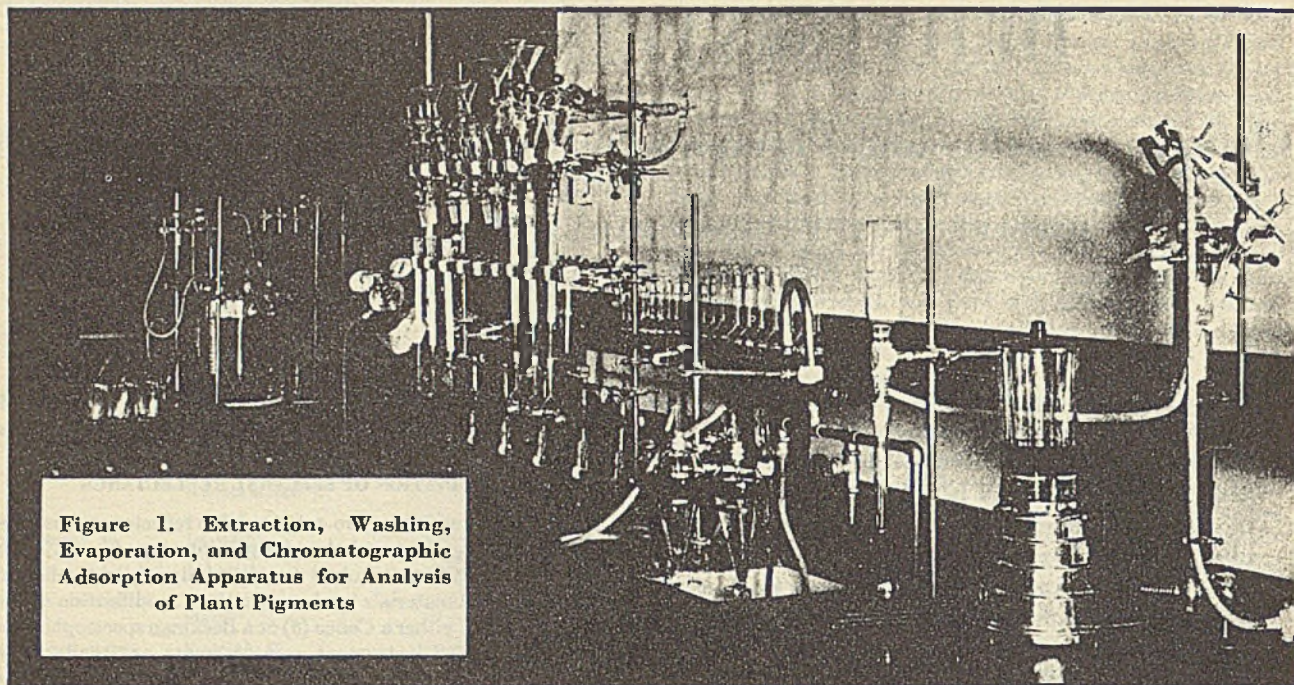


Figure 1. Extraction, Washing, Evaporation, and Chromatographic Adsorption Apparatus for Analysis of Plant Pigments

a Waring Blendor and disintegrated in the presence of 200 ml. of 90 per cent acetone. Approximately 5 grams of Filter-Cel are added during the last 30 seconds of disintegration, and the suspension is filtered under reduced pressure directly into a 500-ml. volumetric flask through a sintered glass funnel. The cake, which is formed upon the filter by means of a tamper and the application of vacuum, is successively washed with a 50-ml. aliquot of 90 per cent acetone, resuspended in an equal aliquot of acetone, reformed, washed, resuspended, etc., until the residue and filtrate are colorless. The filtrate is then made to volume with 90 per cent acetone in a 500-ml. volumetric flask.

In the analysis of fresh samples 25 grams of thinly sliced plant material (50 grams if weakly pigmented) are disintegrated in a Waring Blendor in the presence of 200 ml. of 90 per cent acetone. Subsequent steps are identical with those given above for dehydrated materials. Some difficulty has been experienced in obtaining complete extraction of raw carrots by the procedure described. Steam blanching for 2 to 5 minutes prior to disintegration has been found to facilitate the extraction greatly. Since carotene is stable to steam blanching of this duration, the inclusion of this step is recommended with raw carrots.

**DETERMINATION OF CHLOROPHYLL AND PHEOPHYTIN.** The percentage conversion of chlorophyll to pheophytin is determined by the spectrophotometric method of Mackinney and Weast (11). However, direct spectrophotometric determination in acetone as described in their procedure was not possible upon samples of stored spinach because of the production of interfering pigments during storage, which are extracted by the acetone. These pigments are also water soluble and are largely removed in the hot water wash. Traces of these pigments in the extracts are eliminated in the following manner: Ether is added to the acetone solution of the pigments. The acetone and the interfering pigments are then removed from the ether by washing with water, according to the continuous washing procedure originated by Hubert (8; compare citation 9). The total chlorophyll and pheophytin pigments are determined in the ether solution at wave lengths of 555  $m\mu$  where the specific absorption coefficients of chlorophyll and pheophytin are equal ( $\alpha = 4.16$ ).

This method is based upon several assumptions (11) that make it subject to certain errors and objections, but if an accuracy of  $\pm 5$  per cent is sufficient in the determination of the percentage conversion of chlorophyll to pheophytin, this method gives the results with rapidity and ease.

**DETERMINATION OF CAROTENE AND XANTHOPHYLLS.** A 100-ml. aliquot of the 90 per cent acetone extract, obtained by the method described above, is mixed with 75 ml. of diethyl ether in a 500-ml. separatory funnel and saponified for 30 minutes with 25 ml. of a saturated solution of alcoholic potash. (If the xanthophyll content is not desired, the saponification step may be omit-

ted in materials that have no xanthophyll esters.) The acetone alcohol, and alkali are subsequently removed by the method of continuous washing (8, 9). Traces of water remaining in the hyperphase are forced out with the addition of 20 ml. of petroleum ether and drawn off through the lower stopcock. The hyperphase is then made to volume in a 100-ml. volumetric flask with petroleum ether. Triplicate 25-ml. aliquots of this solution are placed in 50-ml. round-bottom flasks, and the solvents are evaporated off under reduced pressure with a small stream of nitrogen in a constant-temperature bath held at 40° C. Each of these samples is redissolved in a few milliliters of petroleum ether and transferred quantitatively to a CaHPO<sub>4</sub> chromatographic column (12). Carotene is washed through the column with petroleum ether and caught in a 100-ml. volumetric flask. Other pigments are retained on the column. After diluting to volume, the carotene is determined spectrophotometrically by the use of wave length 436  $m\mu$  as suggested by Beadle and Zscheile (1) ( $\alpha = 199$  in petroleum ether) or colorimetrically with a blue filter. In the latter method the colorimeter may be calibrated with known concentrations of pure crystalline  $\beta$ -carotene dissolved in petroleum ether.

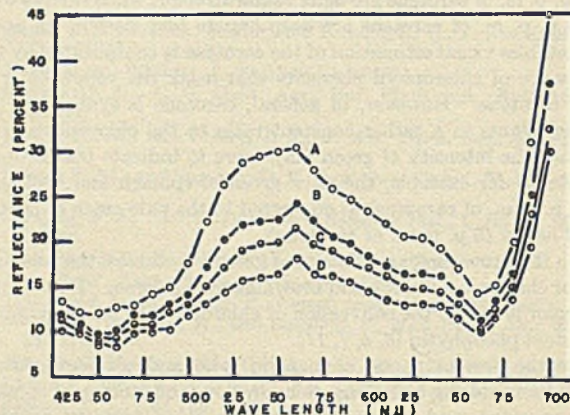


Figure 2. Spectral Reflectance Curves (Cenco Spectrophotometer) of Dehydrated Spinach

- A. Raw, dehydrated
- B. 2-Minute blanch, dehydrated
- C. 4-Minute blanch, dehydrated
- D. 6-Minute blanch, dehydrated



The xanthophylls are determined together by elution from the column with ethyl alcohol. They are caught in a volumetric flask and determined spectrophotometrically at wave length 478  $m\mu$  using the absorption coefficient (14) for lutein ( $\alpha = 232$ ).

Apparatus used in the procedure is shown in Figure 1. By the judicious use of ground glass joints, contact of the solvents and pigment solutions with rubber in the apparatus is eliminated. Pressure rather than vacuum is used to force the solvent through the adsorbent. This method permits pigments to be caught directly in volumetric flasks.

In so far as the determination of carotene is concerned, this method differs from that proposed by Moore (12) chiefly in the techniques of transfer of pigments from polar to nonpolar solvents. By the application of the continuous washing technique, the time required for the transfer has been decreased and troublesome emulsions have been practically eliminated. The subsequent evaporation step takes place at low temperature (40° C.) and eliminates traces of the polar solvent and water, the presence of which are troublesome in Moore's procedure.

In order to test reproducibility of the method for carotene, a series of analyses were performed upon a sample of dehydrated spinach and a sample of dehydrated carrots. In spinach, the standard deviation from the mean on the carotene isolated from any given column was less than  $\pm 4$  per cent. In the test upon carrots, a study was made of the errors that occur in the extraction step and those that occur in the chromatographic step. The standard deviation of the extraction step amounted to  $\pm 1.07$  per cent of the mean value of the carotene. A similar value for the chromatographic step was  $\pm 1.23$  per cent.

#### EFFECT OF BLANCHING

Batches of commercially grown spinach were blanched 2, 4, and 6 minutes with flowing steam prior to dehydration. They were then dehydrated along with a lot of unblanched spinach in a center-exhaust tunnel to a 1 per cent moisture level. After  $3\frac{1}{2}$  hours the temperature had dropped from the initial 190° to 140° F. At completion (7 hours) the temperature had again risen to 190° F. The combined effects of blanching and dehydration upon the conversion of chlorophyll to pheophytin and upon carotene are given in Table I.

The only significant loss of carotene occurred in the raw dehydrated sample. The increased stability of various constituents (in this case carotene) in blanched compared with the raw commodity is frequently attributed to the destruction of one or more enzymes. The 2 minutes of steam blanching were sufficient to give a product having maximum carotene stability.

In the case of the raw dehydrated material, the dehydration process alone resulted in the conversion of 26 per cent of the chlorophyll to pheophytin. Blanching prior to dehydration increased the conversion of chlorophyll to pheophytin in the dehydrated material, the amount depending to some extent upon the duration of the blanching period. The conversion in the batch blanched for 6 minutes and subsequently dehydrated was approximately double that of the unblanched dehydrated batch.

TABLE I. EFFECT OF TIME OF BLANCHING AND DEHYDRATION UPON CAROTENE CONTENT AND CONVERSION OF CHLOROPHYLL TO PHEOPHYTIN

Sample Description	Conversion of Chlorophyll, %	Carotene Content, Mg./100 G. (Dry Basis)	Change in Carotene Content, %
Fresh raw	0	58.5	0.0
Unblanched, dehydrated	26	39.9	-31.8
2-min. blanching, dehydrated	44	55.6	-4.9
4-min. blanching, dehydrated	46	60.4	+ 3.2 <sup>a</sup>
6-min. blanching, dehydrated	50	58.8	+ 0.5 <sup>a</sup>

<sup>a</sup> These are only apparent increases in carotene since they are within the limits of experimental error.

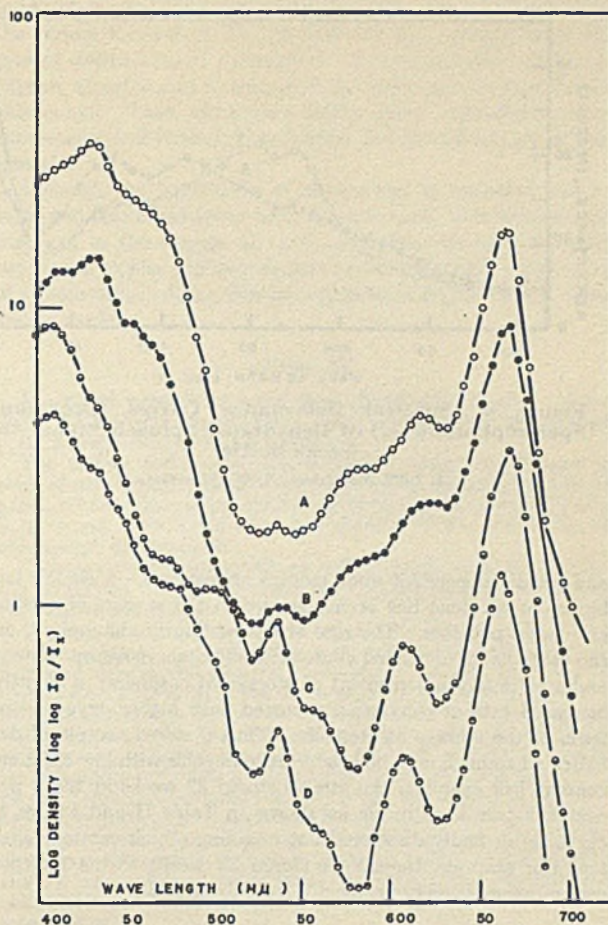


Figure 3. Absorption Spectra (Cenco Spectrophotometer) of Extracts of Fresh Spinach and of Stored Dehydrated Spinach

- A. Fresh spinach
- B. Dehydrated, stored 32 weeks in air, 2.0% moisture
- C. Dehydrated, stored 32 weeks in air, 16.3% moisture
- D. Fresh, chlorophyll converted to pheophytin

The conversion of chlorophyll to pheophytin that occurs during blanching and dehydration is accompanied by a darkening and graying of the color of the dehydrated product. Measurements of reflectance of the four samples with the Cenco spectrophotometer are shown in Figure 2. These changes in reflectance resulting from conversion of chlorophyll to pheophytin consist of a lowering of reflectance for all wave lengths and a disproportionate decrease in reflectance in the green region (530-550  $m\mu$ ) of the spectrum. As will be discussed below, this decrease in reflectance in the green is due to the formation of pheophytin, which has two absorption bands in that region.

#### EFFECT OF MOISTURE CONTENT AND ATMOSPHERE DURING STORAGE

An experiment was carried out in which unblanched dehydrated spinach was stored at two moisture levels in each of four atmospheres: oxygen, air, carbon dioxide, and nitrogen. The temperature of storage was  $31 \pm 2$ ° C. The storage cans were sampled after 2, 4, 8, 16, and 32 weeks, and analyzed for pigment content. The percentage losses of carotene and percentage conversion of chlorophyll during storage are given in Table II.

Two extremes of behavior are shown by these data. The rate of destruction of carotene, within the experimental error of sampling and analysis, was largely independent of moisture content



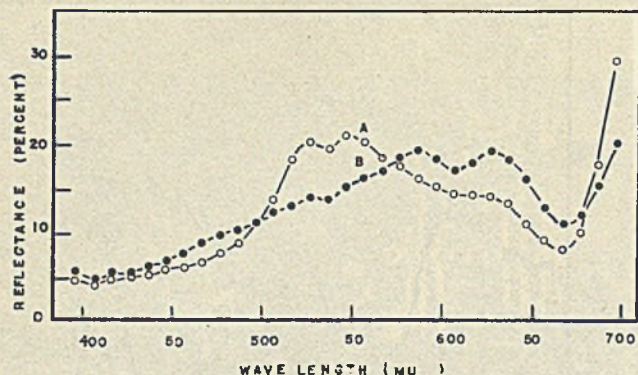


Figure 4. Spectral Reflectance Curves (Beckman Spectrophotometer) of Dehydrated Spinach Stored 32 Weeks in Air

A, 2.0% moisture; B, 16.3% moisture

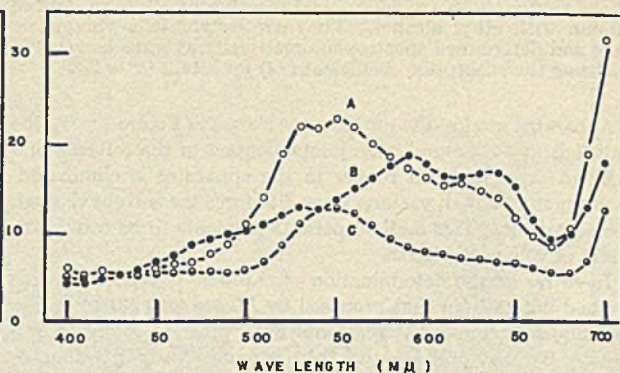


Figure 5. Spectral Reflectance Curves (Beckman Spectrophotometer) of Dehydrated Spinach Stored 32 Weeks in Nitrogen

A, 2.4% moisture; B, 18.7% moisture; C, fresh spinach

and greatly dependent upon storage atmosphere. A similar behavior of carotene has been observed in the storage of carrots and sweet potatoes. The rate of destruction of chlorophyll, on the other hand, depended almost entirely upon moisture content and was nearly independent of storage atmosphere; a slightly increased rate of conversion occurred with higher oxygen contents of the storage atmosphere. Thus a stored sample of dehydrated spinach may be bright green in color with low carotene content (for example, the sample stored 32 weeks at the 2 per cent moisture level in air as shown in Table II and Figure 4, curve A) or badly discolored but retaining a high carotene content (for example, the sample stored 32 weeks at the 18.7 per cent moisture level in nitrogen, Figure 5, curve B).

It is apparent that the samples stored at higher moisture levels were more acid than those at the low levels. This fact probably accounts for the greater conversions of chlorophyll to pheophytin in the high-moisture samples.

The changes in content of pigments as just given are but one of the factors to be considered in the study of color. Color is also dependent upon the specific light absorption properties of the individual pigments. Accordingly, a study was made of the changes in absorption spectra of extracts of the stored dehydrated spinach with particular reference to the two pigments which largely determine the color of dehydrated spinach, chlorophyll and pheophytin.

The effect of the conversion of chlorophyll to pheophytin upon the absorption spectrum of the acetone extract of pigments of fresh spinach is shown in Figure 3. Curve A represents the absorption spectrum of an extract of fresh spinach and curve D, the absorption spectrum of the same extract after conversion of chlorophyll to pheophytin by the addition of oxalic acid.

Some of the changes resulting from the conversion of the chlorophyll are the lowering of the maximum at 665  $m\mu$ , the entrance of an absorption band at 535 and at 500  $m\mu$ , and the shift of the maximum in the blue to shorter wave lengths. For comparative purposes, densities are plotted on semilogarithmic paper. With this method of plotting, the shape of the curves is independent of concentration and any changes in the shape of the curves are due to alterations in the pigment components.

Curves B and C represent absorption spectra of pigments extracted from samples stored in air for 32 weeks. B is for material stored at the 2 per cent moisture level in which the chlorophyll had undergone 15 per cent conversion as a result of storage (Table II). The pheophytin maxima can be detected in this curve.

Curve C is for material stored at the 16.3 per cent moisture level, in which case 100 per cent conversion of the chlorophyll had taken place during storage. The similarity of curve C at wave lengths longer than 525  $m\mu$  to curve D indicates the probable absence of colored chlorophyll decomposition products other than pheophytin. The fact that the absorption at wave lengths shorter than 525  $m\mu$  is relatively less for curve C than for D is due to the loss of carotenoids in the case of the stored sample (curve C). The lower carotenoid content of the stored sample also accounts for the greater prominence of pheophytin bands in the absorption spectra of that sample (curve C).

A qualitative relation between the absorption spectra and the reflection spectra of these two samples is apparent from a comparison of Figures 3 and 4. The wave length positions of the absorption maxima and minima correspond roughly to the position

TABLE II. CAROTENE LOSS AND CHLOROPHYLL CONVERSION FOR UNBLANCHED DEHYDRATED SPINACH DURING STORAGE IN VARIOUS ATMOSPHERES AT DIFFERENT MOISTURE LEVELS

Storage Time, Weeks	Oxygen		Air		CO <sub>2</sub>		Nitrogen	
	2.0% H <sub>2</sub> O	16.5% H <sub>2</sub> O	2.0% H <sub>2</sub> O	16.3% H <sub>2</sub> O	2.7% H <sub>2</sub> O	16.1% H <sub>2</sub> O	2.4% H <sub>2</sub> O	18.7% H <sub>2</sub> O
Carotene Loss, Per Cent								
2	14	26	..	..	..	..	..	..
4	50	57	11	13	..	..	..	..
8	54	61	16	10	7	2	5	..
16	62	74	32	3	0	1	4	+4
32	..	..	50	37	28	..	5	+2
Conversion of Chlorophyll to Pheophytin, Per Cent								
2	10	52	..	..	..	..	..	..
4	16	91	5	93	..	..	..	..
8	15	95	..	..	9	96	1	95
16	17	100	12	100	9	100	6	98
32	..	..	15	100	4	..	6	100

These observations are in accord with the known chemical properties of chlorophyll and carotene. The destruction of carotene takes place by an oxidative process, while the conversion of chlorophyll to pheophytin is a hydrolytic reaction in which the magnesium of the chlorophyll is replaced by hydrogen in the presence of weak acids. As the result of a suggestion by Blair (2) the pH values of the rehydrated samples were investigated in relation to the conversion of chlorophyll to pheophytin. The following measurements were made upon samples after 85 weeks of storage:

Storage Atmosphere	% Moisture	pH
Air	2.0	5.62
Air	16.3	4.88
Nitrogen	2.4	5.58
Nitrogen	18.7	4.81



TABLE III. PIGMENT CONTENT OF DEHYDRATED SPINACH STORED FOR 32 WEEKS AND OF FRESH SPINACH

Pigment	Air Storage		Nitrogen Storage		Fresh Spinach
	2.0% H <sub>2</sub> O	18.3% H <sub>2</sub> O	2.4% H <sub>2</sub> O	18.7% H <sub>2</sub> O	88.3% H <sub>2</sub> O
Mg. pigment per 100 g. (dry basis)					
Chlorophyll	244	0	277	0	493
Pheophytin	109	416	86	278	0
Xanthophyll	55.0	52.5	61.3	75.2	62.9
Carotene	21.4	27.1	40.7	44.1	43.0

of the reflection minima and maxima, respectively. Minima occur in the reflection spectrum for the samples stored at high moisture (Figure 4, curve *B*) at approximately 670, 616, and 540  $\mu$ . This corresponds to the absorption maxima of pheophytin in the absorption spectrum (curve *C*, Figure 3) at wave lengths 662, 607, and 533  $\mu$ . The wave length positions of absorption maxima of extracts cannot be expected to coincide with reflection minima of the dehydrated material. Numerous observers (e. g., Dutton and Manning, 6) have reported that the position of the red absorption maxima of chlorophyll in acetone extract is shifted approximately 200  $\text{\AA}$ . to shorter wave lengths from the position of the absorption maximum in the plant. The reflection spectra of the samples stored at high-moisture levels (Figures 4 and 5, curves *B*) explain the olive-brown color of these samples, and the reflection spectra of the samples stored at low-moisture levels (curves *A*) explain the green color. For comparison a spectral reflection curve for raw spinach is included (curve *C*, Figure 5). It has a generally lower reflectance and lacks the minimum of pheophytin ( $\lambda = 540 \text{ m}\mu$ ) present in the other curves.

To determine whether a relation could be established between carotene content and reflectance measurements, the pigment content and spectral reflectance of samples of the unblanched dehydrated spinach stored for 32 weeks in atmospheres of air and nitrogen were given additional study. The storage samples, along with a sample of fresh spinach, were analyzed for chlorophyll, pheophytin, xanthophyll, and carotene. The results are given in Table III.

Of the pigments studied, chlorophyll undergoes the greatest change under the conditions of storage used. Its change over-shadows all other pigment alterations in its effect upon color (Figures 4 and 5). Little difference is apparent between samples of the same moisture level stored in air and nitrogen (e. g., curve *A*, Figure 4 compared with curve *A*, Figure 5; and curve *B*, Figure 4 with curve *B*, Figure 5) despite the lower carotene content of the former. Since the xanthophyll fraction is present in greater amount than the carotene, it is not surprising that the loss of carotene is not indicated by reflectance measurements. More important, the degradation of chlorophyll introduces strong pheophytin absorption bands in the region of carotenoid absorption and obscures changes due to carotene. It must be concluded that in the storage of green dehydrated vegetables there is little possibility of correlating carotene content and spectral reflectance measurements.

In the results of the storage experiments it is apparent that the conversion of chlorophyll to pheophytin in samples stored at high moisture levels impairs the green color of dehydrated spinach. This alone lowers the quality rating of the product. It is known from tests made in this laboratory that taste and flavor also undergo adverse changes when samples are stored at relatively high moisture levels. However, taste and flavor appear to be lost more rapidly than does color. Thus, while good color may be associated with poor taste and flavor under certain conditions, the discoloration which occurs with the conversion from chlorophyll to pheophytin is invariably associated with poor taste and flavor.

Data on the vitamin C content of these stored samples, obtained by the method of Loeffler and Ponting (10), indicate that

in the absence of oxygen the rate of destruction of vitamin C at the various moisture levels proceeds at a rate comparable to the rate of destruction of chlorophyll. In atmospheres containing oxygen, ascorbic acid is destroyed at a much greater rate than is chlorophyll. Thus, although a bright green color does not assure retention of vitamin C, discoloration does indicate loss of this vitamin.

Although the importance of chlorophyll to nutrition and to taste and flavor has never been demonstrated, it is labile in nature and in the storage of unblanched dehydrated spinach its conversion to pheophytin may serve as an indication of the state of certain other labile substances important to nutritional value and to quality.

#### SUMMARY

Analytical procedures have been described whereby chlorophyll, pheophytin, xanthophyll, and carotene are determined upon a single sample of vegetable.

The visibly and spectrophotometrically observed changes in color of dehydrated spinach from bright green to darker shades of green, which result as the time of blanching prior to dehydration is increased, were found to be correlated with the conversion of chlorophyll to pheophytin.

Carotene, in contrast to chlorophyll, is stable under the blanching conditions used and is protected by blanching against loss in the subsequent dehydration process.

While chlorophyll content can be used as a rough index of the carotene content in fresh green material, in the storage of unblanched dehydrated spinach chlorophyll failed as an index of carotene content because the decomposition of carotene proceeds by a reaction that is different from that involved in the decomposition of chlorophyll. The destruction of chlorophyll is accelerated by increased moisture content and is little affected by storage in an atmosphere of oxygen, air, carbon dioxide, or nitrogen; the rate of carotene destruction is accelerated by oxygen in the storage atmosphere and is unaffected by moisture content. Because changes in color due to changes in chlorophyll content obscure changes in color due to changes in carotene content, it is concluded that in the storage of green dehydrated vegetables there is little possibility of correlating carotene content with spectral reflectance measurements.

Although a nutritional function for chlorophyll has never been demonstrated, it is labile in nature; and in the storage of unblanched spinach its conversion to pheophytin indicates a probable deterioration in palatability and in ascorbic acid content even though it does not necessarily indicate a loss in carotene.

#### ACKNOWLEDGMENT

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# CRYSTALS from PORTLAND CEMENT HYDRATION

## *An Electron Microscope Study*

**D**URING the course of preliminary investigations on miscellaneous industrial solids with the electron microscope, unusual crystal forms were observed when a water-dispersed sample of portland cement was examined. A review of the literature indicated that comparatively few studies of the hydration of cements had been made by either the light or the electron microscope. Consequently it was decided to undertake an electron microscope study of portland cement compounds dispersed in water over a wide range of setting times. Although the photographs presented in this paper do not give complete evidence as to the products of hydration, they do reaffirm certain of the principles previously laid down and demonstrate the applicability of the electron microscope to the study of crystal formation.

According to Bogue in 1928 (2), "exact information on the chemical nature of the major reactions which accompany the setting and hardening of cement has not been advanced materially in the last quarter century and, indeed, but few contributions have appeared which would change in any considerable degree the conclusions reached by LeChatelier on this problem in 1887." The theory postulates that portland cement is composed primarily of five compounds: tricalcium aluminate, tricalcium silicate, dicalcium silicate, tetracalcium aluminoferrite, and calcium sulfate. The first four of these constituents hydrate in contact with water, thus remove the dissolved constituents from the solution, and cause more of the initial material to be dissolved. By this process the initial material enters the solution and forms a crystalline mass, holding together the aggregate and giving strength to the concrete.

Table I lists the compounds and indicates the method of hydration generally accepted (2, 7). In addition to these reactions, hydrolysis reactions have been reported (2, 4, 7). Tricalcium aluminate and tetracalcium aluminoferrite are believed to be the first to react and to give the initial strength to the cement. Tricalcium silicate reacts next and dicalcium silicate last. These studies were based primarily on chemical analyses and on physical measurements on cement test specimens, such as water absorption. Observations on crystal formation added little to the theory.

Since not enough water is usually present in the hydration of portland cement to satisfy all the constituents, the products of reaction take on colloidal properties. White (8) showed that

portland cement takes on permanent growth with the successive wetting and drying over a long period. This growth is accounted for by the hydration of the inner portion of the cement particle, which was previously protected by the colloidal mass around it.

In 1901 Ambronn (1) studied the crystallization of portland cement with a light microscope. During the first few days he observed that the individual particles of the cement became surrounded with a large number of exceedingly fine needles and hexagonal plates. After a few days a third kind of crystal was developed, also consisting of hexagonal plates. Finally, he reported that the presence of air caused the formation of a biscuit-shaped crystal, which he believed to be calcium carbonate.

### TECHNIQUE WITH ELECTRON MICROSCOPE

It is considerably more difficult to obtain a sufficiently dispersed layer for observation in the electron microscope by an air dispersion of the specimen than by a liquid suspension; hence, the latter method was used in this undertaking. The usual dispersion medium is water, although other liquids may be used. Figures 1 and 2 show samples of portland cement and a neat portland cement pat which were dispersed in petroleum ether; in all other instances water was the medium. A small quantity of the solid—about 0.5 to 0.75 gram—was mixed with about 10 cc. of freshly boiled, distilled water and allowed to stand for various periods. At all times there was an excess of solids in contact with the liquid. The specimen is dispersed in a thin layer on a collodion film, supported on a 200-mesh stainless steel screen  $\frac{1}{8}$  inch in diameter, for observation in the electron microscope. A wire with a  $\frac{1}{8}$ -inch end loop is dipped into the vial containing the solution, and the droplet of liquid clinging to it is transferred to the film by contact. The water is allowed to evaporate by standing in a closed dish or desiccator for a few minutes,

and the specimen is then placed in the holder and inserted into the microscope. Most of the micrographs of this paper were taken of samples from glass vials which had not been agitated and from what appeared to be the supernatant liquid. Thus, it is possible that particles were not present in the liquid, but that crystals observed in the microscope resulted from the crystallization during evaporation. In some cases the water and sediment in the test tube were agitated and a cloudy sample was taken, but most of the

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An electron microscope study has been made of crystals resulting from the hydration of portland cement compounds. Calcium hydroxide yielded spheres and a fibrous mass. The dicalcium silicate hydrate appeared as rhombic slabs and possibly as amorphous spherulites. The tricalcium aluminate hydrated to form thin hexagonal plates, rhombic slabs,

needles, and possibly amorphous spherulites. The amorphous spherulites could well be some form of hydrate of both of these compounds, but the photographs show that they bear a resemblance to the known calcium hydroxide. The calcium sulfoaluminate complex formed heavy needles or splines. Amorphous forms of ferrite were also observed.

specimens so observed contained material too dense for observations to be made. However, wherever these specimens were observable, no differences in crystal form between agitated and unagitated samples could be detected. It is possible that Brownian movement or thermoagitation maintains in suspension the finer particles resulting from the hydration of the compound, and that they were present as actual particles when placed upon the screen. The evaporation of the water naturally leaves some solid residue, which either may attach itself to the crystals already present, may form new crystals, or may give a background deposit of more or less amorphous material.

Tyndall effect observations were made on all samples. The results were negative in all cases except those of tricalcium aluminate and calcium hydroxide. As a check on the effects of evaporation, a 3 per cent solution of sodium chloride was used to prepare a specimen. Perfect salt cubes were found, as well as some haze in the background. It thus appears that crystals were formed during the evaporation of water on the film, but the possibility that some small crystals may have been present at the time the specimen was placed on the collodion film is not excluded. When in the microscope the specimen is under a reduced pressure of  $10^{-4}$  mm. of mercury, which evaporates any water not previously vaporized.

The spaces of the 200-mesh screen were examined, and enough photographs were taken of each sample to be representative of the entire field. Special care was exercised to avoid dust contamination, and frequently blanks, of film and screen alone, were observed as a check.

In most of the preparations the water suspensions of portland cement were immediately stoppered at the time of mixing and were kept sealed until the moment at which the sample was placed on the film. Since drying was carried out in a desiccator containing soda lime for removal of carbon dioxide, the maximum contact time of the sample with atmospheric carbon dioxide was about 2 or 3 minutes. The distilled water used in the preparation of the samples was freshly boiled each time as further precaution against carbon dioxide absorption.

TABLE I. SUMMARY OF REACTIONS GIVEN FOR SETTING OF PORTLAND CEMENT (?)

Compound	Reactions
Tricalcium aluminate	$3\text{CaO}\cdot\text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} \longrightarrow 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ $3\text{CaO}\cdot\text{Al}_2\text{O}_3 + 3\text{CaSO}_4 + x\text{H}_2\text{O} \longrightarrow 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$
Tricalcium silicate	$3\text{CaO}\cdot\text{SiO}_2 + x\text{H}_2\text{O} \longrightarrow 2\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O} + \text{Ca}(\text{OH})_2$
Dicalcium silicate	$2\text{CaO}\cdot\text{SiO}_2 + x\text{H}_2\text{O} \longrightarrow 2\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$
Tetracalcium aluminoferrite	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3 + x\text{H}_2\text{O} \longrightarrow 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot x\text{H}_2\text{O} + \text{Ca}(\text{OH})_2 + \text{Fe}_2\text{O}_3\cdot x\text{H}_2\text{O}$

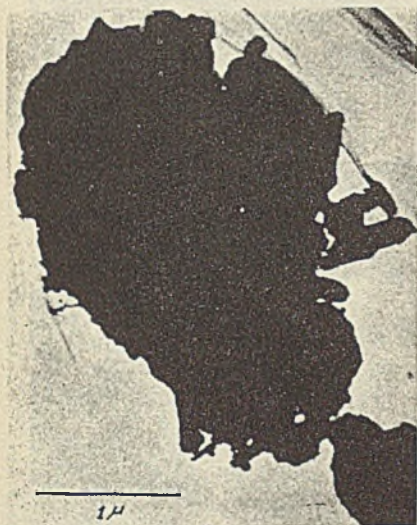


Figure 1. Portland Cement A Dispersed in Petroleum Ether and Left Standing One Week ( $\times 19,000$ )



Figure 2. Neat Cement Pat, Ground in Mortar and Dispersed in Petroleum Ether ( $\times 8000$ )



Figure 3. Calcium Sulfate Hydrated 18 Hours ( $\times 8000$ )



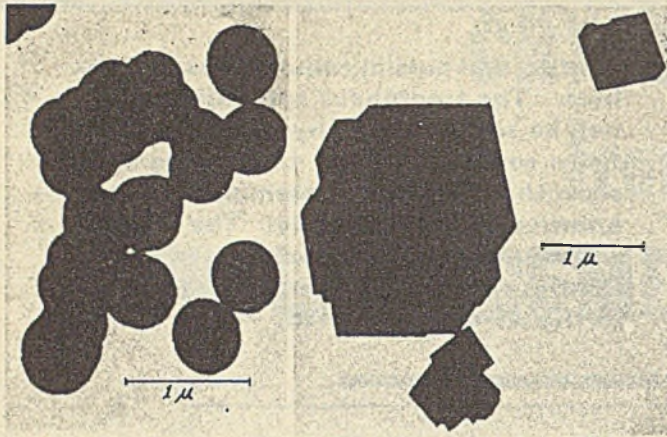
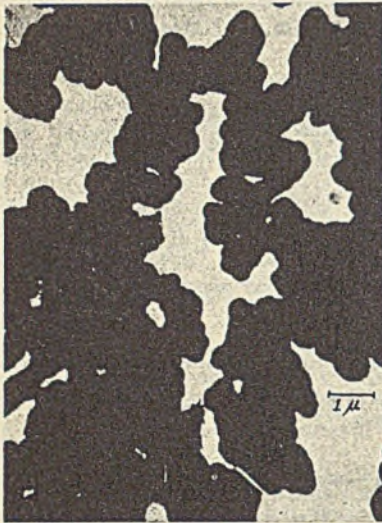
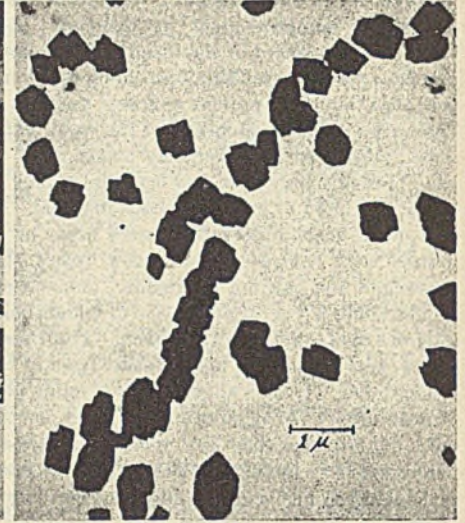
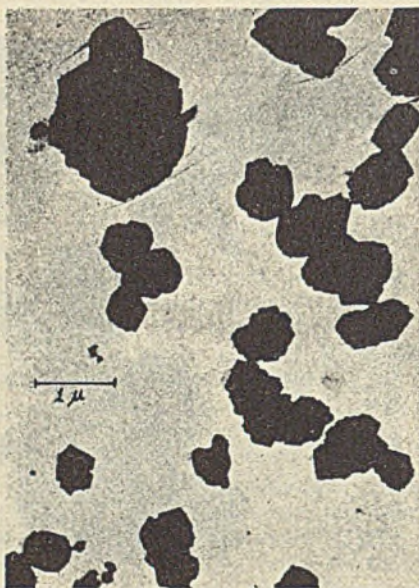
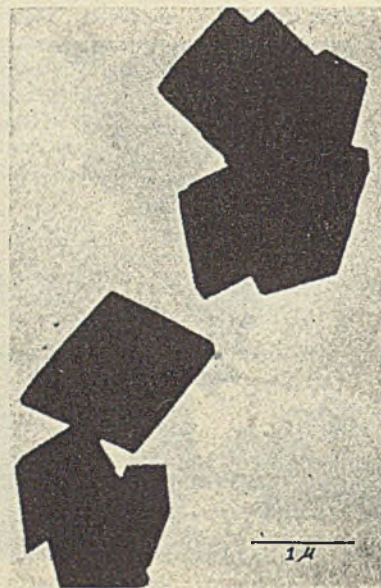
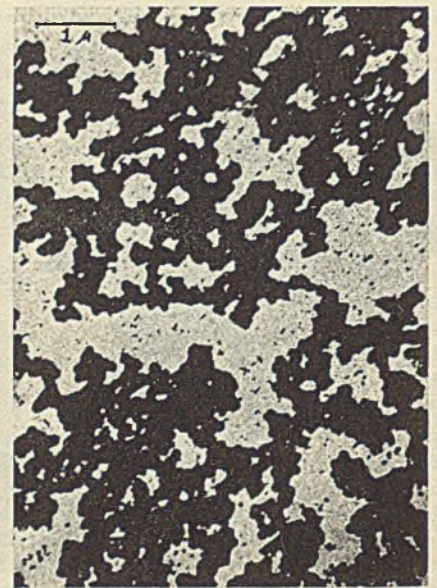


Figure 4

Figure 5

Figure 4. Calcium Oxide Hydrated 2 Days ( $\times 16,500$ )Figure 5. Calcium Oxide Hydrated 4 Days in a Solution Saturated with Carbon Dioxide ( $\times 13,500$ )

Since an excess of liquid (placed on the collodion film) resulted in a specimen which was almost opaque, some care was required as to the quantity deposited. The results of this study include data from a number of observations on specimens which, while not suitable for photographing, were sufficiently defined for visual observation.

Figure 6. Calcium Hydroxide Hydrated 18 Hours ( $\times 6000$ )Figure 7. Calcium Hydroxide Hydrated 7 Days ( $\times 6000$ )Figure 8. Calcium Hydroxide Hydrated 7 Days and Exposed to Atmosphere for 3 Days ( $\times 8000$ )Figure 9.  $\beta$ -Dicalcium Silicate Hydrated 2 Hours ( $\times 10,500$ )Figure 10.  $\beta$ -Dicalcium Silicate Hydrated 16 Days ( $\times 13,500$ )Figure 11.  $\beta$ -Dicalcium Silicate Hydrated 10 Days ( $\times 10,500$ )



Some duplicated results are included to establish the reliability of the samples and the slides, as well as to prove that the sampling procedure is repeatable. However, in some instances duplication of certain results may require that several slides be prepared before a similar field is found.

#### PORTLAND CEMENT CONSTITUENTS

Electron micrographs were taken of the hydration products from the pure constituents, artificial mixtures, and portland cement mixtures. The hydrates of the pure constituents will be presented first so that they may be later used in identifying some of the products found in the complex cement mixtures.

The samples of gypsum, dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite were furnished by T. L. Brownard of the Portland Cement Association. The tricalcium silicate may contain some dicalcium silicate, and the tricalcium aluminate may contain some free lime and some material with a lower ratio of lime to alumina than 3. Since the dicalcium silicate was prepared by using 0.5 per cent borax as a flux, it may also be slightly contaminated. The other two materials, gypsum and tetracalcium aluminoferrite, should be essentially pure.

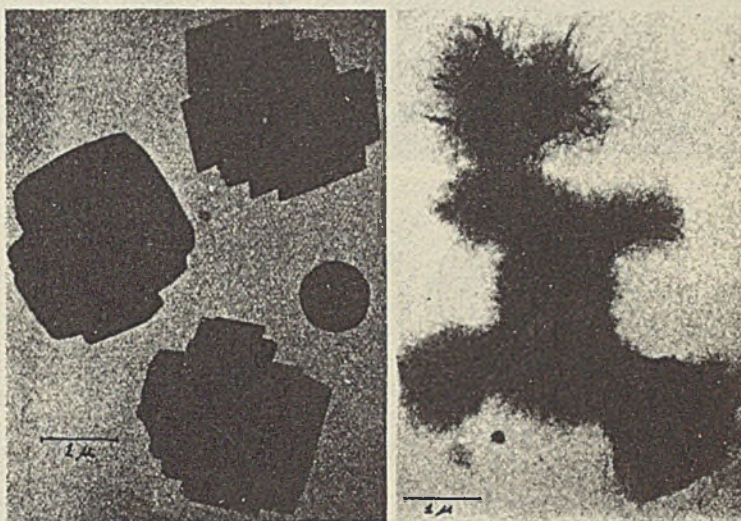
**CALCIUM SULFATE.** Crystals of gypsum (formed by placing a drop of clear supernatant solution on a film and allowing the water to evaporate) were observed after various setting times. Figure 3 shows the type of crystals formed, which are independent of the setting time. This sharp, angular, monoclinic type of structure is characteristic and readily reproducible.

**CALCIUM HYDROXIDE.** Three types of crystals were formed from four different preparations of these samples. Calcium oxide was dissolved in "carbon dioxide free" water, and the suspension was allowed to stand for 2 days before the slide (Figure 4) was prepared from this dispersion; the spheres are believed to be calcium hydroxide<sup>1</sup>. The slide for Figure 5 was prepared from a solution of calcium oxide

which had been saturated with carbon dioxide in order to form rhombohedrons of calcium carbonate.

Another series was prepared from reagent calcium hydroxide suspended in water. Figure 6 shows the spherical calcium hydroxide particles similar to those of Figure 4. The material of Figure 7 is not identified, but similar structures were found repeatedly. This substance might be the result of contamination by carbon dioxide, which caused a calcium hydroxide sphere to recrystallize, or another form of calcium hydroxide resulting from the presence of foreign material. Another photograph of the same slide as Figure 7, but of an adjacent field, was like Figure 6. Figure 8 shows calcium carbonate<sup>1</sup> formed by the carbon dioxide of the air reacting with the calcium hydroxide. The particular grouping of the crystals is typical of the field and would indicate

<sup>1</sup> Similar observations were made by Radczewski *et al.* (5) for calcium hydroxide and for calcium carbonate.



Figures 12 (left) and 13 (right). Tricalcium Silicate Hydrated 18 Hours ( $\times 10,500$ )



Figure 14. Tricalcium Silicate Hydrated 10 Days ( $\times 13,500$ )



Figure 15. Tricalcium Silicate Hydrated 10 Days ( $\times 10,500$ )



Figure 16. Tricalcium Silicate Hydrated 2 Hours ( $\times 12,500$ )



Figure 17. Tricalcium Aluminate Hydrated 2 Hours ( $\times 21,000$ )



Figure 18. Tricalcium Aluminate Hydrated 18 Hours ( $\times 13,500$ )

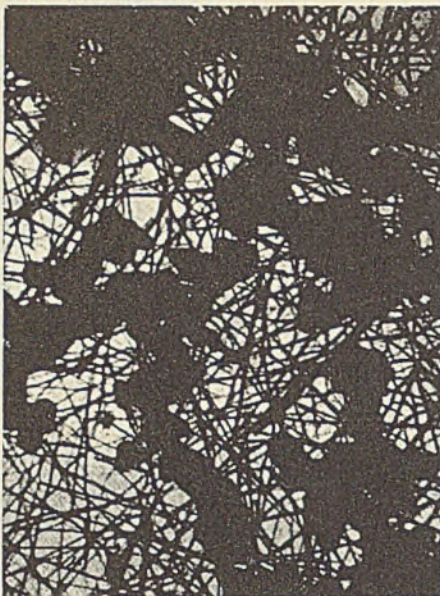


Figure 19. Tricalcium Aluminate Hydrated 18 Hours ( $\times 13,000$ )



Figure 20. Tricalcium Aluminate Hydrated 10 Days ( $\times 10,500$ )



Figure 21. Tricalcium Aluminate Hydrated 10 Days ( $\times 16,500$ )



Figure 22. Tricalcium Aluminate Hydrated 10 Days and Agitated Constantly ( $\times 8000$ )

that they were present as such at the time the solution was placed on the field.

**$\beta$ -DICALCIUM SILICATE.** The dicalcium silicate is supposed to form one hydrate. Figures 9 and 10 show rhombic slabs adhering in the form of accordion-shaped aggregates. Since these structures closely resembled those of calcium carbonate (Figures 5 and 8), an attempt was made to determine the possibilities of carbon dioxide contamination. Samples of dicalcium silicate and calcium hydroxide were prepared from the same carbonate-free water and were treated in exactly the same manner with the usual precautions taken against carbon dioxide contamination. The calcium hydroxide specimen showed the typical spherulites of lime hydrate, and there were no signs of

carbon dioxide contamination. Had any carbon dioxide been present, the lime would have been converted to the carbonate form of Figures 5 and 8. Consequently, it was assumed that the dicalcium silicate sample was likewise carbonate-free, and therefore the rhombic slabs were some form of dicalcium silicate hydrate.

Furthermore, since the figures presented are in all cases representative of the entire field observed, it seems unlikely that sufficient carbon dioxide could contact the specimen and convert all the dicalcium silicate to the carbonate form. On the other hand, Figure 11 resembles the usual hydration product of dicalcium silicate as revealed by the light microscope. However, this type of structure was observed only after hydration periods



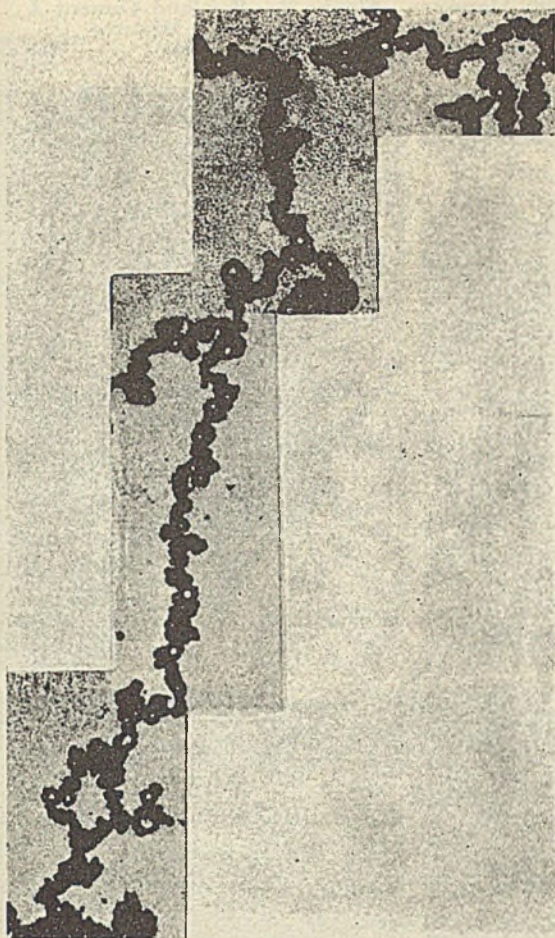


Figure 23. Tetracalcium Aluminoferrite Hydrated 3 Hours in a Stopped Vial ( $\times 2250$ )



of 10 days or longer. The appearance of rhombic slabs in shorter hydration periods remains unexplainable on the basis of existing knowledge, especially since dicalcium silicate is believed not to undergo hydration for several days. Therefore, in the light of these observations it seems that dicalcium silicate may first undergo some intermediate reaction to form the rhombic structure of Figures 9 and 10.

**TRICALCIUM SILICATE.** This compound reacts with water to form dicalcium silicate and calcium hydroxide. Figure 12 gives the spheres of calcium hydroxide and the rhombic slabs similar to those formed from dicalcium silicate. Figure 13 gives the fibrous material of the type found in the calcium hydroxide of Figure 7. Figure 14 again shows the accordion aggregations and possibly either calcium hydroxide or a form of dicalcium silicate hydrate similar to that observed in Figure 11. Figure 15

is comparable with the calcium hydroxide of Figure 6. Figure 16 is the only material found after 2-hour hydration. The large particle may be the original material, while the fine mass resembles calcium hydroxide or a form of dicalcium silicate.

**TRICALCIUM ALUMINATE.** Figures 17 through 21 give the products of reaction from tricalcium aluminate after hydration has progressed from 30 minutes to 10 days. The thin hexagonal plates of Figure 17 resemble kaolin and are probably an unstable form of tricalcium aluminate hydrate. Figure 18 could not be duplicated, even after several attempts; the needles may also represent another unstable form. However, Figure 19 does contain splines and rhombic crystals. These micrographs readily show that four types of crystals may be found—namely, the hexagonal plates of Figure 17, the needles or splines of 18, the rhombic slabs of 20, and the spherulites of 18 and 20. The spheres of Figure 20 may represent either an impurity of calcium hydroxide, a result of hydrolysis, or even some form of a tricalcium aluminate hydrate. Figure 21 was obtained after 10-day hydration and bears a slight resemblance to calcium hydroxide, although they well might be some form of tricalcium aluminate hydrate. Keisermann (3) called the hexagonal plates "tricalcium aluminate hydrate" and the hexagonal crystals "calcium hydroxide". On the other hand, Ambronn (1) failed to identify the fine needles and hexagonal plates which appeared after contact with water for a few days. However, both Ambronn and Read (6) claimed that the large hexagonal plates which appeared after several days were calcium hydroxide.

Figure 22 combines the unintelligible portion of Figure 20 with the hexagonal plate of Figure 17. This specimen was prepared from a suspension that was constantly agitated for 10 days.

The investigations show that tricalcium aluminate containing possible impurities of free lime and mono- or dicalcium aluminate, when dispersed in water, yield hexagonal plates, needles, accordion-shaped aggregations of rhombic slabs, and spherulites.

**TETRACALCIUM ALUMINOFERRITE.** This compound is believed to react with water to form tricalcium aluminate, calcium hydroxide, and some form of ferrite. Figure 23 represents an unusual long-chain structure, the elements of which are perforated with hexagonal holes. Figure 24 shows slabs, previously observed in tricalcium aluminate (Figure 20) and a background,

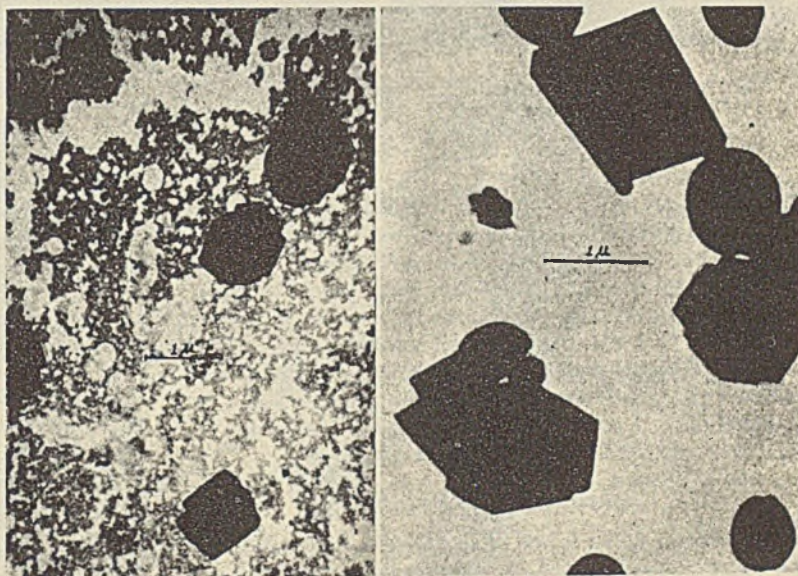


Figure 24. Tetracalcium Aluminoferrite Hydrated 18 Hours ( $\times 10,500$ )

Figure 25. Tetracalcium Aluminoferrite Hydrated 10 Days ( $\times 13,500$ )



Figure 26. Tricalcium Aluminate (4 Parts) and Calcium Sulfate (1 Part) Hydrated 10 Days ( $\times 8000$ )



Figure 27. Tetracalcium Aluminoferrite (3 parts) and Calcium Sulfate (1 part) Hydrated 10 Days ( $\times 6000$ )



Figure 28. Portland Cement A Hydrated 30 Minutes ( $\times 16,500$ )



Figure 29. Portland Cement A Hydrated One Week ( $\times 16,500$ )



Figure 30. Portland Cement A Hydrated One Week ( $\times 12,500$ )



Figure 31. Portland Cement A Hydrated 18 Days ( $\times 16,500$ )

which is probably composed of ferrite. Figure 25 gives the rhombic slabs along with a structure resembling the calcium hydroxide of Figure 20. If tricalcium aluminate is a product of the reaction between water and tetracalcium aluminoferrite, then the same crystals should be formed upon hydration of either of these substances. As a matter of fact, even hexagonal plates similar to those of Figure 17 have been found in samples of tetracalcium aluminoferrite. However, the chainlike structure of Figure 23 is typical only of tetracalcium aluminoferrite; the needles of Figure 18 are of the tricalcium aluminate sample.

#### MIXTURES OF COMPOUNDS

Since calcium sulfate is held to enter the reaction and retard the set of portland cement, a suspension of four parts of tricalcium aluminate and one part of calcium sulfate by weight was studied in an attempt to verify this theory. A similar dis-

position of 3 parts of tetracalcium aluminoferrite and 1 part of calcium sulfate was also prepared. The results of these hydrations are shown in Figures 26 and 27. Again, rhombic slabs, hexagonal plates, and spheres are found, as well as splines, which form a network over the slide. Judging from the results of the investigations on the pure constituents, it is obvious that the heavy needles or splines are a calcium sulfoaluminate complex. During the early stages of this investigation T. L. Brownard suggested that the heavy splines of micrograph III, Figure 32, could possibly be the calcium sulfoaluminate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$ .

#### PORTLAND CEMENTS

Since the constituents described compose portland cement, the electron micrographs of films prepared from solutions of the cement should confirm the observations presented. Two cements were examined: A is a normal, commercial portland





Figure 32. Portland Cement A Hydrated 18 Days  
I,  $\times 4500$ ; II,  $\times 9800$ ; III,  $\times 20,000$ .



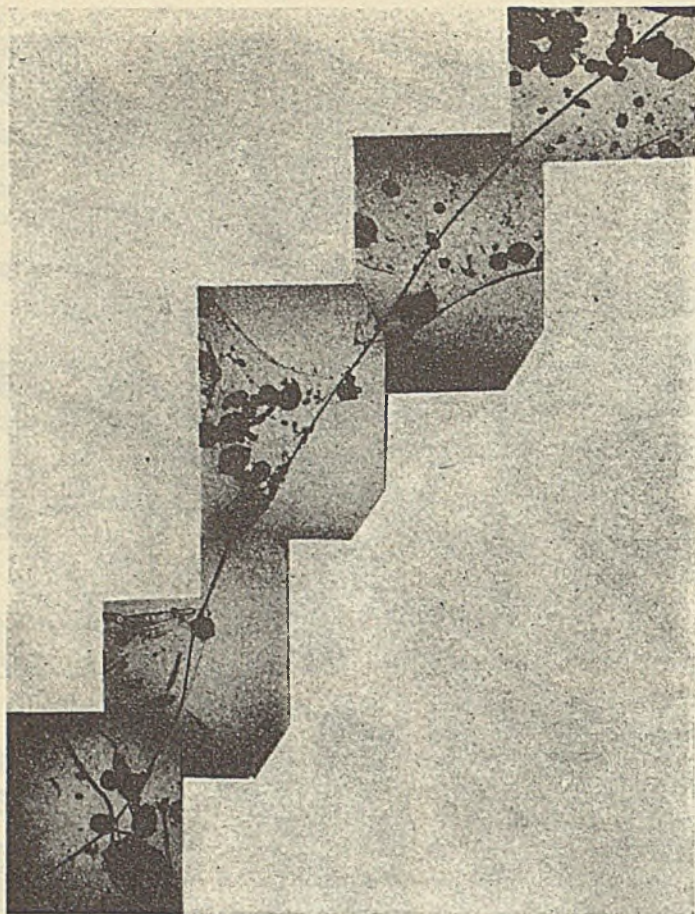


Figure 33. Portland Cement B (Sample 3) Hydrated 24 Hours in Stoppered Vial ( $\times 2250$ )

cement of unknown composition; B was furnished by A. H. White, and has the following composition (in per cent by weight):

SiO <sub>2</sub>	21.55	CaO	63.01
Al <sub>2</sub> O <sub>3</sub>	9.09	MgO	2.73
Fe <sub>2</sub> O <sub>3</sub>	2.56	SO <sub>3</sub>	0.60

The suspensions of cement A were exposed to atmospheric carbon dioxide; those of cement B were well protected from the atmosphere in stoppered vials. Figure 28 is a typical field of hydration for 30 minutes before the film was prepared. Figures 29 and 30 are successive micrographs of a layer prepared from cement A, which had been hydrated 7 days and exposed to the atmosphere; Figure 31 is a sample which had been hydrated 18 days in contact with air. Figure 32 illustrates the effect of a combination of increased magnification and photographic enlargement on the same field.

Cement B gave similar photographs to cement A. Figure 33 is a series of micrographs following the length of a spline (0.0025 inch). Figure 34 shows the effect of 7-day hydration.

Figures 28 and 30 are believed to be original particles of cement girded with the hydration products.

#### SUMMARY AND CONCLUSIONS

1. Crystals, formed by hydration and hydrolysis of portland cement compounds in water with subsequent evaporation of the water during preparation of the specimen, have been examined with the electron microscope.

2. Gypsum forms monoclinic type crystals in all cases.

3. Although calcium hydroxide gives spheres as its principal product, a fibrous or needlelike structure is also often observed.

4. Calcium carbonate forms rhombic slabs which adhere to one another as judged by the products of carbonation of calcium hydroxide.

5. Dicalcium silicate initially hydrates to rhombic slabs which adhere to form accordion-shaped aggregates. Later, amorphous spherulites are found.

6. Tricalcium silicate hydrates to form the same products as dicalcium silicate in addition to calcium hydroxide.

7. Tricalcium aluminate, which may contain small amounts of the mono- or dicalcium compound and lime, gives rhombic slabs, thin hexagonal plates which resemble kaolin, and spherulites. In several instances needles and splines have been observed, but sulfate contamination could possibly have accounted for this third type of crystal.

8. Tetracalcium aluminoferrite decomposes after several hours to form the same products as tricalcium aluminate, plus a background of ferrite and possibly calcium hydroxide. The 3-hour hydration sample gives a unique unstable chain structure not found in any other specimen.

9. Mixtures of gypsum with tricalcium aluminate and with tetracalcium aluminoferrite produce heavy splines. Some fractures of these splines indicate that they may be hollow with fibrous walls.

10. Both dicalcium silicate and tricalcium aluminate hydrolyze or change after several days of hydration in a relatively large quantity of water to yield spherulites which appear similar to calcium hydroxide.

11. Although calcium carbonate, dicalcium silicate hydrate, and one product of hydration of the



Figure 34. Portland Cement B Hydrated 7 Days ( $\times 20,000$ )



tricalcium aluminate all form similar rhombic slabs, the authors believe them to be separate crystals.

12. With the possible exception of gypsum and the thin hexagonal plates formed from the tricalcium aluminate sample, portland cements show all, but no more, crystal forms than those which have been observed from the pure compounds or mixtures.

13. The crystallization taking place in this research may be somewhat different from that when a minimum of water is present and the material is gelatinous. However, when considered on the basis of phase equilibrium, the specimens used here always contained an excess of the original material to keep the solution saturated. Crystallization is likely to come from a saturated solution, and therefore the equilibrium phases should be identical regardless of whether an excess of water is present or whether they are only partially hydrated as a result of the smaller quantity of water used to dissolve the original material. However, the wide dispersion of the samples required in order to observe crystal structure made the dilute dispersion necessary for this study.

14. The 36 electron micrographs presented were selected as representative of more than 250 photographs taken. Approximately a thousand visual observations were also considered in assembling the data.

15. Under the conditions of these experiments all substances show crystalline or geometric shapes except the deposit of ferrite and the material resembling calcium hydroxide. The amorphous material formed from tricalcium silicate, dicalcium silicate, and tricalcium aluminate, after long periods, resemble calcium hydroxide but could be colloidal forms of the silicate and aluminate. If these spherulites are the final form of dicalcium silicate and tricalcium aluminate, the colloidal theory becomes more plausible. However, in that case the hydrate of tricalcium aluminate should be written with a variable water content rather than with 6 molecules of water.

16. If these results can be correlated with portland cement reactions occurring in ordinary industrial proportions of water to cement, it may safely be concluded that the strength of the concrete is attributable to an abundance of crystals in the form of splines, needles, and fibers matted together and bonded by the amorphous mass. Further, strength may be imparted by laminations and the strong surface forces of numerous thin platelike crystals.

#### ACKNOWLEDGMENT

This research was made possible by a grant-in-aid from the Horace H. Rackham Fund. O. S. Duffendack of the Physics Department, under whose supervision the instrument was operated, made valuable suggestions. T. L. Brownard of the Portland Cement Association furnished the pure compounds. A. H. White, of the University of Michigan, furnished cement B and made helpful suggestions. Suggestions also were received from several individuals, including L. S. Ramsdell, G. G. Brown, and L. Thomassen. G. Sawyer, K. Beu, L. Kavanau, and P. Barker were student assistants.

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# Nomograph of Dittus-Boelter Equation

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ACCORDING to Jakob (1) the following equation represents the best practical expression for predicting the heat transfer coefficient of a substance in turbulent flow inside smooth pipe:

$$h = 0.0243 \left( \frac{k}{D} \right) \left( \frac{Du\rho}{\mu} \right)^{0.8} \left( \frac{\mu C_p}{k} \right)^{0.4}$$

This expression is a familiar form of the Dittus-Boelter equation and has been experimentally checked for many liquids and gases (1). Although this form was proposed by Nusselt, it is usually known as the Dittus-Boelter equation because of the outstanding work they did in evaluating the coefficients and exponents. McAdams discussed the various expressions advanced by different workers in this field and their meanings (2).

Often workers shun the use of this rather handy tool because it is necessary to use consistent units, which are seldom found in experimental reports. This, then, entails the use of conversion factors, and it is not uncommon for engineers to misplace a decimal place in the procedure or neglect to use the proper conversion. To remedy the situation, a nomograph of the Dittus-Boelter equation has been prepared and corrected so it will be satisfied when the following system of mixed units are employed:

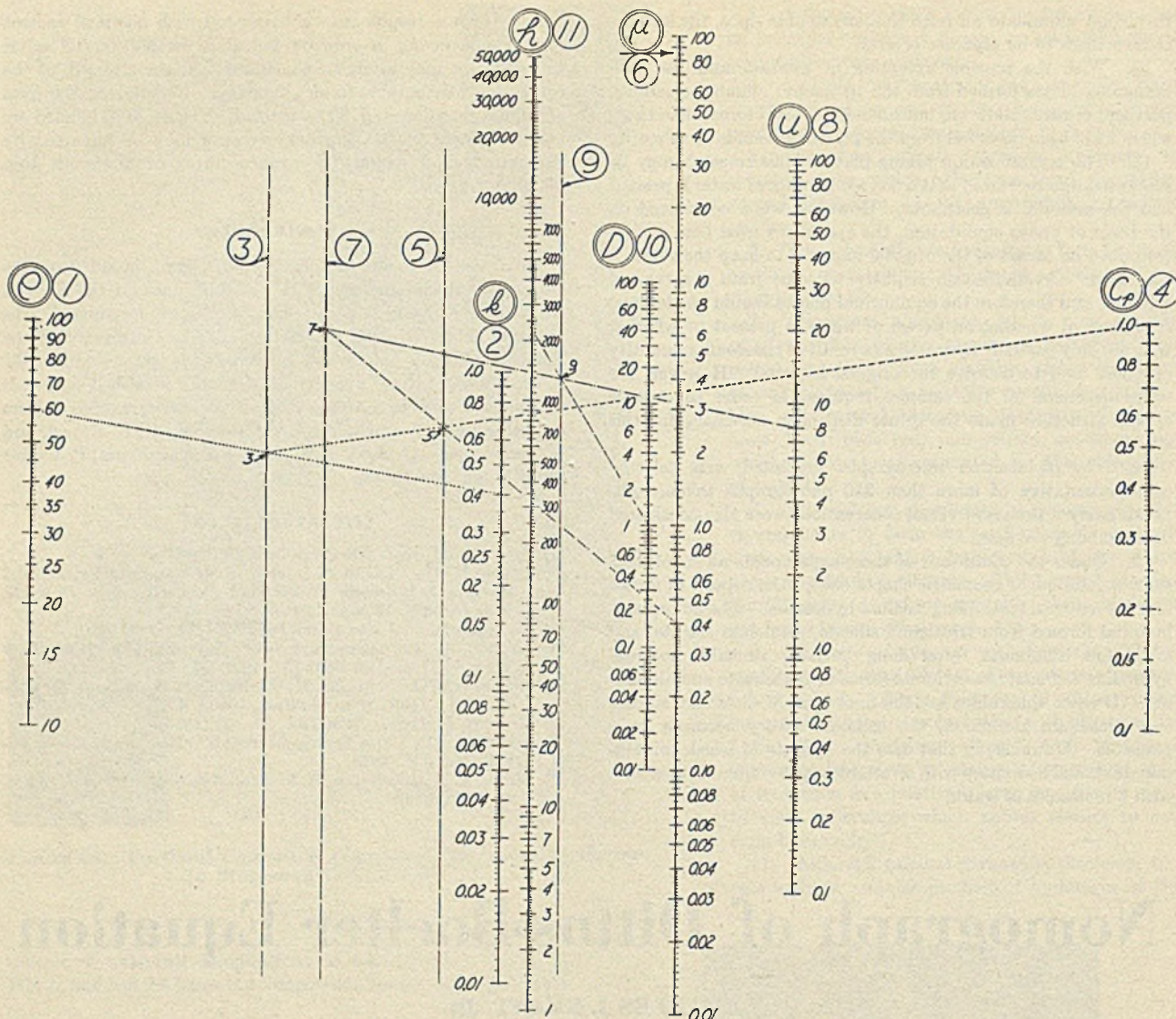
#### SYSTEM OF MIXED UNITS

Symbol	Definition	Unit
$\rho$	Density	Lb./cu. ft.
$k$	Thermal conductivity	B. t. u./(hr.) (ft.) ( $^{\circ}$ F.),
$C_p$	Thermal capacity (numerically equal to sp. heat)	B. t. u./(lb.) ( $^{\circ}$ F.)
$\mu$	Viscosity	Centipoise
$u$	Linear velocity	Ft./sec.
$D$	Characteristic length (diam. for round tubes)	Inch
$h$	Coefficient of heat transfer	B. t. u./(hr.) (sq. ft.) ( $^{\circ}$ F.)

Consider the following example: A waterlike substance (density 60 pounds/cubic foot, specific heat 1.00) is flowing through 1-inch i. d. tubes at a velocity of 8 feet/second. If the viscosity of the substance is 0.4 centipoise and the thermal conductivity is 0.4 B. t. u./hour (foot) ( $^{\circ}$  F.); what heat transfer coefficient should be used in calculating the over-all coefficient? Analysis of the problem shows it to be simply, what is  $h$  when  $\rho$ ,  $k$ ,  $C_p$ ,  $\mu$ ,  $u$ , and  $D$  are given?

To obtain  $h$ , lightly indicate on the nomograph the values of  $\rho$ ,  $k$ ,  $C_p$ ,  $\mu$ ,  $u$ , and  $D$  given in the problem, on the proper axis. These





scales are marked 1, 2, 4, 6, 8, and 10, respectively. A straight line through the points on axes 1 and 2 cuts the auxiliary line 3 at a point. Drawing a line through this point and the value  $C_p = 1.00$ , auxiliary point 5 is obtained. In like manner, connecting 5 and 6 gives 7, 7 and 8 yields 9, and on passing a line through 9 and 10, the line cuts the  $h$  axis at the answer,  $h = 2280$ .

Calculating  $h$ , using the Dittus-Boelter equation and a five-place logarithm table, the value  $h = 2283.7$  B. t. u. / (hr.) (sq. ft.) ( $^{\circ}$  F.) is obtained. With the exercise of a reasonable degree of care in connecting the various scales, it is easy to obtain a solution of the Dittus-Boelter equation which has an accuracy of  $\pm 0.2$  per cent (based on tests made on the original  $38 \times 30$  inch ink drawing of the nomograph).

Constructing the nomograph so that the  $u$  and  $D$  scales are the last to be used, it is easy to obtain all practical combinations of linear velocity and diameter of pipe which will give any desired coefficient of heat transfer, as shown in the following example: Consider the same substance as in the previous example, but determine what velocity and diameter of pipe can be used in order to have a heat transfer coefficient of  $h$ . Proceed as in the previous example until the point on auxiliary line 7 is determined. Assume a value of  $u$ , and obtain the point on auxiliary line 9.

When that point is connected with the desired value of  $h$ , the  $D$  axis is cut at the value which will satisfy all the assumed conditions. Similarly one can assume the  $D$  and find the necessary  $u$ . If  $D$  is assumed, obtain the auxiliary point on axis 9 by passing a straight line through the assumed values of  $h$  and  $D$  on their respective axes. The value of  $u$  needed to realize the desired conditions is obtained by connecting the auxiliary points on axes 7 and 9.

The nomograph can also be used to solve for any unknown in the given equation. If, for example, it is desired to know what  $u$  has been assumed in order to arrive at a certain value of  $h$ , proceed as follows: Work the nomograph as far as possible from each end; that is, in this instance connect 1 and 2, 3 and 4, and then 11 and 10, and 9 and 8. This procedure will result in a point on axes 5 and 7. A straight line through these two points will cross the scale of the unknown at the solution.

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# DRYING OF MEATS

## Rate of Dehydration of Uncooked Cured Ground Meats

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**D**ESPITE the present importance of dehydrated meat products, very little published information regarding the rate of dehydration of such materials under various drying conditions is available. The following data have been selected from experiments carried out over the past few years in the chemical engineering laboratories of the University of Minnesota on the preparation of various types of meat products. These data are principally concerned with the rapid drying in air of uncooked ground pork and beef such as is usually found in dry sausage meats. Some data are also presented on the drying of relatively lean, pre-cooked ground beef.

### DEHYDRATION OF UNCOOKED CURED MEATS

The dehydration of uncooked meat containing a cure of salt, sugar, nitrates, etc., was investigated. Such meats (for example, comminuted pork and beef mixture) have long been dehydrated in casings to produce what is known as dry or summer sausage. This product has been considered an excellent form of dehydrated meat and finds a large market. However, as produced by present methods, it is not a great factor in the current dehydration program, partly because production is limited by the length of time required for the drying process (30 to 90 days). Accordingly, it was believed that a thorough study of the mechanism and rate of drying of such mixtures might result in more rapid processing while retaining, or improving upon, certain qualities present in dry sausage—for example, established consumer acceptance, good keeping quality, and ability to be eaten directly without rehydration or cooking.

Meat mixtures, when intended for use in dry sausage, are usually prepared by comminuting a blend of beef and pork meat, dry cure salts, and spices. After an aging or curing period of a few days at low temperature, the mixture is extruded through a nozzle into casings. The resulting sausages are then slowly dried. The initial composition of such mixtures commonly includes 50 to 55 per cent water and as much as 20 to 30 per cent

An investigation has been made of the air drying under various conditions of samples of uncooked cured meat to form products having properties similar to dry, or summer, sausage. The rate of drying is materially affected by the handling operations and temperature conditions, which may cause the fat to film over the material. As contrasted to the usual dry sausage manufacturing operations, shorter times of drying are necessary to obtain a product containing 25–30 per cent moisture. This is particularly true when the material is dried in the form of small cylinders. The products obtained are similar in color and palatability to the usual dry sausage sold on the market. The small particles, however, do not adhere to form a solid hard mass. If larger samples—for example,  $4 \times 1\frac{1}{8}$  inches in cross section—are dried, solid firm products are formed in about 15 days. Such observations as could be made over the period of a year indicate that the keeping qualities and bactericidal properties of the dried products are decidedly favorable.

fats. The final moisture content varies with the type of sausage; an ordinary dry sausage may, for example, contain about 28 to 30 per cent water.

In this experimental work no casings were used. Rather the ground mixtures of beef and pork containing cure were dried in various shapes without any covering. Under these conditions much more rapid and uniform drying takes place. Since the meat mixtures are quite plastic and adherent, the samples were forced into various shapes by extrusion. Cross sections of the shapes studied ranged from very small cylinders, which dried rapidly, to larger rectangular sections. The latter were investigated in an effort to make possible more efficient packaging than the large cylindrical casings used for present dry sausage and also to obtain a more coherent product.

In this investigation the presence of fat was found to influence greatly the method of preparation of the meat for drying, as well as the actual drying operation.

Such factors as the conditions at which extrusion takes place—that is, meat temperature and amount of surface working—must be considered. The tendency for fat to cover meat particles and thus retard drying is considerable if these conditions are not proper. For the same reason drying operations must be carried out at relatively low temperatures, the range 50–75° F. being investigated in this work. These temperatures are also necessary to minimize microbiological and enzymatic action.

The processes used in dehydrating precooked meat were discussed by Kraybill (2). A common method for beef involves coarse cutting, cooking in a steam-jacketed kettle, and fine grinding. At this stage the material differs considerably from the uncooked type. It is easily disintegrated into granular particles presenting a large specific surface. Drying air temperatures are usually in the 140–170° F. range with the meat temperature between 98° and 150° F. Precooked beef may be dehydrated rapidly, especially when the meats are lean; however, a high fat content causes noticeable interference with the drying rate. In drying precooked pork, this factor becomes more troublesome despite the removal of fat in preliminary operations.

The drying of precooked meat is carried out to a final moisture content of 10 per cent or less. For comparison some data are

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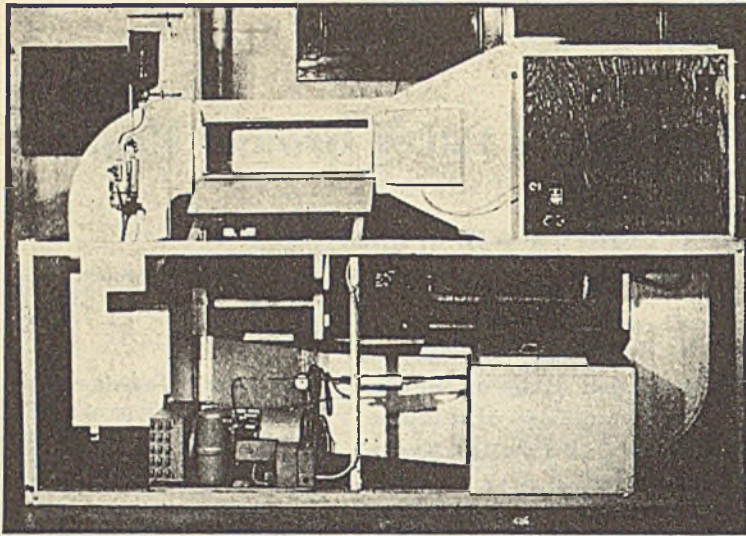


Figure 1. Experimental Dryer

presented in this paper on the drying of precooked beef. In the case of uncooked cured meat, suitable keeping qualities are obtained by drying to a final moisture content of 25-30 per cent. As a consequence, only the latter products are readily edible without being rehydrated.

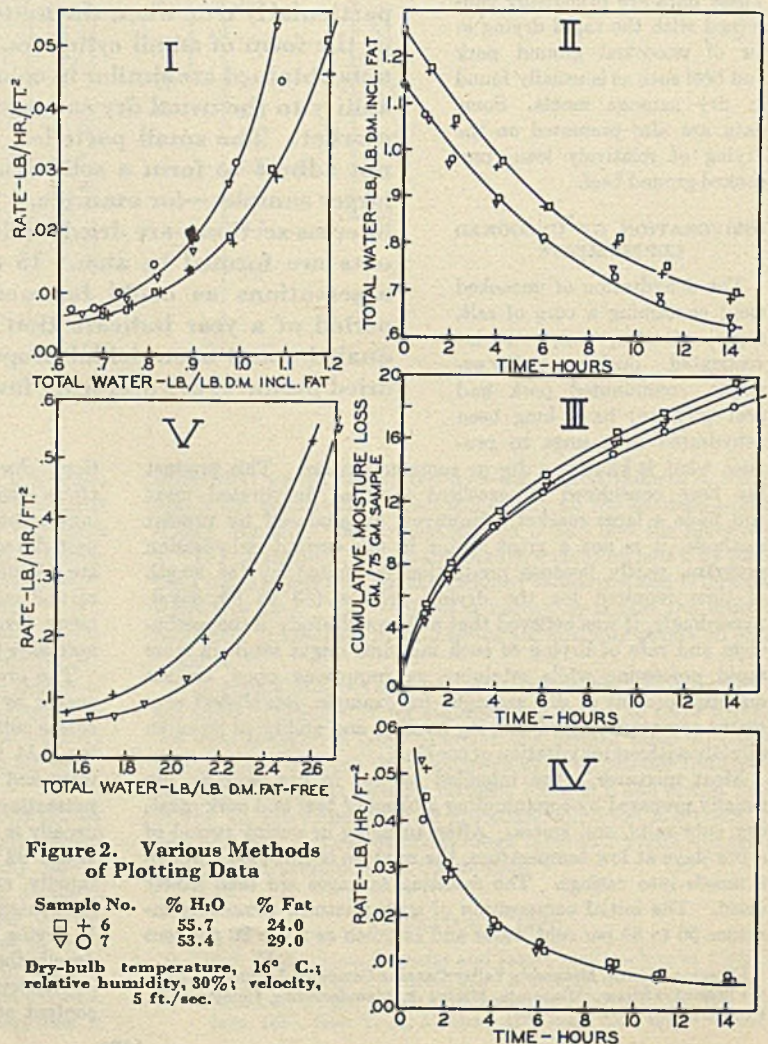
The dried products obtained in this investigation were similar in color and taste to those obtained in the usual process for dry sausage manufacture. The adherent nature of the individual particles also equals that of dry sausage. If, however, very small extrusions having a large specific surface are dried rapidly, it is not readily possible to regrind and then recombine them to form a larger shape possessing adherence. Such products cannot be sliced but can be spread. Further work may lead to a method of obtaining the former property. The principle of recombining meat after grinding is of considerable importance, since it offers a satisfactory utilization of small, rapidly dried shapes. Use of the latter is advantageous since the drying time increases enormously with an increase in cross section. For example,  $\frac{3}{8}$ -inch-diameter cylinders may be dried to 28 per cent moisture in about 10 hours, while  $1 \times 2$  inch slabs require 14 days.

#### KEEPING QUALITY OF UNCOOKED CURED MEATS

The keeping qualities of dry, uncooked, cured meat may be estimated on the basis of the many years of experience the industry has had in the manufacture and handling of common dry sausage. Like the latter, it is not a sterile product but shows similar bacteriological population. Storage temperatures should probably equal those employed for dry sausage with the same moisture content. If the product is canned and pressure-cooked to obtain the complete sterility required for universal military use, most of its attractive qualities are lost.

Some results are given on the keeping qualities of vacuum-tinned uncooked samples of dried cured meats. These tests show a decrease in bacterial count with time, the absence of rancidity, and the absence of mold growth in the product. The last is often troublesome with ordinary dry sausage.

An additional possibility, which was not fully investigated, was to reduce the concentration of cure in the rapidly dried meat from the rather high amount present in ordinary dry sausage. The latter product is often considered to be highly seasoned by the consumer, and a product with a lower level of cure could be attractive. It is believed likely that such large amounts of cure are unnecessary to preserve cured meat when it is in the final dehydrated stage. However, the regular cure is necessary for preservation during a long drying process, particularly when the meat may be rather wet for several weeks in the early stages of drying. It should be possible, as a consequence of a great reduction in drying time, to have greater freedom in the choice of cure.





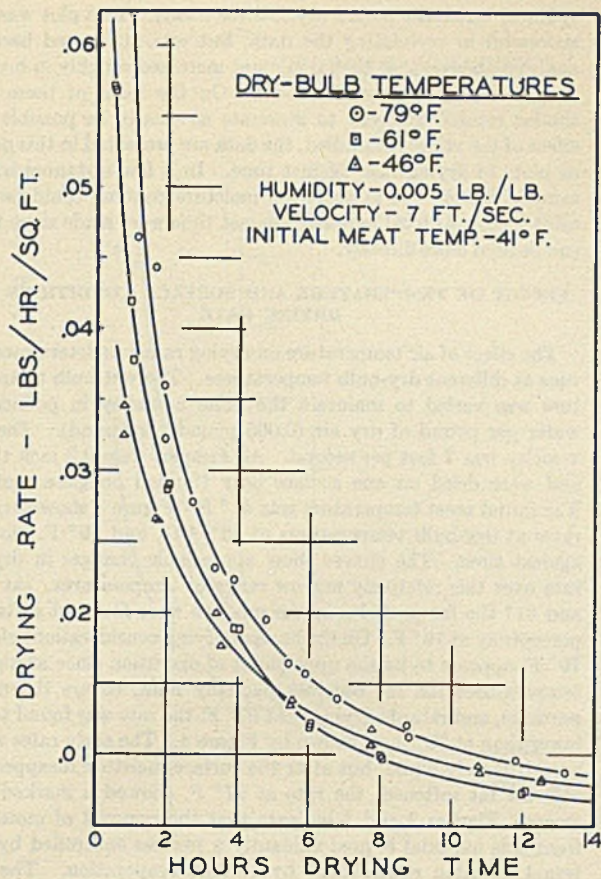


Figure 3. Effect of Air Temperature on Drying Rate

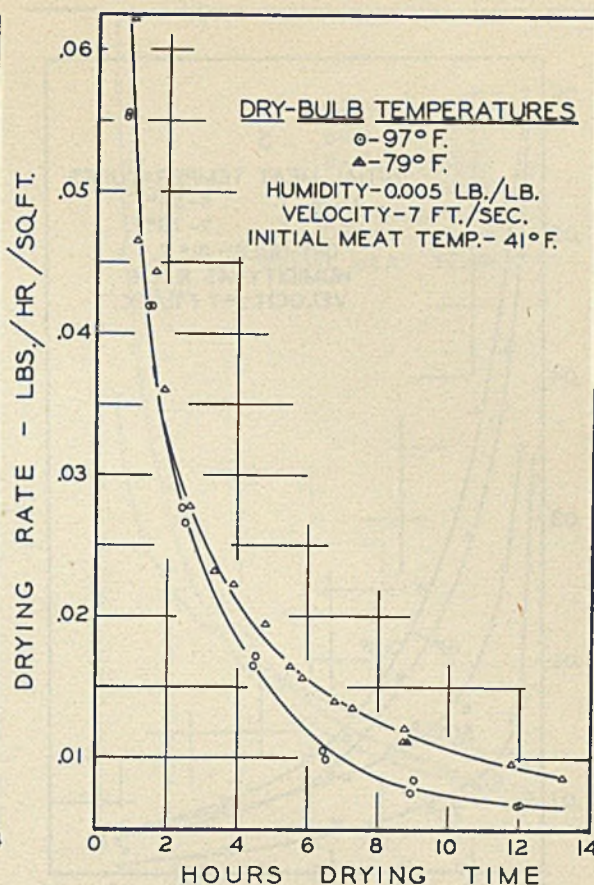


Figure 4. Effect of Extreme Air Temperatures on Drying Rate

#### EXPERIMENTAL PROCEDURE

Experiments were conducted in a test dryer (Figure 1) capable of producing a constant stream of air of variable and controllable temperature, humidity, and air velocity. This apparatus was described in detail by Ritchell, Piret, and Mann (3). It consisted essentially of an insulated sheet-metal duct system fitted with an adjustable speed fan. A contracting section placed immediately ahead of the drying chamber provided a uniform air flow through the drying chamber in which the meat samples were placed on glass plates or screen trays. The air flow was usually parallel to the surface of the material, although through-circulation could be obtained. Temperature and humidity adjustments were made by variation of dampers which allowed a portion of the air to by-pass a refrigerated coil. Manual and automatic control of resistance heaters and steam jets then allowed re-heating and rehumidifying of the air to desired dry- and wet-bulb temperatures (accuracy of control was  $\pm 0.1^\circ \text{C}$ ). For higher temperature drying, the refrigeration system was not used. The cooling and dehumidifying load was taken up by admission of outside air.

The meat samples used in the experiments on uncooked cured meat were taken at various times over a period of two months from several large commercial production batches of meat mixture being prepared for the manufacture of salami sausage. These batches had been prepared in a rotary cutter in which the cure salts used for sausage manufacture had also been added. Following the customary commercial procedure, all samples were aged or cured by storing for two or three days at  $40\text{--}45^\circ \text{F}$ . before use. Previous to drying, the meat was brought to a definite temperature. This temperature was important in order to control, during sample shaping operations, the spreading of a film of fat on the meat particles; as pointed out previously, this procedure decidedly affected the rate of drying. For preliminary experiments it was found convenient to prepare samples by rapidly flattening a weighed quantity of meat (usually 75 grams) on a 5-inch square glass plate. Other shapes on which data are

given were extruded through nozzles under pressure to form shapes of desired cross section.

A few typical curves for precooked meat are given. The meat in this case was chopped into approximately  $1/2$ -inch cubes and cooked with a small amount of added water in a steam-jacketed kettle (30 minutes at  $212^\circ \text{F}$ ). The meat was slowly stirred during the cooking operation. After regrinding through a  $1/8$ -inch plate, the material was dried in the apparatus mentioned above. The requisite amount of salt for keeping qualities (3.5 per cent in the final product) was added before cooking.

**METHOD OF CORRELATION.** Correlation of the data derived from samples on glass plates was difficult because of the variable nature of the material dried. As a result of the long time required for the experiments and the undesirability of long storage periods, it was necessary to use samples from different large commercial batches of meat mixture. These samples varied sufficiently in moisture and fat content to render unsuitable the usual chemical engineering methods of plotting drying rate or drying time against residual moisture content. For example, when two samples having 53.4 and 55.7 per cent initial moisture were dried under identical conditions, the plots of drying data gave two rather widely separated curves (I and II, Figure 2). However, in plotting cumulative moisture loss against time, the points fell more nearly on a single line, showing that drying took place at nearly the same rate for equal times of drying (III, Figure 2). The data plotted as drying rate (pounds per hour per square foot of surface) against drying time (hours), also fell on a common line, justifying the choice of these coordinates in correlating the data (IV, Figure 2). Figure 2 also includes a graph (V) of drying rate against total moisture on the fat-free basis



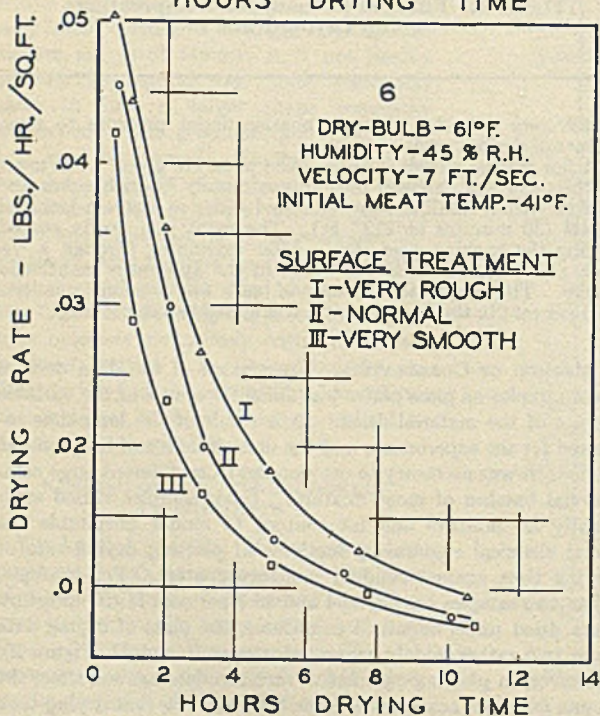
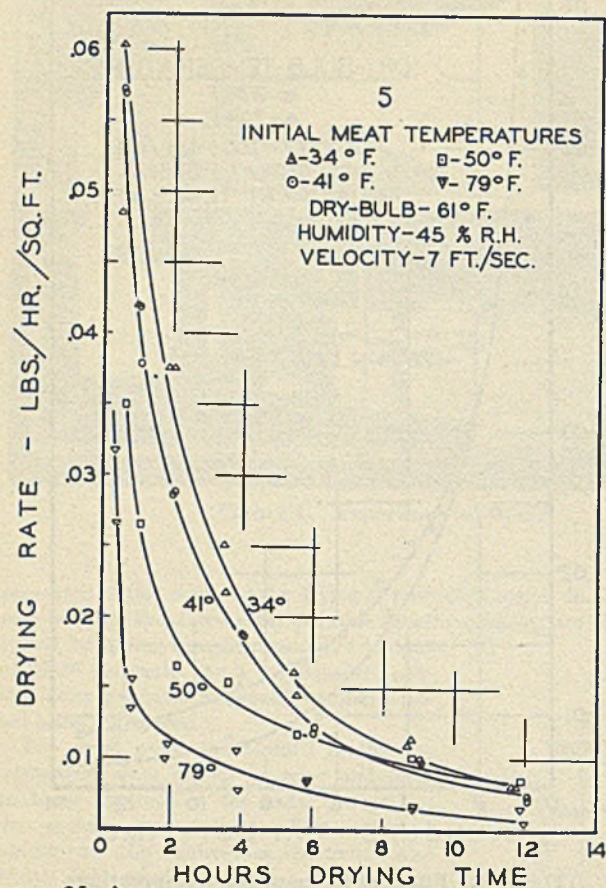


Figure 5. Effect of Initial Meat Temperature on Drying Rate

Figure 6. Effect of Surface Treatment of Meat on Drying Rate

(pounds water per pound dry fat-free meat). This plot was unsuccessful in correlating the data, but was attempted because analyses showed that the fat content increased roughly in inverse proportion to the water content. On the basis of these and similar results, in order to illustrate as clearly as possible the effect of the variables studied, the data are presented in this paper as plots of drying rate against time. In a few instances where samples having the same initial moisture content could be obtained, plots of total moisture against time were made since they can be used more directly.

#### EFFECT OF TEMPERATURE AND SURFACE CONDITIONS ON DRYING RATE

The effect of air temperature on drying rate was determined by runs at different dry-bulb temperatures. The wet-bulb temperature was varied to maintain the same humidity in pounds of water per pound of dry air (0.005 pound per pound). The air velocity was 7 feet per second. All samples were 0.2 inch thick and were dried on one surface only (formed on glass plates). The initial meat temperature was 41° F. Figure 3 shows drying rates at dry-bulb temperatures of 46°, 61°, and 79° F. plotted against time. The curves show appreciable changes in drying rate over this relatively narrow range of temperatures. At 46° and 61° the fat particles in the mixture were firm but softened perceptibly at 79° F. On the basis of drying considerations alone, 79° F. appears to be the upper limit of operation since at higher temperatures the fat becomes partially fluid, covers the meat particles, and retards drying. At 97° F. the rate was found to be lower than at 79° F. as shown by Figure 4. The early rates were approximately equal, but after the surface moisture disappeared and the fat softened, the rate at 97° F. showed a marked decrease. Figures 3 and 4 indicate that the removal of moisture from this material is predominantly a process controlled by internal diffusion rather than by surface evaporation. The increase in drying rate at higher air temperatures is therefore mainly due to the increased rate of moisture diffusion through the material. Since in these experiments the initial temperature of the meat was sometimes far below that of the air, the full increase in rate was not quite realized. The effect of low initial temperature was, however, not great since thermocouple measurements showed that the temperature rose in 30 minutes from the initial 41° F. to approximately that of the wet-bulb temperature of the air. Further increase was slow because of the cooling effect of water evaporation. Eight or nine hours were required for the meat to reach the various dry-bulb temperatures.

A typical evaluation of the effect of dry-bulb temperature on drying time may be obtained by noting the time required to dry the material from an initial moisture content of about 52 to 40 per cent. The latter figure was considered the final moisture content for a product under consideration at the time of these experiments. At 46° F. this moisture content was attained in 10.8 hours; at 61° F. and 79° F. the times were reduced to 9.0 and 5.5 hours, respectively. At 97° F. the time increased to 6.2 hours.

These results show that substantial reductions in drying time may be attained with air temperatures higher than those now used in dry sausage manufacture. The latter temperature is approximately 50° F. The results also show that the choice of temperature is in part limited by the high fat content of the material. The temperature limitations imposed by the occurrence of microbiological action have not been fully investigated. It is believed, however, that the maximum temperature may be well above 50° F. if the drying process is rapid. This is based on repeated organoleptic tests on the dried products, none of which showed signs of deterioration.

The temperature at which the meat was extruded into slabs had a marked effect on drying rate. Figure 5 shows progressively lower rates for several 0.2-inch thick samples formed by the same technique but from meat held at 34°, 41°, 50°, and 79° F. during the forming operations. The lower curves in Figure 5 indicate a



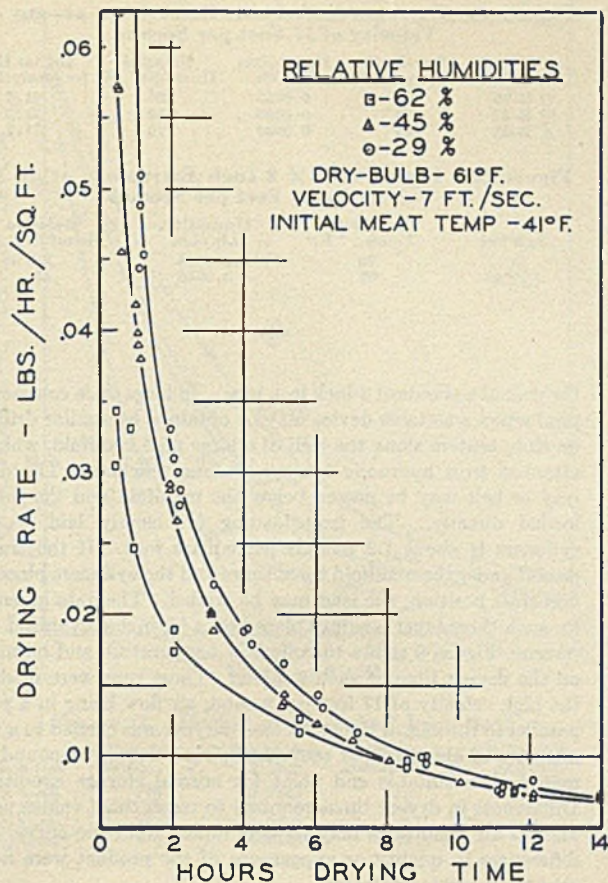


Figure 7. Effect of Humidity on Drying Rate

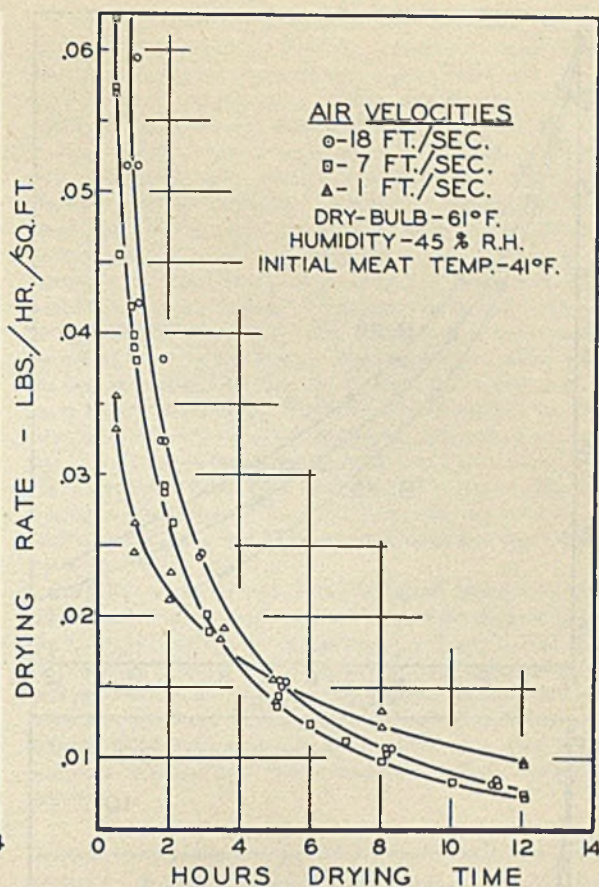


Figure 8. Effect of Air Velocity on Drying Rate

lower drying rate—in other words, a much longer drying time. It is apparent that the low drying rates at high initial meat temperatures were due entirely to covering of meat particles with fat by mechanical action. But for the change of fluidity of fat with temperature, the curves would be superimposed or given in reverse order early in the drying period. The time required to dry samples formed at different temperatures to 40 per cent moisture varied from 6.5 to 24 hours as temperature increased over the range stated. This effect was rather critical. Even at the relatively low temperature of 41° F. the time increased to 9.0 hours. The dry-bulb temperature for these runs was 61° F. Similar behavior was found at dry-bulb readings of 46° and 79° F.

It follows that for any fixed meat temperature the drying rate will be dependent upon the amount of mechanical work expended in forming the sample, especially its surface. That this factor is important is shown by Figure 6 which gives the behavior for meat molded at 41° F. Curve II represents a sample formed with the uniform technique used throughout this experiment, the minimum treatment required to cover the glass plate fully and evenly. The sample shown by curve III was formed in the same manner except that the surface was given several light strokes with the flat of a spatula before drying. This treatment increased the drying time to 40 per cent moisture at the conditions used from 9 to 14 hours. For curve I the samples were flattened over the glass plate with the edge of a spatula. Here the drying rate increased, but the increase was due not only to the lower degree of coverage with fat but also to the larger drying area provided by the rough surface. The drying time to 40 per cent moisture for these rough samples decreased to 7 hours.

Summarizing, it is important to control carefully the conditions during the drying operations and while handling the products previous to drying. As the above examples show, this will result in appreciably shorter drying periods.

#### EFFECT OF AIR HUMIDITY AND VELOCITY ON DRYING RATE

The effect of humidity on the partial drying of 0.2 inch thick samples on glass plates was determined by runs at 29, 45, and 62 per cent relative humidity. The dry-bulb temperature and air velocity remained constant at 61° F. and 7 feet per second. All samples were formed from meat at 41° F. Figure 7 shows that drying occurred more rapidly with low humidity, but that this effect diminished with time as the drying became more dependent upon diffusion. Drying to 40 per cent moisture took place in 7.9 hours at 29 per cent humidity, 9.0 hours at 45 per cent, and 12.5 hours at 62 per cent.

Figure 8 shows the effect of air velocity on the drying rate for the usual type of sample. Dry-bulb temperature and humidity were constant at 61° F. and 45 per cent relative. The velocities used (1, 7, and 18 feet per second) produced some noticeable effects. The drying times to 40 per cent moisture over the above range were 10.5, 9.0, and 6.0 hours, respectively. As shown by the curve for the low velocity of one foot per second, a different type of drying occurred. This was characterized by the absence of a thin, dark-red surface layer found in all other experiments. In this instance the meat surface appeared unaltered, probably due to the fact that the low drying rate made it possible for the internal diffusion mechanism to keep pace with surface evaporation. Observations were made on the behavior of the above surface film after completion of drying. In all cases it virtually



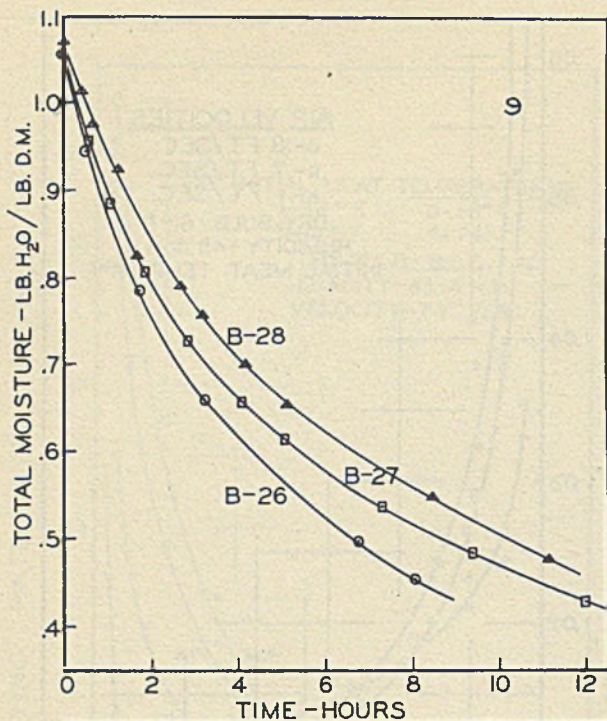
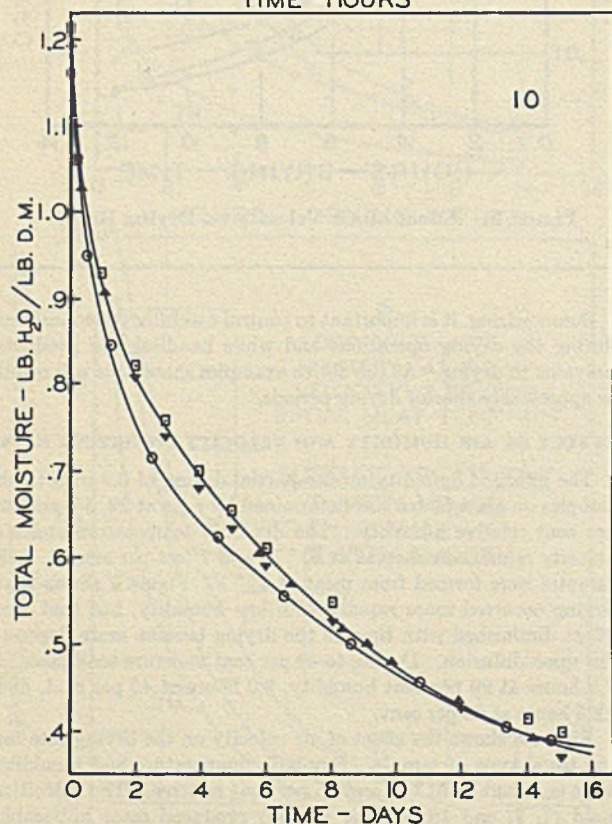


Figure 9. Drying of  $\frac{3}{8}$ -Inch Extrusions at an Air Velocity of 17 Feet per Second

Run No.	Dry-Bulb Temp., ° F.	Humidity, Lb./Lb.	Relative Humidity, %	Initial H <sub>2</sub> O by Analysis, %
○ B-26	70	0.0045	29	51.5
□ B-27	70	0.0080	50	51.5
△ B-28	60	0.0080	70	51.7

Figure 10. Drying of 1 × 2 Inch Extrusions at an Air Velocity of 10 Feet per Second

Symbol	Dry-Bulb Temp., ° F.	Humidity, Lb./Lb.	Relative Humidity, %
○	70	0.0045	30
□▽△	60	0.0045	40



the wall of a standard 3-inch iron pipe. In large scale commercial production a suitable device may be obtained by similar drillings on close centers along the wall of a large pipe manifold, which is attached to a hydraulic sausage stuffing machine. The dryer tray or belt may be passed below the manifold and the former loaded directly. The tray loading for closely laid  $\frac{3}{8}$ -inch cylinders is about 1.2 pounds per square foot. If the tray is passed under the manifold three times and the cylinders placed in crisscross position, the load may be tripled. The data given are for such three-layer loadings placed on a  $\frac{1}{4}$ -inch galvanized wire screen. Figure 9 shows the effect of temperature and humidity on the drying time of such samples. These runs were made at the high velocity of 17 feet per second, air flow being in a plane parallel to the axis of the cylinders. Drying was carried to a final moisture of about 30 per cent (0.43 pound water per pound dry material), a suitable end point for normal storage conditions. Differences in drying times required to reach these values under various air conditions may be determined from the curve. No differences in quality or appearance of the product were noted over the range investigated.

As stated, the drying of 1 × 2 inch extruded slabs is a considerably slower process than that for the small cylinders described above. As Figure 10 shows, about 11 days are required to attain a moisture content of 31 per cent, while 15 days are necessary to reach a value of 28 per cent (0.39 pound per pound). These times are of the order of those necessary for certain small-diameter dry sausages; some time is saved by the absence of a casing.

Drying of these large shapes is so largely controlled by internal diffusion that the air humidity and velocity could not be expected to influence appreciably the time required. For example, differences in drying time at velocities of 10 and 5 feet per second were not appreciable. The runs plotted in Figure 10 show the effect of different dry-bulb temperatures only. Even this variable is of influence only in the early stages of drying. As was the case with samples discussed previously, no permanent surface hardening effects were noted under any of the conditions employed. Samples from different batches of material having lower moisture and higher fat contents than those for which data are given showed similar drying times.

#### DRYING CURVES FOR PRECOOKED LEAN BEEF

The following data on the dehydration of precooked lean beef are included mainly for comparison with the foregoing results on uncooked meat. The method of preparing samples has already been outlined. In carrying out the dehydration, the meat was placed on a 15-mesh screen tray so fixed as to make weighing possible without removal from the dryer. The tray loading was one pound per square foot of surface.

Figure 11 shows representative drying curves obtained at four different air conditions. The latter were selected to provide an approximate indication of the effect on drying time of air temperature, humidity, and velocity. Two sets of runs were made at 150° and 170° F. Air velocities were 4 and 18 feet per second. The air humidity was either 0.0725 or 0.0460 pound water per

disappeared on standing due to reabsorption of moisture from the interior of the sample.

#### DRYING OF EXTRUDED SHAPES

Typical curves are given for the drying of two different sizes of extrusions,  $\frac{3}{8}$ -inch cylinders and slabs of 1 × 2 inch cross section. The former were obtained by forcing the mixture through the short nozzle formed by drilling a  $\frac{3}{8}$ -inch hole into



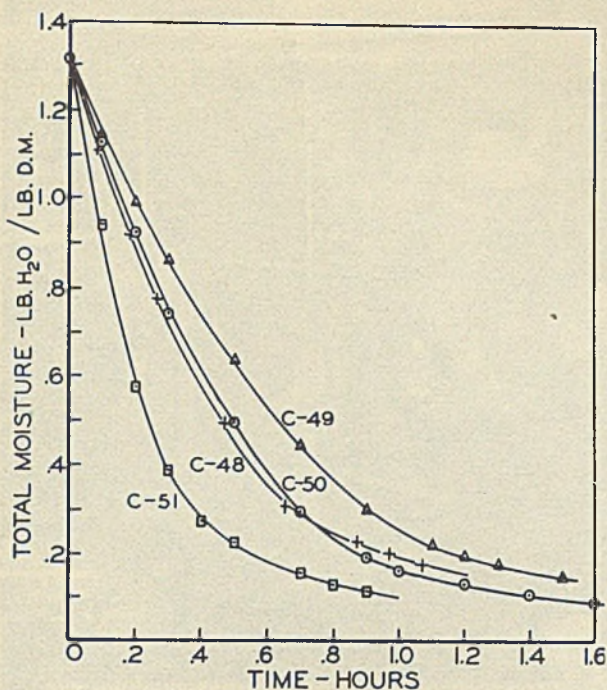


Figure 11. Drying of Precooked Lean Beef

Run No.	Dry-Bulb Temp., ° F.	Humidity, Lb./Lb.	Relative Humidity, %	Air Velocity, Ft./Sec.
+ C-48	170	0.0725	17	4
△ C-49	150	0.0725	34	4
○ C-50	150	0.0460	22	4
□ C-51	170	0.0725	17	18

pound dry air. The important effect of velocity under these conditions can be readily seen by comparing the curves for runs C-48 and C-51. The effect of humidity at 150° F. is evident from the curves for runs C-49 and C-50. The more rapid drying at a dry-bulb temperature of 170° F. over that at 150° is shown by the plots of runs C-48 and C-49.

A comparison of this family of curves with those previously presented on uncooked cured meats shows the decided effect of cooking and possible lack of cure in greatly increasing the rate of drying. The product is of widely different character and properties.

#### KEEPING QUALITIES OF PRODUCTS

The possibility of dehydrating this material in a wide range of shapes requiring widely different drying times gives rise to a considerable number of problems concerning quality and keeping characteristics. This is particularly true if it is not possible to follow directly the well established Bureau of Animal Industry regulations (5) for the manufacture of dry sausage. These are mainly concerned with the elimination of danger from trichinae and demand various storage periods under specified temperature conditions and a specific cure content. In the ordinary process of manufacture, the curing or holding period before drying and the drying period itself suffice to fulfill these conditions. If a rapid process is used, the pork muscle in the mixture must be either subjected to proper frozen storage before use in the mixture or must be suitably stored after the dehydration stage in order to comply with present Bureau of Animal Industry regulations on trichinae control.

Considerable research has been done on the bacteriology of uncooked meats cured with salt, nitrates, nitrites, sugar, etc.; this has been reviewed by Jensen and Hess (1). Further research is necessary on the products made by rapid drying since the method

of manufacture differs so widely from established practice. It was possible to study the keeping qualities of a number of samples of sausage meat dried without casings which had been packaged in vacuum-closed cans. The meat mixtures had been prepared in accordance with Bureau of Animal Industry regulations. The slabs of meat were of such size ( $4 \times 1\frac{1}{8}$  inches cross section) that the drying time exceeded the minimum required by the Bureau of Animal Industry. A standard cervelat mixture was employed. Samples were canned at final moisture contents of 28 and 25 per cent. It was found that over a one-year period rancidity and mold growth were absent, a factor attributable in part to vacuum packaging. In addition to periodic organoleptic tests, bacterial counts were also made over a one-year storage period at room temperature. The organoleptic tests indicated no loss in palatability and the product was appetizing and of good flavor throughout. Further observations will be made to determine whether these properties are retained on longer storage. The color of the stored material was a normal red, indicating a negligible formation of undesired hematin pigments (4) during or after drying. Enameled cans were not used in this experiment, but they are recommended since the unprotected tin plate was badly stained.

Bacterial counts (Table I) on the canned product show that a high population was present after completion of drying but that the count fell rapidly during storage to very low values. Parallel tests run on ordinary dry sausage showed approximately equivalent populations during drying and storage. Measurements of pH were also made on the canned material after prolonged storage. The resulting values likewise agreed with those determined on ordinary dry sausage. These values were all in the pH range 5.8-6.2.

TABLE I. BACTERIAL COUNTS ON VACUUM-CANNED SAMPLES OF DRIED CERVELAT

Time after Vacuum Sealing, Weeks	Bacteria per Gram	
	28% water samples	25% water samples
0	21,800,000	24,300,000
1	10,000,000	2,540,000
3	510,000	400,000
7	315,000	314,000
12	34,000	21,000
18	3,100	2,100
25	290	750
49	180	110

Owing to the lack of facilities for dehydrating sufficiently large quantities of meat in such shapes as  $\frac{3}{8}$ -inch cylinders, bacterial counts like those described above could not be carried out on rapidly dried material. However, organoleptic tests were made whenever possible. A common procedure was to seal hermetically a can of material, such as reground dried  $\frac{3}{8}$ -inch extruded cylinders, and examine the contents after various periods of storage at room temperature. In all cases the color, aroma, and flavor were good.

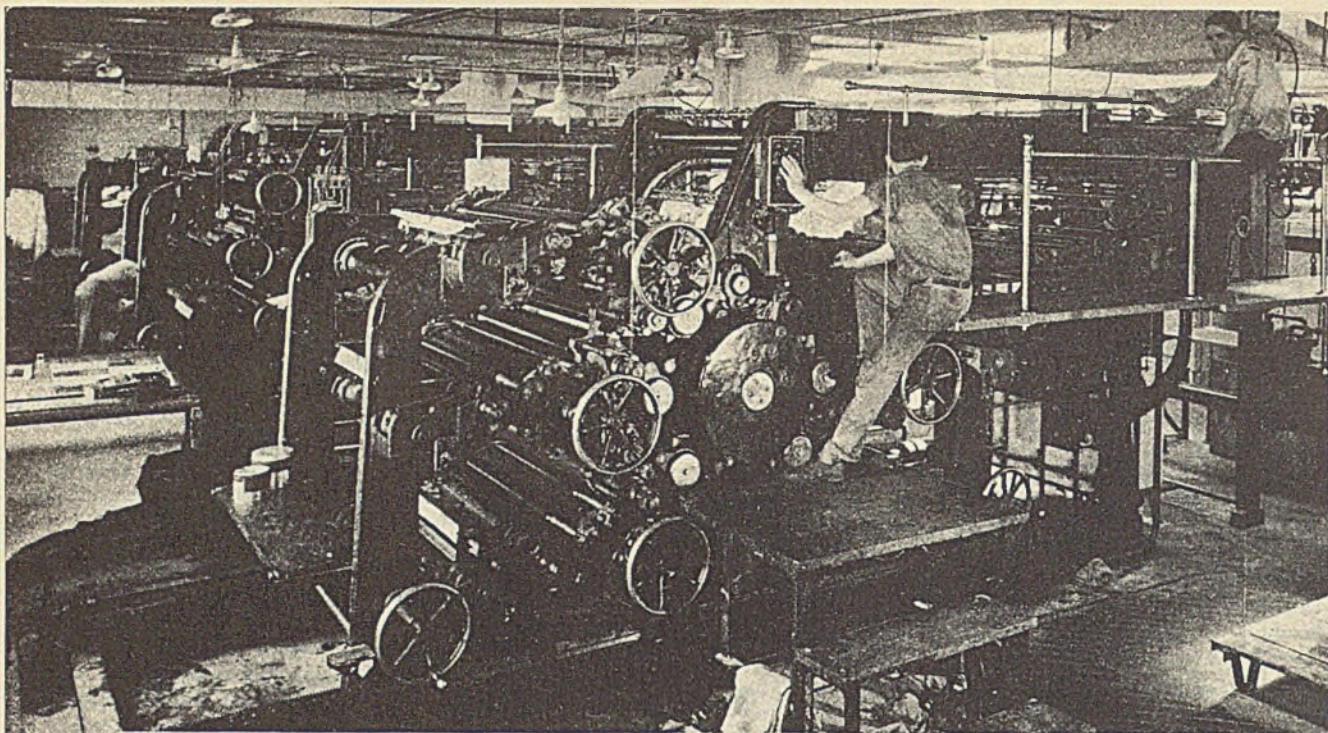
#### ACKNOWLEDGMENT

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## SOYBEAN PROTEIN DISPERSIONS AS PRINTING INK VEHICLES

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IN RECENT years, zein, an alcohol "soluble" protein, has been used in diethylene glycol and other polyhydric alcohols to give a new type of printing ink (4) which does not harden by oxidation of the binder or by evaporation of the thinner but is caused to set to a hard film by precipitation (4, 6). This change from a liquid or plastic state is accompanied by absorption of moisture which lowers the "solubility" of zein in polyhydric alcohols (3, 7). When the water content exceeds a critical limit, zein separates. In printing inks, zein seems to occlude the pigment particles; and by exposing a printed film to steam or water, the zein is precipitated with the pigment.

Other simple proteins of commercial importance are casein, blood albumin, an alkali-extracted protein from maize (Maco. 13), and soybean alpha-protein. When these substances are substituted for zein, they have to be dispersed in polyhydric alcohols in the presence of peptizing reagents. Diethylene glycol is the common dispersant for moisture-sensitive inks because of its slow evaporation rate, a result of hygroscopicity and low vapor pressure. In very thin ink films it tends to absorb water from the atmosphere during the process of evaporation. During the hardening of a print, excessive moisture content causes the binder and pigment to separate from diethylene glycol. Part of the water-polyhydric alcohol mixture evaporates, while the other part penetrates into the paper and leaves pigment and binder on the surface.

Among the above-mentioned proteins, glycinin, the protein from soybeans (also called soybean alpha-protein) was investigated, and blood albumin, casein, and Maco were used in dispersions for comparison. Glycinin belongs to the class of globulins, which are insoluble in polyhydric alcohols but form colloidal dispersions in some of them.

Egg albumin, casein, and gelatin are more readily dispersed in alcohols than globulins, as indicated by the way some spinning solutions and resinous products are made. The first three proteins can be dispersed in tetrahydrofurfuryl alcohol, cyclohexanone glycerol phthalate, etc. (14), or in acetone (11), 80 per cent alcohol (11), or even an alcohol-benzene mixture (1). Modified alkyd resins are made by heating glycerol, casein, and a dicarboxylic acid together at about 160° C., and similar products were obtained by heating casein, egg albumin or gelatin with glycerol, sometimes with small amounts of catalysts such as alkalis or mineral acids. When globulins are used instead of the previously mentioned proteins, they have to be degraded to simpler units. According to Sly (15), casein is readily dispersible in glycerol at elevated temperatures, whereas globulins must be partially hydrolyzed before dispersion can be accomplished. However, formaldehyde-hardened soybean protein is compatible with diethylene glycol. Plastics have been prepared from this modified protein with small amounts of polyhydric alcohols as plasticizers (2). Treatment with aldehydes at elevated temperatures modifies proteins sufficiently to change their characteristics.

The investigation on the use of soybean alpha-protein in printing inks is divided into two parts: search for efficient

The above photograph shows several five-color sheet-fed rotary presses in a printing plant (courtesy, C. B. Cottrell & Sons).



dispersing agent, and determination of optimum or most suitable dispersion procedure. The colloidal dispersions were used solely in steam-setting printing inks, but they are adaptable as a starting point for paper coatings, artificial fibers, and bases for emulsions. Chemical modifications of soybean protein dispersions will be discussed in a later report.

The search for efficient dispersing agents included acids, ammonium salts, and various other nitrogen compounds. The resin-forming properties with aldehydes and the cost of the compounds were taken into consideration.

#### DISPERSION PROCEDURE

The dispersion was conducted in a 400-ml. Griffin beaker (Corning Catalogue No. 1000); its tin cover had circular openings for stirrer and thermometer. This arrangement permitted the removal of a crust formed on the walls of the beaker. The beaker was immersed into a bath of peanut oil, the temperature of which was observed by a second thermometer with the bulb near the bottom of the beaker. Temperature fluctuations in the reacting vessel could be controlled within  $\pm 2^\circ$  C. during operation. The oil bath was first heated rapidly to about  $15^\circ$  C. above the chosen temperature and held there until the temperature in the beaker had risen to about  $10^\circ$  C. below that chosen. Then the source of heat, a gas flame, was removed. When both thermometers gave readings within  $2^\circ$  C., the gas burner was adjusted for the chosen condition. Sometimes the bath had to be cooled by addition of small quantities of cold oil.

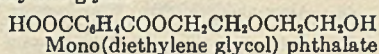
If there was no visual evidence that a reaction had taken place after one hour, the temperature was raised as indicated in Table I. The top temperature of  $160^\circ$  C. was arbitrarily chosen although it allowed for a substantial loss of polyhydric alcohol due to evaporation. Adjustments were made after the end of the reaction period by adding an amount of dispersing medium equal to the loss of weight. All determinations were based upon adjusted batches. Loss of weight caused by volatile substances other than the dispersing medium, such as water, carbon dioxide, etc., was regarded as a loss of dispersing medium and was adjusted as such.

#### DISPERSING AGENTS

**ACIDS.** Organic acids or the respective anhydrides were used to effect degradation of the protein to a less complex, dispersible substance. It was intended then to esterify any free carboxylic groups after dispersion. When anhydrides, such as those of maleic and phthalic acid, are heated with alcohols, alcoholysis of the anhydride proceeds at about  $80^\circ$  C., as illustrated with phthalic anhydride (8):



Phthalic anhydride Diethylene glycol



Mono(diethylene glycol) phthalate

Colloidal dispersions of soybean protein in polyhydric alcohols with the aid of proper dispersing reagents were made in three stages: mechanical suspension in polyhydric alcohols at temperatures up to about  $70^\circ$  C.; formation of a semisolid gel between  $70^\circ$  and  $125^\circ$  C., due to the action of the dispersing reagent; and conversion of the gel into liquid at more elevated temperatures. At  $135^\circ$  C. this transformation is accompanied by considerable swelling, which can be eliminated by an intermediate maceration period at  $125^\circ$  C., ranging from 1 hour for the 20 per cent dispersion to 2

hours for the 30 per cent protein dispersion. The 20 per cent dispersions are suitable vehicles for high-oil but not for low-oil absorption pigments, such as chrome yellow and cadmium red; for the latter, the 30 per cent dispersion has to be used for printing inks. These inks are distinguished by their dull appearance, after hardening by exposure to steam. Comparison with other commercial proteins shows that blood albumin, casein, and alkali-extracted protein from maize disperse more readily in diethylene glycol than does soybean protein.

The yields consisted merely of grainy gels, and they indicate that long digestion and high temperature favor at least partial dispersion. This procedure is probably applicable for plastics and resins, but it is not feasible for printing ink vehicles.

Concentrated nitric acid dispersed soybean protein readily, but the dispersions are very corrosive and their odor is stifling. Therefore they could not be recommended for printing inks.

**NITROGEN-CONTAINING COMPOUNDS.** Soybean protein is more soluble in alkaline than in acid aqueous solutions (16). Since many derivatives and salts of ammonia are soluble in ethyl alcohol, it might be assumed that they are also soluble in diethylene glycol and impart peptizing potentials to the alcohol.

Experiments 9 to 41 were conducted for 3 hours at  $160^\circ$  C. Selected results are given in Table II. The consistency of uniform dispersions were measured by the Stormer viscometer, which had been calibrated with oils of known viscosities, using weights of 100, 200, 500, and 1000 grams. The readings were taken in seconds and converted to poises by means of Stormer viscosity charts (Figure 1). Since protein dispersions are thixotropic, the readings from the graphs (called "relative viscosity") depend upon the rate of rotation of the revolving cone; and varying readings can be observed on the same dispersion. With low-viscosity dispersions the variations are small, but with the more viscous compositions the error is appreciable.

A number of nitrogen compounds were found to be effective dispersing reagents for soybean alpha-protein at  $160^\circ$  C. in a 15 per cent concentration in diethylene glycol (Table III). The desire to remove the reagent after it had served its purpose as a peptizer led to the consideration of those materials which are reasonably volatile or are suitable for resin formation. While almost all of the amines and ammonium salts of organic acids can be made to form resins, the more important nitrogen compounds suitable for formaldehyde condensations are melamine, urea, dicyandiamide, and guanidine carbonate. The resins of urea (5, 9) and melamine (10) are well established; it was expected that their condensation reactions, which are conducted in water, would be the same in polyhydric alcohols. Guanidine carbonate and dicyandiamide are also raw materials for resinous products (5) but might also change to melamine or its derivatives (12), and as such are capable of forming resins.

Several of the peptizing reagents were chosen on the basis of these considerations and tried at a concentration of only 5 per cent in diethylene glycol. The compounds which showed

hours for the 30 per cent protein dispersion. The 20 per cent dispersions are suitable vehicles for high-oil but not for low-oil absorption pigments, such as chrome yellow and cadmium red; for the latter, the 30 per cent dispersion has to be used for printing inks. These inks are distinguished by their dull appearance, after hardening by exposure to steam. Comparison with other commercial proteins shows that blood albumin, casein, and alkali-extracted protein from maize disperse more readily in diethylene glycol than does soybean protein.



TABLE I. ACIDS AS DISPERSING REAGENTS

(Reaction mixture: 10 grams soybean alpha-protein, 75 diethylene glycol, and acid as shown)

Expt. No.	Dispersing Reagent		Observations after 2 Hr. at 115° C. Followed by 3 Hr. at 160° C.
	Acid	Grams (millimoles)	
1	Phthalic anhydride	15 (101)	Grainy gel at 115° C. becomes smoother at 160° C., but is still heterogeneous
2	Maleic anhydride	10 (102)	Grainy gel at 115° C. becomes smoother at 160° C., but is still heterogeneous
3	Maleic anhydride	Added in 4 portions of 2.5 g. each every 40 min. at 160° C.	No difference from expt. 1 Same appearance as that of expt. 2 after 4 hr.
4	Adipic	20 (137)	Very grainy after 3 hr. at 160° C.
5	Oxalic anhydrous	9 (100)	Grainy gel at 115° C. becomes almost uniform at 160° C.
6	Acetic anhydride	15	Initial swelling when reacted 2 hr. at 95° C.
7 <sup>a</sup>	Nitric concd.	5	Initial swelling, reacted for 2 hr. at 65° C.; complete dispersion at 95° C. for 3 hr.; viscosity, 5 poises.
8 <sup>a</sup>	Nitric	4	Complete dispersion, for 3 hr. at 95° C.; viscosity, 7 poises

<sup>a</sup> Experiments 7 and 8 yielded uniform dispersions, but products are very corrosive and their odor is stifling.

good results were tried again in a 5 per cent concentration at 145° C. (Table III). At the lower temperature the only suitable compounds are triethylene tetramine and guanidine carbonate. Because of the lower cost and the possibility of resin formation, guanidine carbonate was chosen even though triethylene tetramine is the better peptizing agent.

## OPTIMUM DISPERSION PROCEDURE

In determining optimum or most suitable conditions for the dispersion procedure, consideration was given to concentration of soybean alpha-protein (Figure 2), temperature of dispersion (Figure 3), concentration of guanidine carbonate (Figure 4), and time for reaction (Figure 5). Severe swelling to twice its normal volume occurred in all of these experiments. The dispersions are dark brown.

There is a gradual increase in the relative viscosity of the dispersions as the concentration increases up to about 20 per cent, above which the increase in viscosity is relatively large (Figure 2). A 30 per cent soybean protein dispersion has a viscosity of 36.0 poises, determined with a 500-gram plummet on the Stormer viscometer (experiment 62). There is a considerable decrease in the relative viscosity as the reaction temperature is raised from 120° to 130° C., after which the decrease is gradual (Figure 3).

The dispersions made at 125° C., although turbid, are homogeneous and have a greenish color. Those made at 130° and 135° C. are brownish; however, they are more desirable than the very viscous ones (318 poises) at 125° C.

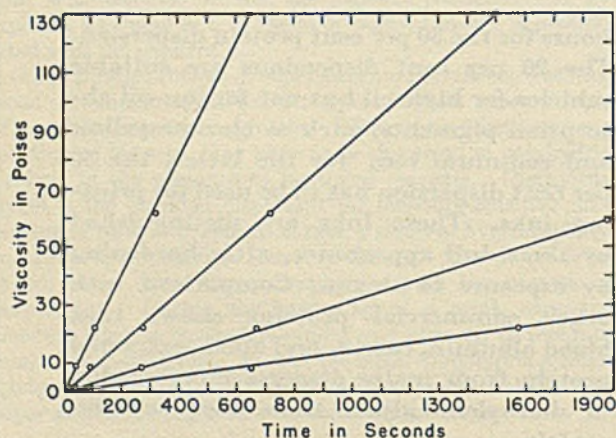


Figure 1. Relation of Viscosity and Time of Stormer Viscometer Calibrations

When the concentration of guanidine carbonate is decreased below 4.5 per cent, the relative viscosity is not consistent, probably owing to the fact that the dispersions are not homogeneous; they contain varying amounts of translucent gel-like aggregates. The experimental points below 4.5 per cent are therefore not consistent and were omitted from Figure 4.

TABLE II. DISPERSION WITH NITROGEN COMPOUNDS

(Composition of mixture: 10 grams soybean alpha-protein (low viscosity), 75 diethylene glycol, 15 dispersing reagent; reacted at 160° C. for 3 hours)

Expt. No.	Reagent <sup>a</sup>	Appearance	Relative Viscosity, Poises <sup>b</sup>	Beckman pH Meter Reading
11	Ammonium thiocyanate C. P.	Uniform brown liquid	1.29	6.27
12	Ammonium acetate	Same; odor of acetamide	1.00	5.59
13	Ammonium oxalate	Uniform brown dispersion with abundant ppt. of white, slightly water-sol. crystals (m. p. 415° C., decomposed)	4.03	5.38
14	Ammonium nitrate	Protein dispersed readily but decomposed after 45 min. with excessive spattering; uniform orange-red, very viscous, tacky dispersion; burns readily	..	..
15	Ammonium chloride	Homogeneous brown liquid	2.75	3.93
16	Ammonium thiocyanate, technical	Homogeneous brown liquid	1.65	4.47
18	Urea, commercial, 50%	Homogeneous brown liquid	2.53	6.99
19	Dicyandiamide	Homogeneous brown liquid	3.56	8.33
20	Guanidine carbonate	Homogeneous brown liquid	1.25	10.45
25	Monoethanolamine	Homogeneous brown liquid	1.53	9.46
26	Hexamethylene tetramine	Brown gel-like agglomerates, break up readily to uniform dispersion on grinding	1.40	8.85
28	Thiourea	Uniform, brown dispersion	1.02	6.96
29	2-Nitro-2-methyl-1,3-propanediol	Same	3.04	6.14
32	Triethylene tetramine	Same	1.07	9.35
33	Triethanolamine, commercial (mixt. di- and triethanolamines)	Same	1.54	7.82
37	Di-n-butylamine	Same	1.29	9.98
38	Monoisopropanolamine	Same	0.61	9.13
41	2-Amino-2-methyl-1-propanol	Same	1.02	9.20

<sup>a</sup> Unsatisfactory dispersions resulted from the use of ammonium carbonate and bicarbonate, ammonium ferrocyanide, ammonium nitrate (experiment 14), aniline, monomethylaniline, dimethylglyoxime, ethyl monoethanolamine, melamine, phenylmorpholine, and triisopropanolamine.<sup>b</sup> Read in the Stormer viscometer; weight reading was 100 grams in each case.



The appearance indicates that at 135° C. guanidine carbonate should not be less than 4.5 per cent. Figure 4 indicates that below 5.0 per cent there is a steep increase in the viscosity, while above 5.5 per cent the decrease is almost negligible. Since guanidine carbonate is not a pure compound and its composition might vary, it was assumed that the most suitable concentration is 6 per cent of guanidine carbonate.

During the dispersion process, the mixture was heated to 135° or 145° C. within 15 minutes. At room temperature the protein particles and guanidine carbonate are held in suspension by mechanical agitation. As the temperature rises to about 70° C., the mixture becomes a soft gel which liquefies at 135° C. in about 30 minutes. The time recorded in experiments is taken from the moment at which the thermometer in the reaction vessel reads 135° or 145° C., respectively. As heating continues, the dispersion becomes more liquid. According to Figure 5, at 135° C. the viscosity of the colloidal soybean protein dispersions diminishes rapidly during the first 3 hours; the decrease after 3 hours is comparatively small. At 145° C. the dispersion proceeds faster than at 135° C.; the rapid decrease in viscosity is accomplished after about 2 hours of heating at 145° C.

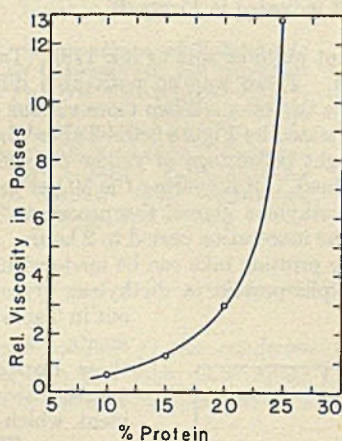
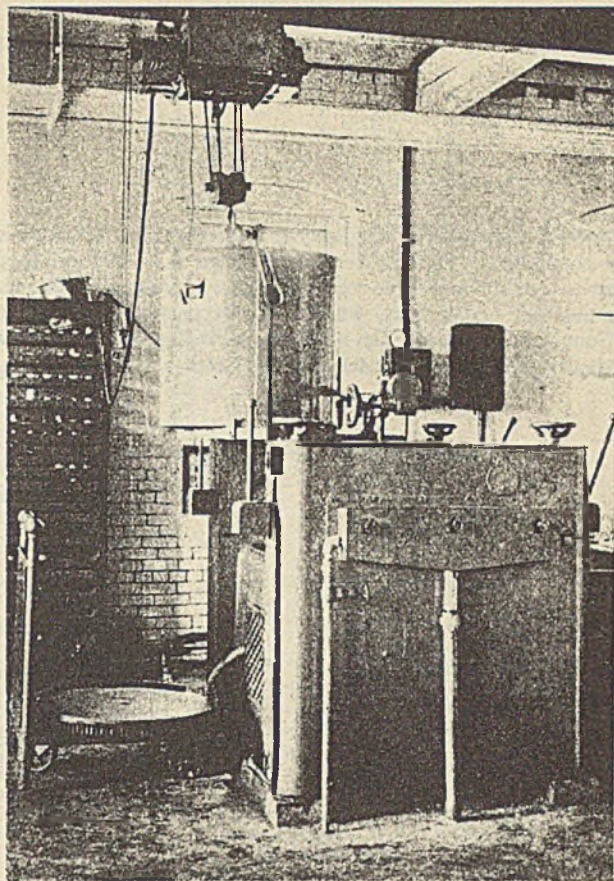


Figure 2. Relation of Concentration and Viscosity of Colloidal Dispersions of Soybean Alpha-Protein (Low Viscosity) in Diethylene Glycol (Reacted with 5% Guanidine Carbonate for 5½ Hrs. at 160° C.)

Soybean alpha-protein is dispersed more readily in the less complex polyhydric alcohols (Figure 5). Propylene glycol, diethylene glycol, triethylene glycol, and glycerol were found to be good dispersing agents in the presence of 6 per cent guanidine carbonate at 135° C. Under the same conditions, tetraethylene glycol does not yield uniform dispersions; amounts up to 10 per cent guanidine carbonate are not sufficient for peptization. Dispersions were accomplished in the presence of 15 per cent guanidine carbonate, but their use in printing inks is not feasible.

The dispersions of glycerol are too viscous for consideration at present; however, they might find some useful application in water color inks.

For steam-setting inks, the ink must not dry on the press. The ink films on the rollers of the press sometimes measure 0.001 inch or less. Alcohols boiling below 200° C., such as ethylene and propylene glycol, evaporate too fast for usual conditions, but might be applicable for fast-drying inks where the films are not exposed to steam after printing.



Courtesy, Kent Machine Works, Inc.

An Ink Mixer Discharging a Batch on a Three-Roller Mill

Diethylene and triethylene glycols are suitable for steam-setting inks. Since diethylene glycol yields the less viscous dispersions, it was chosen for the remainder of the investigation. A relative viscosity of 15-50 poises is probably suitable for most printing inks.

The conditions adopted for the dispersion of soybean alpha-protein are a composition of 20 per cent soybean alpha-protein, 6 per cent guanidine carbonate, and 74 per cent diethylene glycol, and a reaction temperature of 135° C.

TABLE III. CHOICE OF MOST EFFECTIVE DISPERSING REAGENT  
(Composition of reaction mixture: 10 grams soybean alpha-protein (low viscosity), 85 diethylene glycol, 5 reagent; reaction time, 3 hours)

Expt. No.	Reagent	Appearance	Relative Viscosity, Poises <sup>a</sup>
Reaction at 160° C. <sup>b</sup>			
42	Guanidine carbonate	Uniform dark brown	0.85
46	Thiourea	Brown uniform dispersion	1.65
48	Triethylenetetramine	Same	0.85
50	Di-n-butylamine	Same	1.65
Reaction at 145° C.			
51	Guanidine carbonate	Uniform, light brown	0.85
55	Thiourea	Not quite homogeneous, brown dispersion	10.7
56	Triethylenetetramine	Light brown dispersion	2.27

<sup>a</sup> Read in the Stormer viscometer; weight reading was 100 grams in each case.

<sup>b</sup> Unsatisfactory dispersions resulted from the use of dicyandiamide, hexamethylenetetramine, 2-nitro-2-methyl-1,3-propanediol, triethanolamine, and urea.



## APPLICATION IN PRINTING INKS

Printing inks were made from the following dispersions:

Time, Hr.	Ink No.
1	94 black
2	88 black
3	87 black
5.5	85 black
7	95 black

The ink was made of 80 grams of dispersion and 20 grams of carbon black. The two items were mixed uniformly and then ground on a small three-roller laboratory paint mill. The examination of the inks, which are soft pastes, is empirical. Comparisons are usually made by spreading the ink with a spatula and testing for tack; for the latter, a small amount of

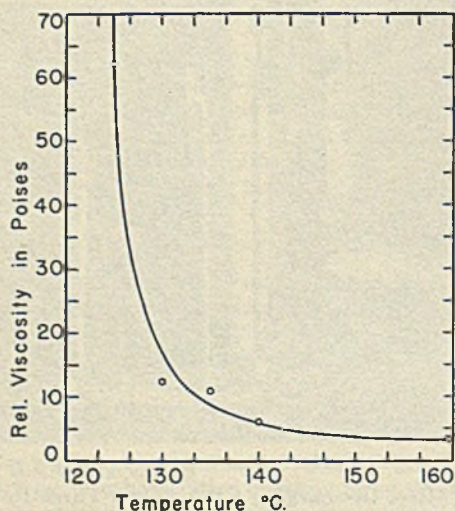


Figure 3. Effect of Reaction Temperature on Viscosity of Colloidal Dispersions of Soybean Alpha-Protein (Low Viscosity) in Diethylene Glycol (20% Protein Reacted with 5% Guanidine Carbonate for 5½ Hrs.)

ink is applied to the finger and tapped out on a glass slab or paper. The consistency and tack can vary widely for any type of ink, as long as the ink does not pull off the coating from the paper. Black ink 95 had the heaviest consistency and the greatest tack. The inks grew softer and less tacky, according to the time of the dispersion; i. e., black ink 88 is softer and less tacky than 94, black ink 87 is softer and less tacky than 88, etc.

Printing was done on a Vandercook proofing machine (No. 219), equipped with split rollers so that two inks could be printed simultaneously. The prints were passed over steam issuing from a steam bath, in order to set the ink to a hard film. All of the inks set well, and no difference was noticeable.

In the preparation of larger quantities of dispersion, swelling of the gel formed in the early stages of the peptization process is an undesirable feature, for oversized equipment is needed. A study of the behavior of the protein during peptization was made in a 1000-cc. beaker in experiment 172 with the following mixture:

160 grams soybean alpha-protein  
48 grams guanidine carbonate  
592 grams diethylene glycol  
500 grams

Observations of peptization features of soybean alpha-protein during dispersion led to the adoption of the following procedure:

1. Rapid heating to 125° C. in about 10–15 minutes while stirring.
2. Maceration at 125° C. for 1 hour with stirring discontinued.
3. Heating to 135° C. in about 30 minutes while stirring. (The slow increase corresponds to a rise of 3° C. per minute.)
4. Continued heating at 135° C. until foam settles.
5. Determination of consistency of dispersion at that time and estimation of time of heating required for desired viscosity.
6. Completion of final heating period.

The resulting product corresponds to a 2-hour dispersion. It was used in printing inks with pigments of both high and low oil absorption. These data are presented and discussed in Table IV.

By using a 30 per cent dispersion (experiment 62, conducted at 160° C.), the concentration of the pigment in the ink can be raised. The pigment-binder ratio in experiment 191 was kept at 2.5:

33.3 grams chrome yellow = 42.8% of pigment  
44.5 grams dispersion 62 = 57.2% of pigment  
77.8 grams (30% soybean protein, dispersion as prepared by method indicated in Figure 2)

Although not quite so soft as ink 178E (Table V), it was still too fluid. There was no noticeable difference in the qualities of the two inks. When more viscous dispersions are made, as illustrated by Figure 6 and Table VI, and used with the same weight percentage of yellow pigment, satisfactory inks are obtained. In preparing the 30 per cent protein dispersions in diethylene glycol, the procedure was varied by lengthening the maceration period to 2 hours.

Satisfactory printing inks can be made with the dispersion of soybean alpha-protein in diethylene glycol. As pointed out in Table IV, not all pigments can be used with these dispersions—for example, calcium lithol pigment which changes color on aging. The lack of water resistance of inks 173–190 and 192Y–196Y limits the use of the dispersions. The difference between soybean protein and casein, blood albumin, and Maco is demonstrated in Figure 7.

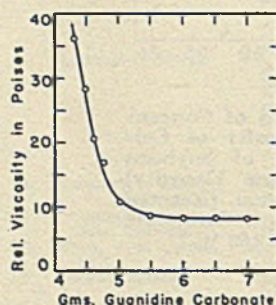


Figure 4. Effect of Concentration of Guanidine Carbonate on the Viscosity of Colloidal Dispersions of 20 Per Cent Soybean Alpha-Protein (Low Viscosity) in Diethylene Glycol (Reacted for 5½ Hrs. at 135° C.)

## COMPARISON OF SOYBEAN WITH OTHER COMMERCIAL PROTEINS

The dispersions of casein in diethylene glycol in the presence of as little as 2 per cent of guanidine carbonate and temperatures as low as 80° C. are uniform. They leave a small amount of undispersed inorganic material as residue. Qualitative analysis showed the presence of sodium, calcium, and phosphoric acid. In the very viscous dispersions some of the salts remain suspended during the dispersion process but settle out on standing. This feature suggests a method of separating salts from casein and similar proteins so that the latter might become suitable for photographic films; it is recommended for investigation. Although a reaction temperature of 80° C. is suitable, the viscosity relation vs. time was



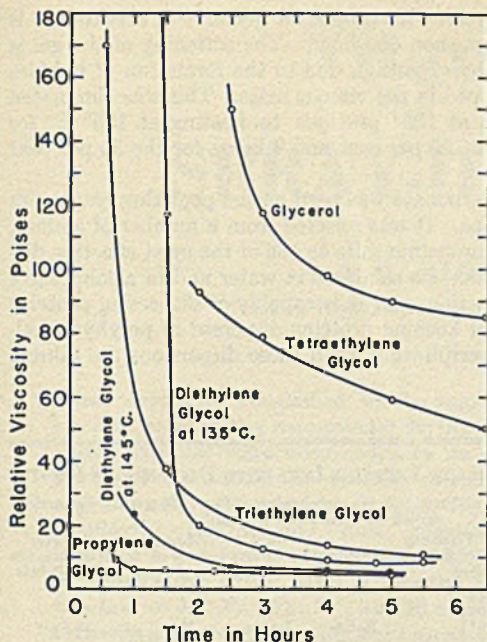


Figure 5. Comparison of Polyhydric Alcohols as Dispersants for Soybean Alpha-Protein (Low Viscosity), Showing Relation of Heating Time and Relative Viscosity (20% Protein Reacted with 6% Guanidine Carbonate in All except Tetraethylene Glycol, in Which 15% Guanidine Carbonate Was Used)

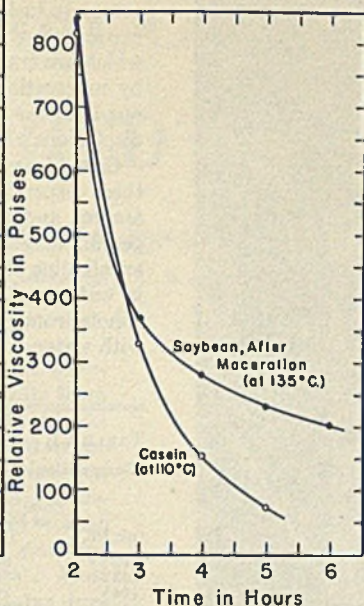


Figure 6. Relation between Casein and Soybean Alpha-Protein (Low Viscosity), Showing Effect of Heating Time on Viscosity of 30% Colloidal Protein Dispersions in Diethylene Glycol

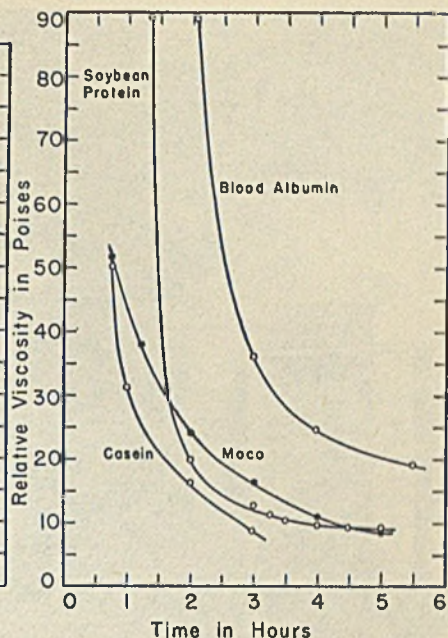


Figure 7. Comparison of Colloidal Dispersions of Commercial Proteins, Showing Relation of Heating Time and Relative Viscosity, with Diethylene Glycol as Dispersant (Casein Reacted with 3% Guanidine Carbonate at 110° C.; Maco with 3%, Blood Albumin with 4%, and Soybean Protein with 6% Guanidine Carbonate at 135° C.)

also determined at 110° C., as condensations with aldehydes probably do not take place much below this temperature. Three per cent of guanidine carbonate is sufficient

TABLE IV. PRINTING INKS MADE WITH 2-HOUR DISPERSION OF SOYBEAN ALPHA-PROTEIN AT 135° C.

Expt. No.	Pigment* and Concn., %	Behavior on Proofing Press	Water Resistance of Prints <sup>b</sup>	
			Initially	After 24 hr.
173	Victoria blue, 31.6	Satisfactory	Poor	Poor
174	Calcium lithol <sup>c</sup> red, 28.6	Satisfactory	Poor	Poor
175	Naphthol yellow, 28.6	Satisfactory	Poor	Poor
176	Iron blue, 34.8	Satisfactory	Poor	Poor
177	Carbon black, 20	Satisfactory	Poor	Poor
178	Medium chrome yellow, 60	Unsatisfactory	...	...
179	Molybdate orange, 60	Unsatisfactory	...	...
190	Cadmium red, 60	Unsatisfactory	...	...

\* The printing qualities of the inks made with pigments of high oil absorption, such as 173-177, are satisfactory; those made with pigments of low oil absorption do not transfer from distribution rollers. The cause seems to be lack of sufficient binder. By the addition of more protein dispersion, this difficulty was eliminated, as illustrated in Table V.

<sup>b</sup> The water resistance of the dry ink films was tested by pulling a wetted piece of filter paper over the dry print. A Whatman filter paper No. 1, 3 inches in diameter, was soaked with water, held on one side, and allowed to drain, until 10 seconds elapsed for successive drops to fall. All inks made with dispersion 172 smeared.

<sup>c</sup> The proofs on aging for 2 weeks turned chocolate brown; the original color was Bordeaux red.

for 20 per cent dispersions of casein and Maco. For blood albumin, 4 per cent guanidine carbonate is probably the optimum. The most suitable temperature for the last two proteins seems to be 135° C.

These conclusions serve to illustrate that the dispersion of soybean protein is the most difficult of the four materials investigated. Casein dispersions compare more favorably in color than any other but, since the object is the use of soybean alpha-protein in steam-setting inks, the dispersions of casein, blood albumin, and Maco were used merely for comparison.

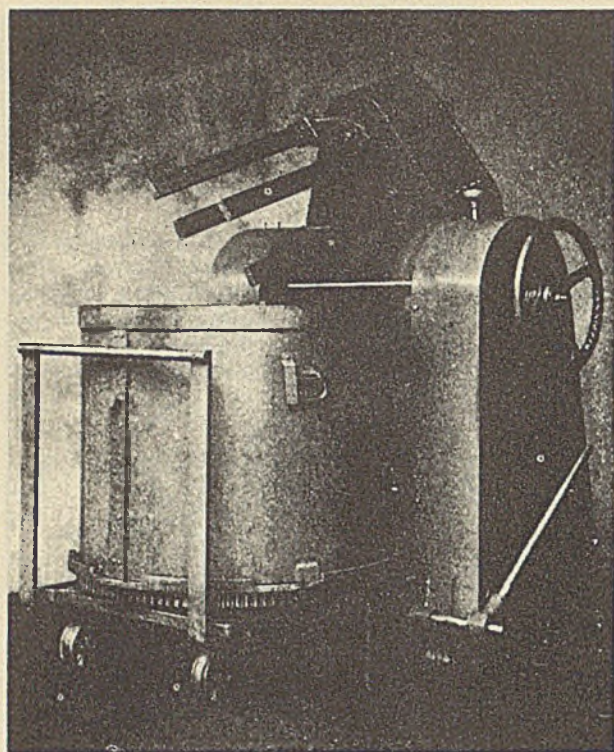
The dispersions of 30 per cent casein in diethylene glycol were carried out at 110° C. with 4.5 per cent guanidine carbonate. Their consistencies are much softer than those for soybean alpha-protein, as illustrated in Figure 6. An outstanding feature of the 30 per cent casein dispersion is the short heating period required to obtain uniform vehicles; no maceration previous to dispersion is necessary as with soybean protein.

During the regular dispersion procedure, peptization proceeds gradually with blood albumin, casein, and Maco, and no excessive expansion of the contents in the reaction beaker is noticeable. Preparation of large quantities with these proteins will not require the modified procedure outlined for soybean alpha-protein in experiment 172.

#### SUMMARY AND CONCLUSIONS

Although soybean alpha-protein is insoluble in polyhydric alcohols, it forms colloidal dispersions in glycerol and in low-molecular-weight glycols, such as propylene, diethylene glycol, and triethylene glycol. Although dispersion in tetraethylene glycol is possible, good results cannot be had with 10 per cent of guanidine carbonate or less. The concentration





Courtesy, Kent Machine Works, Inc.

**Ink Mixer for Mixing Pigment with Vehicle, Previous to Milling on Three-Roller Mill**

must be about 15 per cent to obtain a uniform product. The low-molecular-weight glycols are better dispersing media than the more complex homologs, as indicated by the graph comparing the relative viscosity with time of heating.

The colloidal dispersions of soybean alpha-protein in diethylene glycol were used as vehicles in steam-setting printing inks. When the printed surfaces of these inks are exposed to steam, the protein is precipitated with the pigment from diethylene glycol onto the paper.

In the preparation of the dispersions, soybean alpha-protein forms soft plastic gels with the polyhydric alcohols in the initial stages of the reaction. These gels become liquid on heating at elevated temperatures. At least 2 hours are necessary to soften the dispersion in glycerol, diethylene glycol, and

**TABLE V. DECREASE OF PIGMENT-BINDER RATIO IN YELLOW INKS<sup>a</sup>**

Ink No.	% Concn. of Chrome Yellow	Behavior on Proofing Press	Chalking of Prints after Steam Setting	
			Immediately	After 3 days
178	60	Unsatisfactory	.....	.....
178A	50	Unsatisfactory	.....	.....
178B	45	Satisfactory	Bad	Slight
178C	40	Satisfactory	Slight	Hardly noticeable
178D	35	Satisfactory	Hardly noticeable	None
178E	33 1/2	Satisfactory	Hardly noticeable	None

<sup>a</sup> Made by mixing additions of protein dispersion (experiment 172) with ink 178. These combinations are too soft for flat-bed printing processes and probably are too liquid for rotary presses. Since it is desired for experimental purposes to have soybean alpha-protein as the only binder, the ratio of chrome yellow to protein should not be more than that for 33 1/2 per cent pigment. The ultimate composition of this mixture is the following:

33.33% of chrome yellow pigment	=	13.33	
13.33% of soybean alpha-protein	=	13.33	= 2.50
4.00% of guanidine carbonate	=	13.33	= 1.00
49.34% diethylene glycol	=	13.33	

The pigment protein ratio is 2.5/1.0 or 2.5.

triethylene glycol. In propylene glycol the breakdown is complete in less than one hour. The softening of the gel is accomplished by expansion due to the formation of bubbles which are trapped in the viscous mass. This was eliminated by maceration at 125° previous to heating at 135° C. for one hour for the 20 per cent and 2 hours for the 30 per cent dispersions.

Guanidine carbonate was used as the peptizing reagent in these dispersions. It was selected from a number of amines, amides, and ammonium salts as one of the most effective dispersing reagents. Its solutions in water and in alcohol have an alkaline reaction, and it is capable of dispersing proteins in water and of keeping proteins dispersed in polyhydric alcohols from precipitating when these dispersions are diluted with water.

**TABLE VI. YELLOW PRINTING INKS WITH DISPERSIONS 192-196**

(Composition of mixture: 43 grams chrome yellow, 57 grams dispersion; milled on laboratory ink mill)

Ink No.	Relative Viscosity of Dispersion, Poises	Printing Qualities	Rate of Steam Setting	Appearance of Prints	Water Resistance of Prints
192Y <sup>a</sup>	843				
193Y	399				
194Y	281	Satisfactory	Immediate	No chalking	Fair
195Y	234				
196Y	207				

<sup>a</sup> Mixing of ink 192Y was very difficult. Wetting of the pigments became easier with a decrease in viscosity of the dispersion. No difference was noticeable in the qualities of the inks. They have good steam-setting qualities, but the water resistance of the prints is poor.

This undesirable feature can be changed by modifying the dispersions in order to form resinous complexes from guanidine carbonate and soybean alpha-protein. This will be discussed in a later report.

Casein, blood albumin, and Maco disperse more readily in diethylene glycol than does soybean alpha-protein. Casein can be dispersed at 80° C. in the presence of 3 per cent guanidine carbonate and at somewhat lower temperatures with larger amounts of guanidine carbonate to form suitable printing ink vehicles. Blood albumin and Maco do not disperse so readily as casein; they require about 4 per cent of guanidine carbonate at about 135° C., while the minimum for soybean alpha-protein at this temperature is about 5 per cent of guanidine carbonate. Regardless of the amount of alkaline peptizing reagent used in casein, blood albumin, and Maco, all the dispersions could be diluted with water, an indication that they would have the same lack of water resistance as soybean alpha-protein dispersions.

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# Vitamin Content of SPRAY-DRIED WHOLE EGG

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Spray drying of emulsified whole eggs, as practiced in most of the commercial drying units from which samples were obtained, has no significant destructive action on the vitamins contained in the egg—namely, vitamin A, vitamin D, thiamine, riboflavin, pantothenic and nicotinic acids. Vitamin A was found to be unstable during storage of dehydrated eggs; after 9 months 60 per cent was lost at 15° F., 75 at 70°, and 80 at 98.6°. Pantothenic and nicotinic acids were quite stable during 9 months of storage of spray-dried whole eggs under the conditions used in these experiments. Only slight destruction of riboflavin occurred at 98.6° F. during the 9 months and essentially none at lower temperatures. Thiamine in spray-dried whole eggs was stable at 15° F. for 9 months; during the same period the losses were 46 per cent at 70° F. and 50 at 98.6°.



THE quantity of eggs spray dried in the United States has recently been greatly increased; in fact, a new industry has virtually been established. Information concerning the retention of vitamins during the drying and storing of eggs is, however, scanty. Since dried eggs will probably supply important fractions of the daily vitamin requirements to consumers, information concerning vitamin retention is very desirable. The present communication reports the results from experiments designed to supplement available information (3).

## STORAGE AND VITAMIN ASSAYS

The emulsified whole eggs and the egg powders used in these investigations were obtained from several sources. Efforts were made to get samples of egg meats and powders which, when collected at the dryers, would be representative of the batches being processed. Ten pairs of samples of emulsified and dried eggs were obtained from six commercial dehydrators. Some engineering data were obtained on the temperature at which the eggs were dehydrated, the nozzle pressures, and air volumes (Table I). The eggs were transported to this laboratory while held at the temperatures of solid carbon dioxide, and after being received were immediately stored at -30° F. until vitamin analyses could be carried out. All samples were examined to determine the effect of spray drying on the vitamin content of the eggs, and a selected sample was used in studies of vitamin retention during storage.

Storage studies were carried out at three temperatures, 15°, 70°, and 98.6° F. The dried eggs were stored in lined barrels

and in sealed No. 2 tin cans. Those in barrels were subsampled and examined for their vitamin content after 1, 3, 6, and 9 months; those in tin cans were examined only after 9 months of storage.

The samples were assayed for vitamin A, vitamin D, thiamine, riboflavin, pantothenic acid, and nicotinic acid. Three types of assays were used: biological for vitamins A and D, microbiological for pantothenic and nicotinic acids, and physical-chemical for thiamine, riboflavin, and vitamin A.

Vitamin A was determined by the U. S. P. rat bioassay technique (6) with only minor modifications. The same vitamin was determined by the Carr-Price colorimetric procedure as modified by Koehn and Sherman (4), using U. S. P. reference cod liver oil as the standard; since agreement of results from the two methods was good, some of the later results were obtained by the physical-chemical method only. Vitamin D was determined by the A. O. A. C. chick assay method (1); thiamine and riboflavin were determined by the fluorometric method of Conner and Straub (2).

Pantothenic and nicotinic acids were determined by the microbiological methods of Pennington, Snell, and Williams (5) and Snell and Wright (7), respectively. The pantothenic acid procedure was modified by substituting hydrochloric-acid-hydrolyzed casein for sulfuric-acid-hydrolyzed casein and by substituting a mixture of pure vitamins for the alkali-treated yeast extract. The vitamin mixture used in the assay was prepared by using 5 µg. thiamine, 5 µg. pyridoxin, 5 µg. nicotinic acid, 2 µg. riboflavin, and 0.1 µg. *p*-aminobenzoic acid in each 10 ml. of culture media. The method of Snell and Wright for nicotinic acid was also slightly modified. Sulfuric-acid-hydrolyzed casein was replaced by hydrochloric-acid-hydrolyzed casein, and the mixture was composed of 5 µg. thiamine, 5 µg. pyridoxin, 1 µg. pantothenic acid, 2 µg. riboflavin, 0.1 µg. *p*-aminobenzoic acid, and 0.004 µg. crystalline biotin (free acid). Control assays showed that results obtained by the modified and original methods were in good agreement.

## VITAMIN RETENTION

**DURING DEHYDRATION.** Dehydration of whole liquid eggs by the spray process did not result in any marked loss of vitamin A in a majority of the samples tested (Table II). The apparent losses were, in general, well within the errors of the assay methods and cannot be considered significant. That losses may occur dur-

TABLE I. PROCESSING, MOISTURE, AND PROTEIN SOLUBILITY DATA ON SPRAY-DRIED EGG SAMPLES

Sample No.	Type of Egg	Moisture Content, %	Protein Soly., Gram, Dry Egg	Temperature, F.		Pressure, Lb./Sq. In.	Air Vol., Cu. Ft./Min.	
				In-take	Ex-haust			
2	Shell, storage	3.9	0.265	260	160	120	2500-2800	27,000
4	Shell, oil-processed	3.5	0.277	260	160	120	2500-2800	27,000
6	Same	3.1	0.265	260	160	120	2500-2800	27,000
8	Same	3.6	0.273	260	160	120	2500-2800	27,000
10	Same	4.5	0.296	260	160	120	2500-2800	27,000
12	Shell, storage	6.5	0.271	283	142	...	.....	.....
14	50% frozen, shell	4.6	0.284	316	144	...	.....	.....
16	26.4% frozen, 73.6% fresh shell	5.4	0.258	308	160	...	.....	.....
18	20% frozen, 10% storage shell, 70% fresh shell	4.6	0.271	425	160	125	3200	9,000
20	Shell	3.3	0.252	315	144	90	7000	8,500



TABLE II. RETENTION OF VITAMINS IN EGGS DURING SPRAY DRYING

Sample No.	Sample Description	Vitamin A, U. S. P. Units/G. Dry Wt. <sup>a</sup>	Vitamin D, A. O. A. C. Units/G.	Thiamine, $\mu\text{g./G.}$ Dry Wt.	Riboflavin, $\mu\text{g./G.}$ Dry Wt.	Nicotinic Acid, $\mu\text{g./G.}$ Dry Wt.	Pantothenic Acid, $\mu\text{g./G.}$ Dry Wt.
1	Emulsified whole egg	60	1.4	2.1	8	2.4	69
2	No. 1 dehydrated	53	3.6	2.8	8	2.1	65
3	Emulsified whole egg	38	3.0	7.0	13	2.9	127
4	No. 3 dehydrated	38	1.4	7.4	13	2.3	127
5	Emulsified whole egg	37	1.4	3.3	9	2.4	53
6	No. 5 dehydrated	32	1.3	3.2	10	2.4	53
7	Emulsified whole egg	42	3.9	6.9	12	3.1	142
8	No. 7 dehydrated	39	3.3	6.9	12	2.5	137
9	Emulsified whole egg	38	1.0	3.3	8	2.9	60
10	No. 9 dehydrated	33	1.1	3.5	9	3.1	62
11	Emulsified whole egg	39	...	3.2	8	2.0	71
12	No. 11 dehydrated	41	...	2.7	12	2.1	73
13	Emulsified whole egg	44	...	3.4	10	2.2	80
14	No. 13 dehydrated	21	...	2.8	14	2.1	80
15	Emulsified whole egg	58	...	3.2	10	2.3	59
16	No. 15 dehydrated	56	...	2.7	12	2.2	63
17	Emulsified whole egg	42	...	3.1	10	2.1	83
18	No. 17 dehydrated	38	...	2.7	11	2.1	81
19	Emulsified whole egg	36	...	...	...	...	...
20	No. 19 dehydrated	37	...	2.8	ii	...	...

<sup>a</sup> Samples 1 to 10 were assayed for vitamin A by the biological method, and samples 11 to 20 by the chemical method.

ing dehydration is indicated by the values obtained by assaying samples 13 and 14. Comparison of the analytical data indicates that about 50 per cent of the vitamin A present in the liquid meats of sample 13 was lost during dehydration. The reason for this exception is not known. The solubility of the protein in this powder does not appear to be notably different from the protein solubilities found in the other samples of powders examined (Table I).

The data indicate that vitamin D is retained during dehydration (Table II). The variations found are well within the experimental error of the chick bioassay method.

The data on the effect of spray drying on the water-soluble vitamins shows clearly that no loss of these vitamins took place during drying (Table II). Slight variations in values for the liquid eggs and the dehydrated products can be ascribed to errors in sampling and other experimental errors inherent in the methods. All determinations were made in replicate.

**DURING STORAGE.** The data show that vitamin A was very unstable during storage (Table III). When stored in barrels at 98.6° F. for 1 month, the loss, as measured by bioassay, amounted to 56.6 per cent of the amount originally present in the powder. At the end of 9 months of storage under the same conditions, 81.0 per cent of the vitamin was lost. The retention of the vitamin in powder stored at 70° F. was somewhat better than that at 98.6° F. At the end of 6 months the loss at 70° F. was approximately half as great as that found at the higher temperature. Reduction of the storage temperature to 15° F. served to retard the rate of destruction further, but probably not enough to warrant the use of the lower temperature, except possibly for a relatively short time following packaging. Storage in sealed cans resulted in somewhat improved retention. The differences in retention resulted in the preservation of 10 to 15 per cent more of the original vitamin content in the canned as compared to the barreled powders held at the two higher temperatures.

In the storage studies vitamin A was determined by the biological assay method and by the physical-chemical

procedure (4). Table III and Figure 1 show the close correlation of the data obtained from the two methods in the majority of samples assayed. From the character of the curves it is clear that the results by the colorimetric method are subject to less variation than those obtained by the biological method; at the same time the two sets of data are in such close agreement that the reliability of the chemical method for the determination of this vitamin in eggs seems to be adequate.

The losses of vitamin D in powdered whole egg during storage were studied at two temperatures, 15° and

98.6° F. The values obtained by analysis of samples stored at 15° F. do not indicate loss (Table III). A loss of 29 per cent was found in the powder held at 98.6° F. for 9 months.

Of the water-soluble vitamins studied, thiamine was found to be the least stable, as was to have been expected (Table III). No loss took place when the egg powder was stored at 15° F. for 9 months; at 70° F. very little destruction had taken place during 6 months of storage, but at the end of 9 months only about 50 per cent of the original thiamine remained; at 98.6° F., 25 per cent was lost during the first month of storage, followed by a gradual decrease which reached 50 per cent at the end of 9 months. No loss of nicotinic or pantothenic acids occurred during storage of spray-dried eggs under the conditions of these experiments. Any variation in the values is well within the experimental error of the method. Riboflavin was also found to be comparatively stable during storage. At 98.6° F. some loss took place, which amounted to 16 per cent after 9 months of storage.

#### DISCUSSION OF RESULTS

The results of these investigations, obtained from a study of three samples of eggs, demonstrate that the vitamin A content of

TABLE III. RETENTION OF VITAMINS IN DEHYDRATED EGGS DURING STORAGE<sup>a</sup>

Storage Time, Mo.	Vitamin A, U. S. P. Units/G. Dry Wt. Bio-assay	Vitamin A, U. S. P. Colorimetric	Vitamin D, A. O. A. C. Units/G. Dry Wt.	Thiamine, $\mu\text{g./G.}$ Dry Wt.	Riboflavin, $\mu\text{g./G.}$ Dry Wt.	Nicotinic Acid, $\mu\text{g./G.}$ Dry Wt.	Pantothenic Acid, $\mu\text{g./G.}$ Dry Wt.
0	53	52	1.4	2.8	7.9	2.1	65
Storage Temperature, 98.6° F.							
1	23	38	0.9	2.1	7.9	1.9	66
3	20	22	1.1	2.1	6.9	1.9	66
6	10	13	0.9	1.9	6.8	2.2	64
9	10	11	1.0	1.4	6.6	2.2	66
9 <sup>b</sup>	15	..	...	...	...	...	..
Storage Temperature, 70° F.							
1	56	48	...	2.9	7.6	2.1	65
3	26	33	...	2.9	7.9	2.0	65
6	29	24	...	2.4	7.4	2.5	67
9	16	11	...	1.5	7.0	2.3	67
9 <sup>b</sup>	19	..	...	...	...	...	..
Storage Temperature, 15° F.							
1	58	48	1.3	2.9	8.0	2.2	69
3	42	41	1.5	2.8	7.9	2.2	61
6	27	30	1.8	2.8	7.9	2.3	62
9	27	19	1.4	2.6	7.6	2.4	68
9 <sup>b</sup>	26	..	...	...	...	...	..

<sup>a</sup> Sample 2 was used in the storage studies.

<sup>b</sup> These subsamples were stored in sealed tin cans; all others were stored in barrels.



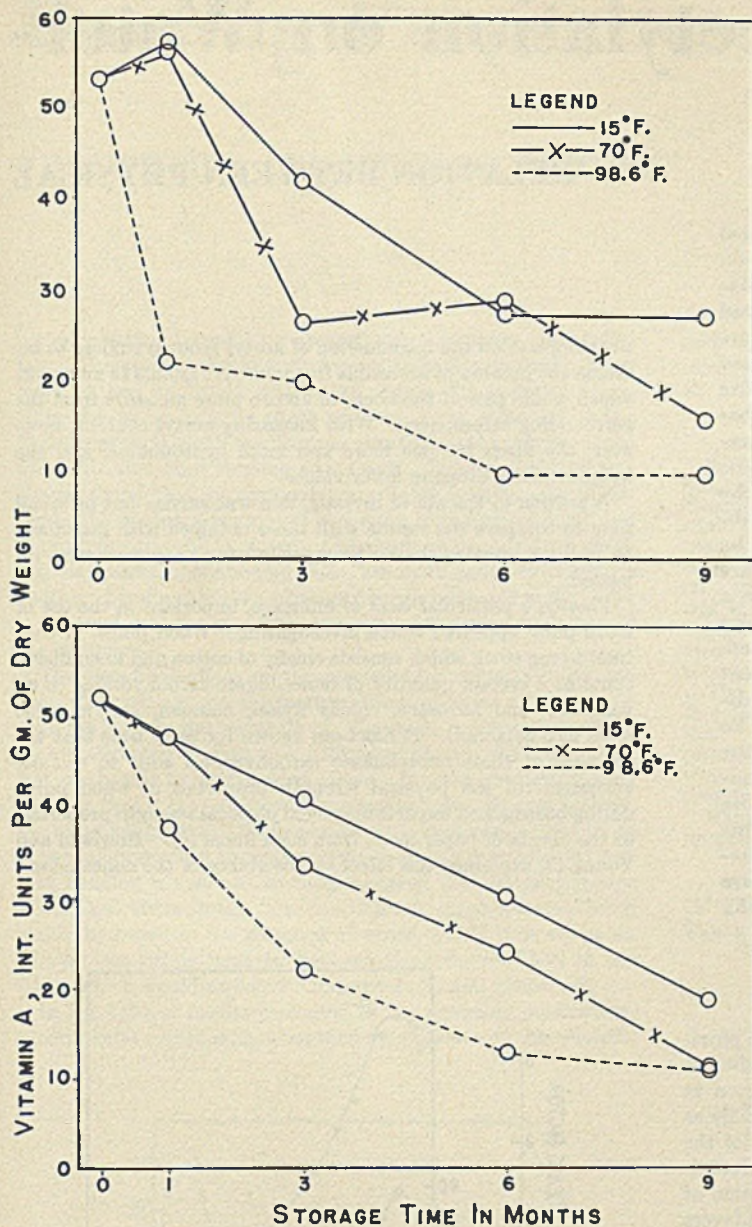


Figure 1. Effect of Storage on Vitamin A Content of Powdered Dehydrated Whole Egg as Determined by U. S. P. XI Rat Bioassay Method (above) and by a Modification of the Carr-Price Colorimetric Assay Method (below)

dehydrated eggs may be markedly and rapidly reduced while the eggs are in storage. This destruction is relatively rapid even under conditions which might be expected to stabilize the vitamin A. Even at 15° F. the major part of the vitamin A was destroyed in 9 months. The loss of thiamine may also be a matter of concern, when unfavorable conditions of storage obtain, as it amounted to approximately 50 per cent when the eggs were stored for 9 months at 98.6° F.

Presumably the inactivation of vitamin A is due to oxidative processes. It was apparent in these experiments that the destruction of vitamin A results from changes which are quite independent of those resulting in quality deterioration as indicated by off-odors and -flavors. The egg powder stored for 9 months

at 15° F. had not undergone the marked changes that are usually indicative of deterioration in quality. However, the vitamin A destruction was very marked. It is evident, therefore, that preservation of vitamin A is a separate problem and may not be related to maintenance of other desirable qualities of egg powders.

A possible explanation of the rapid oxidation of vitamin A in egg powders is found in the structure of the particles making up the powder. Microscopic examination showed that they were thin-walled, perforated, hollow globules. In effect, egg powders are made up of thin membranes which provide maximum exposure to the air and offer favorable conditions for oxidative processes.

Two methods appear likely to be useful in retarding vitamin A destruction. One of them is the incorporation of antioxidants in the liquid egg prior to drying and in such fashion that the likelihoods of dissolving the antioxidant in the fat particles is assured; the other is that of mechanically compressing egg powders to such an extent that much of the air is expelled and the total surfaces are greatly reduced. It is possible that these two measures may be combined and their protective action accentuated. Experiments undertaken with the view of investigating the possible usefulness of such measures are in progress in this laboratory. Preliminary results indicate retarded destruction by some antioxidants and by compression.

#### ACKNOWLEDGMENT

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# Effect of Acetylation on Water-

## RELATION BETWEEN PHYSICAL

A previous paper indicated that the physical strength properties of sheets prepared from beaten acetylated rag stock show a maximum after a relatively small amount of acetyl had been introduced and then drop rapidly as the acetyl content is further increased. These results have been confirmed on another rag stock material as well as on a sulfite pulp prepared from spruce. The coincidence between the maximum in physical strength properties and a maximum in hygroscopicity of the acetylated fibers, which was to be expected on the basis of the hypothesis advanced, was actually observed. The previously made observation that the more highly acetylated cellulose fibers, which are incompatible with water, may be converted into a satisfactory sheet of paper, if acetone is the beating and sheet-forming medium, could be confirmed. The effect of the addition of xylan and acetylated xylan to the pulp, as well as the effect of the addition of xylan to acetylated pulp, was studied. The results seem to support the hypothesis that the strength-increasing effect of noncellulosic carbohydrates is brought about by mutual bonding between their hydroxyl groups and those of cellulose. If those hydroxyl groups which are responsible for the mutual bonding in either material are covered with acetyl groups, no strength-increasing effect is observed.

THE previous paper in this series (1) showed that the physical strength properties of sheets prepared from beaten acetylated rag stock first increase, reach a maximum at about 6 per cent acetyl content, and then drop rather rapidly as the acetyl content is further increased. This behavior of the acetylated fibers was explained by the assumption that the micellar structure of the fibers is opened up by the introduction of acetyl groups and that the looser structure thus produced favors the development of external surface on beating; the result is increased accessibility of hydroxyl groups to water (hydration) and subsequent increased bonding between the hydroxyl groups of adjacent fiber surfaces when the water is removed. However, this effect ceases when the acetyl content is increased above the optimum value because of the increasing hydrophobic character of the fibers; the result is an ever increasing resistance to hydration and to bonding and thus a considerable decrease in the physical strength properties of the sheet.

It is now shown that a maximum in physical strength properties is also obtained merely by subjecting the cellulosic material to sufficient defibration (in the British disintegrator)—i. e., without actual beating, although the maximum is less pronounced than on beating.

If the maximum in physical strength properties is a result of maximum hydration, it should coincide with a maximum in hygroscopicity of the dried fibers of limited acetyl content. In fact, this coincidence was observed. Moreover, the hygroscopicity maximum occurred with acetylated fibers which had not even undergone a process of defibration. Hence, it would appear that the mere opening of the micellar structure of the fibers (assumed

to take place on the introduction of acetyl groups) suffices to increase the number of accessible free hydroxyl groups to an extent which would permit the fibers to absorb more moisture from the surrounding atmosphere. With increasing acetyl content, however, the fibers become more and more hydrophobic, and the hygroscopicity drops to lower values.

A portion of the above investigation was carried out on wood pulp to compare the results with those obtained with rag stock. In addition, some of the earlier experiments on rag stock were repeated.

Finally, a particular item of influence, important in the use of wood pulp, appeared worth investigating. Wood pulps, in contrast to rag stock which consists chiefly of cotton and linen fibers, contains a certain quantity of noncellulosic carbohydrates (i. e., pentosans and hexosans, chiefly xylan, mannan, and in some cases also galactan). It has been known for some time that the presence of these noncellulosic carbohydrates adds to the development of the physical strength properties of wood pulps during beating and imparts improved physical strength properties to the sheets of paper made from such fibers (6). Rowland and Young (8) explained this effect by the ability of the noncellulosic

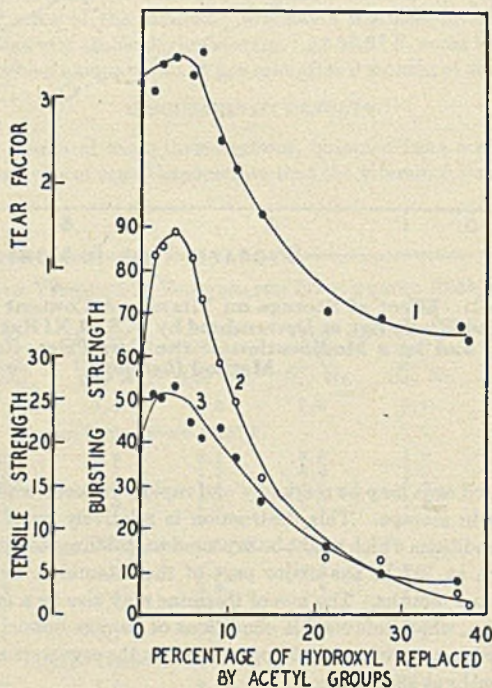


Figure 1. Physical Properties of Sheets Prepared from Rag Stock of Increasing Acetyl Content

1. Tearing strength
2. Bursting strength
3. Tensile strength



# Binding Properties of Cellulose

## PROPERTIES AND HYGROSCOPICITY

carbohydrates to swell to a greater extent in water than cellulose. They assumed that the presence of these substances, being more or less uniformly distributed within the cellulose fibers, gives rise to an osmotic effect whereby water surrounding the fiber is drawn through the fiber membrane into the interior of the fiber with increased swelling as a result. Indeed, Rowland and Young found that an approximately linear relation existed between the pentosan content of a number of hardwood pulps and their ability to swell in water. As a result of the increased swelling, the pentosan-containing fibers are more easily hydrated on beating; bonding between adjacent fibers is increased as the water is removed, and the physical properties of the sheet thus formed are improved.

The beneficial effect of the noncellulosic carbohydrates has been observed also on the mere addition of these substances to cellulose fibers in the beater (6, 7). However, in this case in which we are obviously dealing only with a mechanical mixture, the effect can hardly be explained as above. But the assumption may be made that it is a result of the mutual bonding effected between the hydroxyl groups of the noncellulosic carbohydrates and those of the cellulose when the water is removed, in much the same way that bonding is assumed to occur between the hydroxyl groups of cellulose fibers alone. The noncellulosic carbohydrates, being highly hydrated in the presence of water, would thus act as an efficient cementing material between the cellulose fibers in the sheet, which would explain its improved physical properties.

In the light of results presented in the foregoing publication, experimental evidence showing that the presence of noncellulosic

carbohydrates would fail to be beneficial if their hydroxyl groups were replaced by acetyl groups would substantiate the hypothesis.

### EXPERIMENTAL PROCEDURES

Samples of rag stock similar to that used by Bletzinger and having a degree of polymerization of 1441 (viscosity method, Staudinger equation) were acetylated by the modified Hess and Ljubitsch method (1). The samples with the lower acetyl contents (1.24 to 4.42 per cent) were prepared by allowing the rag stock to stand in the acetylating mixture at room temperature for a fixed period and by increasing the acetic anhydride concentration. To obtain the samples with the higher acetyl content, the time of acetylation was increased under the conditions previously described (1). The acetyl content of the samples was determined according to the method of Genung and Mallat (2).

The acetylated samples and the original material were beaten in a Lampén mill (3) which permitted the use of 24 grams at a time. In this device the original rag stock developed its optimum physical strength properties after a beating time of 30-45 minutes. A period of 45 minutes was chosen for beating the acetylated samples.

Handsheets were prepared and tested for physical strength properties, as previously described by Bletzinger.

TABLE I. PHYSICAL PROPERTIES OF SHEETS PREPARED FROM BEATEN RAG STOCK OF INCREASING ACETYL CONTENT

Acetyl Content, %	Hydroxyl Groups Substituted, %	Bursting Strength, Lb./Sq. In./100 Lb. Basis Weight <sup>a</sup>	Tensile Strength, Lb./100 Lb. Basis Weight <sup>a</sup>	Tear Factor <sup>a</sup>
0.00	0.00	56.06	19.35	3.160
1.24	1.58	83.36	25.94	3.096
2.08	2.67	85.44	25.56	3.375
3.11	4.03	89.64	26.64	3.481
4.42	0.16	82.89	22.31	3.271
5.31	7.03	73.01	20.51	3.522
6.85	9.23	58.39	22.18	2.527
8.16	11.14	50.04	18.25	2.170
10.36	14.47	31.90	13.46	1.671
14.76	21.66	13.88	8.06	0.537
18.24	27.28	13.13	5.14	0.440
22.92	37.09	4.97	4.39	0.354
28.40	38.09	2.41	...	0.212

<sup>a</sup> Calculated to cellulose basis.

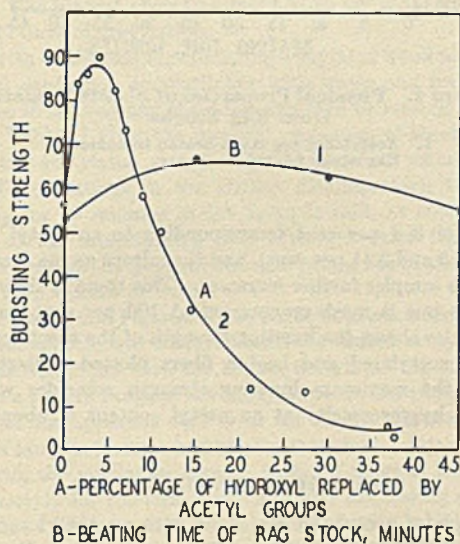


Figure 2. Bursting Strengths of Rag Stocks at Various Beating Intervals

1. Unacetylated rag stock
2. Acetylated stocks beaten 45 minutes

**HYGROSCOPICITY.** Absorption isotherms were obtained at 30° C. by weighing samples of the several materials after they had come to equilibrium in air, conditioned to each of a number of relative humidities distributed throughout the range of interest. A constant temperature cabinet was conditioned by circulating the air over trays of saturated salt solutions having the desired equilibrium relative humidities. The actual relative humidities were measured by wet- and dry-bulb thermometers. The wire-screen buckets which held the samples were weighed on an analytical balance; they were hung from a hook attached to a fine wire which passed through a small hole in the top of the cabinet, through a hole in the base of the balance mounted on the cabinet, and then to the hook from which the left-hand balance pan was normally suspended.

The hygroscopicity measurements were made on average samples of the acetylated material, which had been subsequently washed with alcohol and ether and from which the ether had been removed in a vacuum desiccator over calcium chloride. These samples were subjected to no defibration or beating.



TABLE II. PHYSICAL PROPERTIES OF SHEETS PREPARED FROM ACETYLATED WOOD PULP

Acetyl Content, %	Bursting Strength, Lb./Sq. In./100 Lb. Basis Weight		Tensile Strength, Lb./100 Lb. Basis Weight		Tear Factor		Apparent Density	
	Disintegration only	Disintegration + beating	Disintegration only	Disintegration + beating	Disintegration only	Disintegration + beating	Disintegration only	Disintegration + beating
0.00	32.7	155.7	11.09	41.91	2.482	0.988	10.24	14.79
2.61	37.8	173.9	12.16	41.95	2.821	0.889	11.43	16.09
4.05	43.5	173.9	11.80	44.87	3.007	1.000	12.00	15.90
6.75	33.0	109.3	11.33	51.69	2.624	1.089	9.28	14.56
7.95	23.8	161.9	8.94	51.67	2.101	1.038	8.68	13.54
12.08	13.7	148.6	5.60	42.20	1.395	1.168	7.70	11.70
15.37	13.3	95.8	4.89	30.57	1.137	1.165	7.00	12.47
18.97	9.8	35.2	4.00	16.23	0.971	0.907	6.26	10.71
23.26	0.0	7.3	...	...	0.586	0.269	5.10	7.75

EFFECT ON PHYSICAL STRENGTH PROPERTIES

Data on the influence of acetyl content upon the physical strength properties of sheets made from the beaten acetylated fibers are presented in Table I and Figure 1. The physical strength properties first increase with increasing acetyl content, reach a maximum, and then drop sharply to almost zero values as the acetyl content is further increased. This result confirms those found by Bletzinger, with the difference that the maximum in this work was reached with an acetyl content of about 3 per cent, whereas previously the maximum appeared with an acetyl content of about 6 per cent. This difference is probably due to a difference in the nature of the two rag stocks. It may be added that the freeness of the beaten material, particularly if the acetyl content was above about 15 per cent, was much higher than that of the unacetylated rag stock and that the apparent density values showed the same trend. Likewise, the general behavior of the acetylated fibers in the aqueous suspension was similar to that previously observed—i. e., the easy defibration of the samples with an acetyl content up to 3-4 per cent, the increasing tendency of the material to flocculate and to resist beating action, and the failure to form a coherent sheet as the acetyl content was increased.

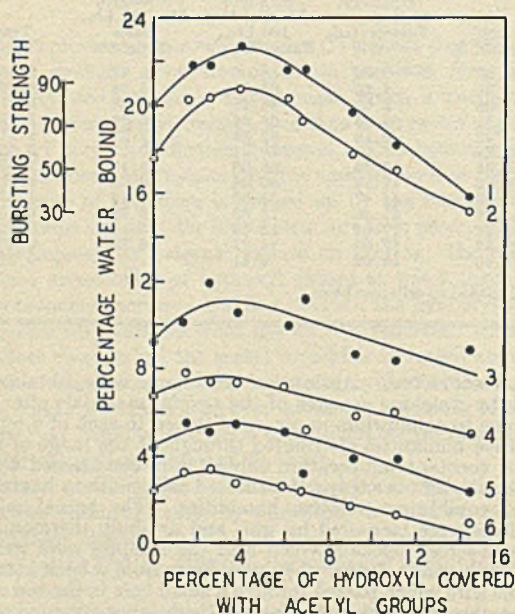


Figure 3. Hygroscopic Results on Acetylated Rag Stocks Compared with Bursting Strengths

6. Hygroscopicity at 20% relative humidity
5. Hygroscopicity at 40% relative humidity
4. Hygroscopicity at 60% relative humidity
3. Hygroscopicity at 80% relative humidity
1. Hygroscopicity at 100% relative humidity
2. Bursting strength

The beneficial effect of limited acetylation upon the physical strength properties is further illustrated in Figure 2. Comparison of the two curves shows that the bursting strengths of acetylated rag stock samples having acetyl contents from zero to about 7 per cent (developed by 45 minutes of beating) are considerably above those developed in the unacetylated rag stock at any beating interval. The maximum bursting strength obtained with the sample containing 3.11 per cent acetyl is about 40 per cent above the optimum bursting strength of the unacetylated rag stock.

EFFECT ON HYGROSCOPICITY

The results of the influence of acetyl content upon the hygroscopicity of the acetylated rag stock samples are shown in Figure 3. It is seen that the hygroscopicity (obtained by interpolation and extrapolation of the measured values) increases with increasing acetyl content, reaches a maximum between an acetyl

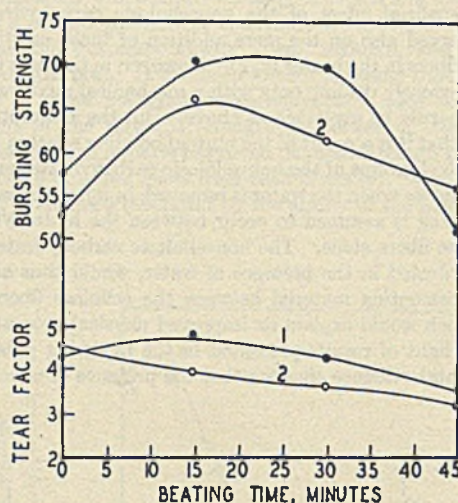


Figure 4. Physical Properties of Sheets Prepared from Rag Stocks

1. Acetylated rag stock beaten in acetone
2. Rag stock beaten in water

coverage of 3-4 per cent (corresponding to an acetyl content between 2.5 and 3.11 per cent), and then drops as the acetyl content of the samples further increases. This trend is shown at all humidities but is most pronounced at 100 per cent humidity. Figure 3 also shows the bursting strength of the sheets prepared from the acetylated and beaten fibers plotted against acetyl content; the maximum bursting strength coincides with the maximum hygroscopicity at an acetyl content of about 3 per cent.

EFFECT OF BEATING IN ACETONE

A sample of acetylated rag stock with an acetyl content of 23.49 per cent was soaked in acetone, defibered in the British disintegrator, and then beaten in the Lampén mill as previously described. For comparison, another portion of the sample was treated in the same way but water was used instead of acetone. Bletzinger's observations were fully confirmed: It was difficult



to prepare a sheet from the acetylated stock beaten in water, but easy and satisfactory to do so with the acetylated stock beaten in acetone. Figure 4 compares the bursting and tearing strengths of sheets prepared from the acetylated fibers beaten in acetone with those of sheets from unacetylated rag stock beaten in water.

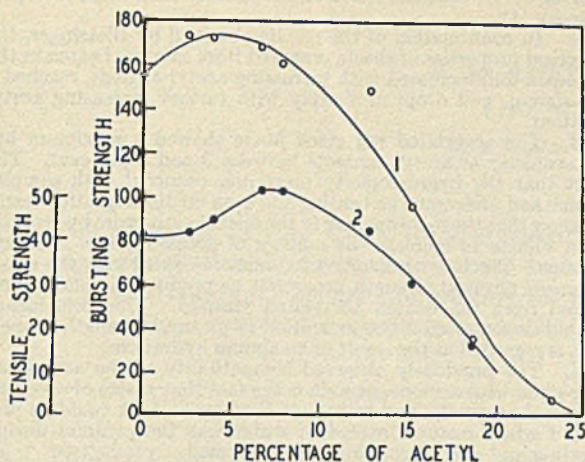


Figure 5. Physical Properties of Acetylated Wood Pulp Beaten in Water

1. Bursting strength
2. Tensile strength

Beating of the acetylated material in acetone resulted in a sheet of very satisfactory strength properties. Although the improvement over the original rag stock beaten in water was not so striking as that found by Bletzinger, it was definitely evident.

#### BEHAVIOR OF ACETYLATED WOOD PULP

Commercial bleached Mitscherlich pulp, having a degree of polymerization of 1027 (corresponding to a molecular weight of 166,400) derived from specific viscosity measurements in cuprammonium hydroxide (using Staudinger's equation), was acetylated as before to give a series of samples with increasing acetyl contents. The highest acetyl content (23.26 per cent) was obtained after 41 days of acetylation.

As with acetylated rag stock, the acetylated wood pulp samples showed decreasing compatibility with water and increasing resistance to beating and sheet forming with increasing acetyl content. Table II gives the physical properties of sheets prepared from the acetylated samples after defibration without beating (75,000 revolutions in the British disintegrator), followed by beating for 40 minutes in the Lampén mill, as compared with those of the unacetylated pulp after the same beating time. Figure 5 shows the physical strength properties of the acetylated wood pulp beaten in water.

As Table II and Figure 5 show, the same phenomenon, although less pronounced, was observed with the beaten acetylated wood pulp as was found with the beaten acetylated rag stocks; i. e., within a certain range of low acetyl content, the physical properties and the apparent density of the sheets prepared from the beaten samples increase and reach a maximum. For the bursting strength, the maximum appears within a range of 2.61–4.05 per cent acetyl; for the tensile strength and the tearing strength, it appears at 6.75 per cent. The apparent density is highest at 2.61 per cent acetyl. With higher acetyl contents the bursting and tensile strengths and apparent density decrease rapidly and become almost zero at an acetyl content of 23.26 per cent. The tear values vary relatively little, but the sharp drop (Table II) when an acetyl content of 23.26 per cent is reached is quite noticeable.

A similar though less pronounced trend is shown by the figures referring to the sheets prepared from the samples which were disintegrated but not actually beaten (Table II). Maximum values for bursting strength and tear, as well as for apparent density, are observed at an acetyl content of 4.05 per cent, whereas maximum tensile strength appears at a somewhat lower degree of substitution. That no maximum was observed for sheets prepared from unbeaten acetylated rag stock samples in the earlier investigation is probably explained by the fact that those materials were subjected to considerably less mechanical agitation in the British disintegrator than the samples here discussed. In addition, the greater resistance to defibration of rag stock as compared with wood pulp may aid in accounting for the difference.

When the water was replaced by acetone in the processes of beating and sheet preparation, the compatibility of the acetylated samples with acetone increased with the acetyl content. The sample with 23.26 per cent acetyl gave a very uniform sheet of high water and ink resistance. Its bursting strength, although lower than that of the unacetylated wood pulp beaten in water, was quite satisfactory (116.3 against 154.3 after 30 minutes of beating), and its tearing strength was somewhat higher than that of the unacetylated pulp (1.392 against 0.988). The indications were that the acetylated wood pulp should have been beaten for a longer period than 30 minutes (as for the unacetylated material) to develop its maximum strength values and that the maximum would have approached, if not surpassed, that of the unacetylated stock at optimum beating time.

#### INFLUENCE OF NONCELLULOSIC CARBOHYDRATES

Of the noncellulosic carbohydrates present in wood and wood pulp, xylan was selected as the most frequently occurring representative:

The crude xylan which was available and had been prepared from wheat straw by the Salkowsky method as modified by Heuser and Braden (4) contained 8.06 per cent ash and had a rather dark color. It was purified by trituration with hydrochloric acid and by subsequent treatments with chlorine gas and liquid bromine (according to a suggestion made by E. Anderson), followed by washing with alcohol and water. The color had been much improved and the ash content had been reduced to 0.66 per cent; the ash was free of copper. The purified xylan was acetylated according to the method of Heuser and Schlosser (5) by heating it with a mixture of acetic anhydride and pyridine at 70° for an hour. The acetyl contents of the products thus obtained were

TABLE III. EFFECT OF XYLAN ON PHYSICAL STRENGTH PROPERTIES OF RAG STOCK SHEETS

	Beating Time, Min.	Bursting Strength, Lb./Sq. In./100 Lb. Basis Weight	Tensile Strength, Lb./100 Lb. Basis Weight	Tear Factor
Rag stock alone	5	56.25	15.72	5.839
	10	71.18	19.52	4.628
	20	65.35	20.71	2.705
	40	60.19	20.00	2.626
	60	56.69	19.95	2.247
5% xylan added	5	55.05	14.18	4.579
	10	71.53	19.72	4.640
	20	70.21	23.75	3.877
	40	65.90	22.45	2.535
	60	58.43	21.33	1.955
10% xylan added	5	63.32	14.59	5.488
	10	77.56	21.90	4.146
	20	78.07	23.44	3.582
	40	67.34	22.61	2.528
	60	61.47	23.11	1.912
10% acetylated xylan added	5	60.63	16.28	3.869
	10	63.46	18.15	4.023
	20	55.54	19.60	3.246
	40	50.49	14.31	2.407
	60	36.70	15.12	1.342



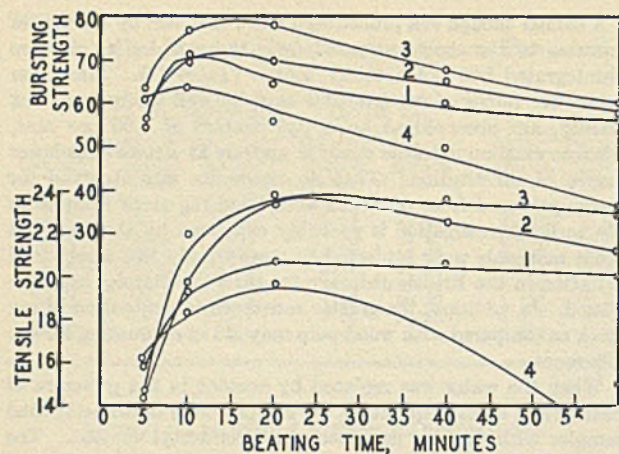


Figure 6. Effect of Xylan on Bursting and Tensile Strength of Rag Stock

1. Rag stock alone
2. 5 per cent xylan added
3. 10 per cent xylan added
4. 10 per cent acetylated xylan added

39.37 and 39.10 per cent. Theoretically, xylan diacetate requires 39.82 per cent.

The rag stock was that used in the earlier part of this investigation; it was practically free of noncellulosic carbohydrates, its alpha-cellulose content being 98.15 per cent.

To ascertain the effect of unacetylated and acetylated xylan upon the strength properties of sheets prepared from beaten rag stock, certain quantities of xylan and of the acetylated product were added to the rag stock, and the mixtures were beaten in the Lampén mill for various times. The results are shown in Table III and Figure 6.

It is seen that the physical strength properties of the sheets prepared from rag stock to which xylan had been added were increased over those of sheets prepared from rag stock alone; the findings of previous investigators were thus confirmed. However, the addition of acetylated xylan did not cause an increase but rather a decrease. This result seems to support the hypothesis advanced above—namely, that the strength-increasing effect of noncellulosic carbohydrates added to cellulose fibers is brought about by mutual bonding between their hydroxyl groups and those of the cellulose. If the hydroxyl groups of the noncellulosic carbohydrate are replaced by acetyl groups, bonding fails to occur. The decrease in physical strength properties seems to indicate that the acetylated xylan acts merely as a filler.

The hypothesis advanced appears to be further supported by the results of an experiment in which a relatively large amount of xylan was beaten with a sample of acetylated rag stock which had lost all of its papermaking properties (23 per cent acetyl content). It would be expected that those hydroxyl groups which are responsible for hydration and bonding in the unacetylated rag stock would no longer be available for a combination with the free hydroxyl groups of the xylan in an acetylated cellulosic material, in which about 37 per cent of the hydroxyl groups had been replaced by acetyl. Thus, the addition of even a large amount of (unacetylated) xylan should result in no increase in physical strength properties.

The addition of about 50 per cent xylan to the acetylated rag stock had no strength-increasing effect but rather a tendency in the opposite direction. Although it was difficult to prepare homogeneous sheets from the highly acetylated material, small portions could be defibered by a combined treatment in the Lampén mill and the British disintegrator to the extent that a few sheets could be prepared for testing. The bursting and tensile strengths

of the acetylated rag stock without xylan were 4.97 and 4.39, respectively, and the values of the material to which 50 per cent xylan had been added were 4.34 and 3.94, respectively.

#### SUMMARY

1. The study of the effect of acetylation upon the water-binding properties of cellulose was extended to rag stock samples having acetyl contents closer to one another than those used previously (1).

2. In confirmation of the results obtained by Bletzipger, the physical properties of sheets prepared from samples beaten in the Lampén mill increased with increasing acetyl content, reached a maximum, and dropped sharply with further increasing acetyl content.

3. The acetylated rag stock fibers showed a maximum hygroscopicity at acetyl contents between 3 and 4 per cent. The fact that the hygroscopicity maximum occurred with samples which had undergone no beating and even no disintegration seems to show that the mere opening of the micellar structure by acetylation suffices to increase the number of accessible free hydroxyl groups. The hygroscopicity maximum coincided with the maximum in physical strength properties as produced in sheets prepared from the beaten acetylated samples. This coincidence would be expected if the maximum in physical strength properties is regarded as the result of maximum hydration.

4. The previously observed compatibility of the acetylated rag stock with acetone, as well as the fact that sheets of excellent physical properties and resistance to water and ink could be prepared when acetone instead of water was the medium during beating and sheet formation, was confirmed.

5. Commercial bleached sulfite pulp (Mitscherlich type) showed a behavior with increasing acetyl content, when beaten in water or in acetone, very similar to that of the acetylated rag stock. Moreover, a maximum in physical strength properties was also obtained with sheets prepared from samples which were merely subjected to disintegration in the British disintegrator in the presence of water—i. e., without actual beating.

6. The addition of acetylated xylan to unacetylated rag stock in the Lampén mill failed to produce the improvement in physical strength properties observed with the addition of unacetylated xylan to rag stock. This result seems to support the hypothesis that the strength-increasing effect of the added xylan is brought about by mutual bonding between its hydroxyl groups and those of the cellulose.

7. Likewise, the addition of a large amount of (unacetylated) xylan to highly acetylated rag stock failed to improve the physical strength properties of the latter. Obviously, those hydroxyl groups in cellulose which are responsible for hydration and bonding were no longer available in the acetylated material for a combination with the free hydroxyl groups of the xylan.

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- (7) Obermanns, *Paper Trade J.*, 103, No. 7, 83 (1936).
- (8) Rowland and Young, *Ibid.*, 97, No. 15, 44 (1933).

PORTION of a thesis submitted in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of doctor of philosophy from Lawrence College, Appleton, Wis.; carried out under the direction of F. Heuser.

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# WATER FOR Grain Alcohol Distilleries

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The shortage of cool water for the continuous operation of grain distilleries converted to high-proof alcohol for war purposes has led many plants to water conservation and mechanical cooling. About 700 gallons of water are required for the processing and total recovery of feed by-products per bushel of grain converted to 95 per cent alcohol.

**A**T PRESENT the beverage alcohol (whisky) industry is completely converted to and operates full time on the production of high-proof alcohol, furnishing about half the total alcohol needed in our war program. The majority of the molasses alcohol plants are converting to grain or grain concentrate, and the new plants (if any) to be built by the Government are to be high-proof alcohol plants operating on grain. Of the raw materials used in distillery operations, water is one of the essentials; and since large quantities are required, these plants must be located where an adequate supply is available. In peacetime many of the distillers shut down during the summer months mainly on account of water shortage and/or its increase in temperature. With present conditions creating a large demand for alcohol and by-product feeds, this must be avoided. A review of the water demands of a high-proof alcohol plant operating on grain therefore becomes pertinent.

In modern distillery practice the conservation of both water and heat is essential, and as a result an economic balance is maintained through the re-use of water at various temperatures. The total water used in the larger plants, as in the case of Hiram Walker & Sons, amounts, in round figures, to 700 gallons for each bushel of grain processed. This includes water for processing, boilers, condensers, by-product feed recovery, and domestic services. The water demands of the various operations naturally vary with the temperature of the water, but on the basis of using well waters running 60° F. (16° C.) for the mashing, fermenting, and distilling departments, and using 70° F. (21° C.) river water for operating the stillage evaporators, the breakdown is substantially as given in Table I.

For the purpose of discussion, the waters used in a distillery may be divided into three main classes—namely, processing waters, cooling waters, and boiler waters. In many plants these waters all come from the same source but the general decline in the static level of ground waters throughout the country is forcing not only distillers but other processing plants as well to use surface waters whenever possible.

## PROCESSING WATERS

In the main, distillers prefer ground waters for processing purposes—that is, for the mashing of grains and conversion of the solubilized starch to sugar, in growing their yeast and in the fermentation of their saccharine mashies by the yeast to alcohol. This processing water should be free of sediment, should possess no foreign taste or odor, and should be clean bacteriologically,

even to the extent of meeting drinking water standards. It should also be chemically constituted in order to furnish the desired inorganic salts for optimum fermentations and, if chlorinated, should carry only a trace of free chlorine. Lime-soda ash treated waters should not be used for processing because they are too alkaline. A limestone-bearing type water is preferred because it contains those inorganic salts which are necessary for optimum conversion and yeast propagation—namely, the bicarbonates of calcium and magnesium with traces of other cations and a moderate quantity of sulfates. The effect of various salts in these operations is recognized by fermentologists, and a discussion of the subject would be too lengthy to include here. Most of these limestone-bearing well and spring waters also run low in bacterial count and are usually cool so that they may be used for cooling purposes, preferably after they have been treated to remove or stabilize the bicarbonate hardness. The analysis of a typical well water found satisfactory for the processing of cereal grains to whisky and high-proof alcohol is given in Table II.

It is not so essential today as it was years ago for the distiller to find a "natural" satisfactory processing water. By combining what is known regarding the inorganic salt requirements of yeast and the effect of various salts on the mashing and malt conversion steps with present day knowledge regarding treatment, he can remodel or reconstitute almost any available water supply to meet his demands and even his whims.

TABLE I. WATER AND STEAM REQUIREMENTS OF A MODERN GRAIN DISTILLERY PRODUCING HIGH-PROOF ALCOHOL

	Gal. Water per Bu.	Lb. Steam per Bu.
Processing <sup>a</sup>		
Cooking (batch-pressure) and sterilizing	36	36
Mash coolers, double pipe	78	...
Fermenter cooling (coils)	70	...
Stilla, high-proof alcohol	94	100
Total processing	278	136
Stillage recovery (screenings and solubles) <sup>b</sup>		
Evaporators, stillage	430	87
Dryers	...	55
Power house <sup>a</sup>	12	...
Administration <sup>a</sup>		
Sanitary + air conditioning	5	...
Solid carbon dioxide <sup>a</sup>	5	...
Bottling <sup>a</sup>		
Sanitary + air conditioning	35	...
Grand total	765	...

<sup>a</sup> Well water at 60° F.

<sup>b</sup> Illinois River water supply at 70° F.







This water need not be treated to remove or stabilize the bicarbonate hardness because it never reaches more than 90° F. (32° C.).

The hot water used in the Yeast Department to maintain the temperature of mashers undergoing lactic acid production, as well as the cold well water used to keep down the temperature of large batches of yeast under propagation, are collected; through the use of a thermostatic control valve, they are directed to the hot water recovery system if warm or to the well water recovery storage tank if cool. In summer when well water is used in the fermenter cooling coils, it is also collected and re-used through the well water recovery system.

The gradual decline in the ground water level in many parts of the country is leading distillers to substitute surface waters wherever possible. For example, instead of the standard heat exchanger type of mash coolers (double pipe, countercurrent) it is possible to reduce the temperature of hot mashers to the desired conversion point by vacuum cooling, using barometric and jet condensers. A large number of distillers have already gone to cooling water recovery systems (from mash, back-slop, and whisky coolers and condensers), and are cooling these recovered waters through spray towers and/or refrigeration systems. When the temperature of a surface supply of water exceeds that necessary for the heat exchanger type of cooling, this water may still be used for refrigeration equipment or for vacuum cooling although a larger quantity is required.

The successful use of lake water through a hot portion of double pipe coolers followed by the use of a spray tower and vacuum cooling system to give a water of 50° F. (10° C.) as practiced at a distillery in Bardstown, Ky., has been reported (1).

The water used in operating multiple-effect evaporators for the concentration of screened stillage may be of any type as long as it is not too warm and contains only a moderate amount of suspended solids. At the Hiram Walker plant in Peoria, river water is used in the barometric and jet condensers the year round although the temperature varies from freezing to 85° F. (29° C.). Naturally more water is required at the warmer temperatures.

#### BOILER WATERS

The powerhouse uses well water direct from one well in order to have a constant source of water with definite softening requirements. This water is conditioned by a hot lime-soda ash process capable of treating 3,500,000 pounds per day. The treated water, together with returned condensates, is fed to two Sterling bent-tube boilers (rated at 1379 horsepower each), delivering approximately 7,000,000 pounds of steam per day at 250 pounds pressure. This high pressure steam is passed through two turbines to develop electricity for the plant and deliver 80- and 15-pound processing steam to the distillery. The natural sulfate ion concentration in this well water is adequate to provide the A. S. M. E. recommended sulfate-alkalinity ratio. Operations have shown that the hot lime-soda ash process removes only approximately half of the silica; therefore internal anhydrous disodium phosphate treatment is given the boilers. This combination treatment prevents boiler scale and provides clean steam for processing. The steam quality is good enough to permit use of the condensate from the alcohol still calandrias for distilled water for reducing proof. Analysis of this water from the collecting tank shows less than 2 p. p. m. of solids and less than 0.1 p. p. m. of iron. An additional quantity of distilled water is required above that supplied by the alcohol still calandrias; therefore powerhouse condensate is redistilled in a multiple-effect water still. This practice eliminates the necessity of chemical treatment of the water fed to the water still. Research has indicated that cation and anion exchange material can be used to produce a satisfactory deproofing water from the well supply.

The quantity of steam required for producing high-proof alcohol from corn containing 12-13 per cent moisture at a recovery

yield of 5.1 proof gallons per bushel, varies with the method of processing and the type of stills used. In the batch pressure cooking method, using modern continuous stills not equipped for vapor re-use, about 36 pounds per bushel of grain are required for mashing and sterilizing and about 100 pounds per bushel for distilling. The complete recovery of by-products requires about 142 pounds of steam per bushel of grain ground to obtain a total by-product feed recovery of 17 pounds per bushel of original grain ground (Table I). The processing of wheat or rye to high-proof alcohol requires about the same quantity of water and steam as does corn.

#### WATER SYSTEM

The well water supply at the Hiram Walker plant is taken from an underlying gravel strata, its temperature ranging from 56° F. (13° C.) in summer to 62° F. (17° C.) in winter (note the temperature lag). Three of these 50-60 foot wells are capable of furnishing a total of 7000 gallons of water per minute. City water of the same type as the plant well supply is available in limited quantity in case of necessity.

TABLE II. REPRESENTATIVE ANALYSIS OF RIVER AND WELL WATERS

	River Water	Well Water <sup>a</sup>
pH	7.8	7.0
Chemical analysis, p. p. m.		
Calcium	4.97	125.7
Magnesium	10.1	40.1
Sodium	23.9	24.2
Sulfate	42.0	153.7
Nitrate	5.3	23.0
Chloride	25.0	29.0
Alkalinity as CaCO <sub>3</sub>	134.0	305.0
Manganese	0.0	0.0
Fe (filtered)	1.0	0.1
Silica	8.0	14.0
Suspended solids	27.0	None
Organic and volatile	95.0	
Total dissolved solids	253.0	608.0
Total hardness	166.0	479.0

<sup>a</sup> H<sub>2</sub>SO<sub>4</sub>-treated water has a pH of 6.4-6.7 and contains 150-180 p. p. m. of alkalinity as CaCO<sub>3</sub>.

The river water system includes traveling screens through which the water flows into a sump; from there it is pumped by centrifugal pumps delivering a maximum of 11,700 gallons per minute to the distillery. The river water temperature ranges from 33° F. (1.0° C.) in winter to 85° F. (29° C.) in summer. So far it has not been found necessary to treat this water to control biological growths in the exchangers.

Each water supply is kept separate in the distillery since it is necessary to change piping when equipment is shifted from one supply to another. This eliminates the possibility of cross connections which might lead to pollution of the well supply used for processing and drinking purposes.

This discussion does not warrant a review of the various types of ground water wells used in the industry. However, attention should be called to the lateral type water collecting system being installed by the Ranney Water Collector Corporation which has been found satisfactory by the Joseph E. Seagram & Sons distilleries as well as many other industries where it is necessary to obtain a large quantity of water from one structure or water from aquifers of poor permeability.

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PRESENTED before the Division of Water, Sewage, and Sanitation Chemistry at the 105th Meeting of the AMERICAN CHEMICAL SOCIETY, Detroit, Mich.



Phase Equilibria in

# Hydrocarbon Systems

## HEAT OF SOLUTION OF ETHANE AND PROPANE

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Experimental measurements were made to determine the change in enthalpy involved when either ethane or propane is dissolved in a relatively nonvolatile hydrocarbon oil. Comparison is made between results obtained from calorimetric determinations and those calculated from the volumetric behavior of the system.

A CHANGE in phase of a component of a hydrocarbon mixture is often associated with transfers of thermal and mechanical energy to or from the system. The magnitude of thermal energy transfers of this type associated with processes of industrial interest is sufficiently great to make its evaluation desirable in engineering calculations. Experimental information concerning the "heat of solution" of the lighter hydrocarbons is scarce, and for this reason a study of the change in enthalpy resulting from the solution of ethane and propane in a relatively nonvolatile, water-white oil was undertaken. The experimental program included both calorimetric and volumetric measurements for temperatures between 100° and 220° F. and at pressures up to 500 pounds per square inch.

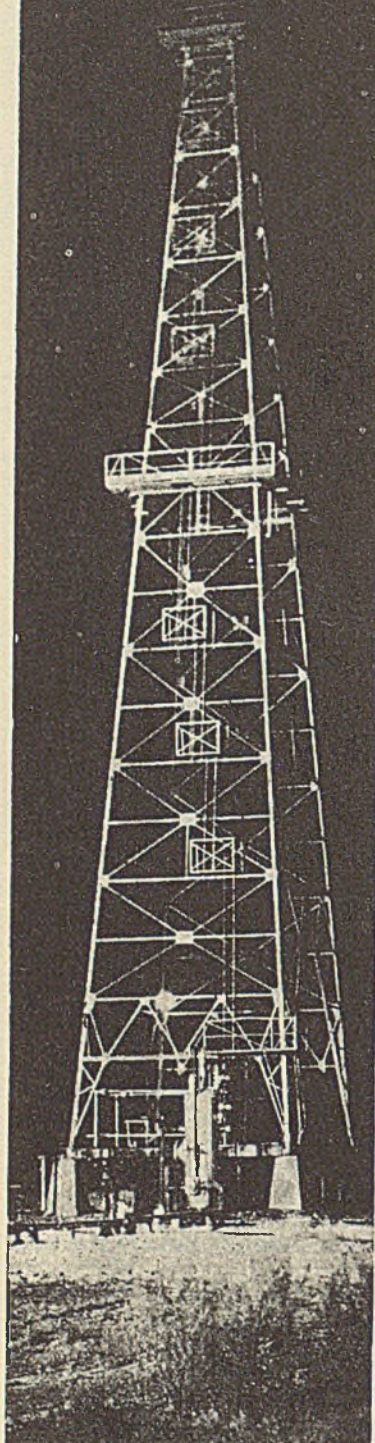
Information is available concerning the change in enthalpy during the solution of propane (12) in a nonvolatile hydrocarbon liquid. Fischer (1, 2) discussed the thermodynamic relations applying to the heat of vaporization of binary and ternary mixtures. These relations indicate that the isothermal changes in enthalpy of any complex system may be ascertained from volumetric measurements alone. However, if attention is directed to the component rather than to the system as a whole, it is desirable to determine the change in the partial enthalpy (6) of the component as a result of a change in phase. This procedure may also permit a simpler correlation of the thermal properties of multicomponent hydrocarbon systems from the behavior of the individual components. The thermodynamic relations for multicomponent systems have been developed in detail by Gibbs (3) and by Goranson (4).

The difference between the partial enthalpy of a component in a gas phase and that in a liquid phase may be ascertained from volumetric data by suitable application of thermodynamic methods. In the case of two phases at equilibrium in a binary system containing one essentially nonvolatile component for a change in state in which the composition of the liquid does not change, it can be shown that

$$H_{1g} - \bar{H}_{1l} = T(V_{1g} - \bar{V}_{1l})\left(\frac{\partial P}{\partial T}\right)_{x_1} \quad (1)$$

This equation permits the direct evaluation of the change in enthalpy due to the change in phase of a component in this type of binary system in terms of the absolute temperature, the specific volume of the gas phase, the partial specific volume of the component in the liquid phase, and the rate of change of bubble point pressure with

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temperature at a fixed composition. It is rigorous when applied to systems satisfying the restraints indicated above.

The corresponding equation for the general case is more complex. It requires for its solution rather complete volumetric data concerning the binary system at states from infinite volume to the pressure in question.

#### EXPERIMENTAL METHOD

In some cases it is advantageous to determine the enthalpy change during solution by means of direct calorimetric measurements. This was the purpose of the present investigation.

In principle the apparatus employed is illustrated schematically in Figure 1. It consisted of an isochoric chamber, *A*, located within the adiabatic vacuum jacket, *B*. Chamber *A* was arranged so that liquids could be added or withdrawn through valve *C*, located outside of the vacuum jacket. Gaseous components were introduced or withdrawn from the system through tube *D*. Provision was made for the measurement of the pressure existing within vessel *A* through small conduit *E* which connected the apparatus to pressure balance *F* through an appropriate mercury U-tube. Mechanical agitation was provided by centrifugal pump *G*, which was driven by a small wire shaft within tube *H*, entering the calorimeter system through packing gland *J*. Arrangement was made for precise measurement of the temperature of the fluids within vessel *A* and of the temperature difference between jacket *B* and the exterior of calorimeter vessel *A*. Known quantities of electrical energy were added to the system when desired by means of resistance element *K*.

Two types of process for the study of the enthalpy of solution of binary systems may be carried out conveniently with equipment of this nature. The first involves the addition of a known weight of the less volatile component to chamber *A* through conduit *C* or *D*. The necessary amount of the second component is then added to the system in order to reach the desired initial composition. Electrical energy is added, if necessary, to bring the calorimeter to the temperature in question. The component whose change in partial enthalpy is to be investigated is then admitted as a gas through conduit *D* from weighing bomb *L*, its rate of admission being controlled by adjustment of valve *M*. The change in temperature of the calorimeter and contents resulting from the addition of this material is determined, and from this information and the heat capacity of the calorimeter the change in enthalpy of the component resulting from its solution in the liquid phase may be calculated. This procedure may be applied to systems involving more than two components as well as to binary systems. However, except in cases involving systems with only one volatile component certain auxiliary volumetric information pertaining to the behavior of the system is necessary in the interpretation of the results, and in any event the volumetric behavior of the component in question must be available.

In the case of systems in which only one component need be treated as volatile, a somewhat simpler procedure may be employed. The system is brought initially to the desired composition and temperature by the suitable addition of material and electrical energy. After equilibrium has been attained, the volatile component is gradually withdrawn through conduit *D* into weighing bomb *L*, its rate of withdrawal being controlled by valve *M*. Electrical energy is added to the calorimeter at a known rate to maintain isothermal conditions during the withdrawal process. This procedure is somewhat simpler to interpret than the more generally applicable addition process described earlier, since the changes in temperature are small and the electrical energy added to the system, in conjunction with suitable correction terms, is a direct measure of the change in the partial enthalpy of the volatile component in passing from the liquid to the gas phase. However, it is limited in application to systems involving only one volatile component and therefore cannot be applied to a number of situations of industrial interest. The

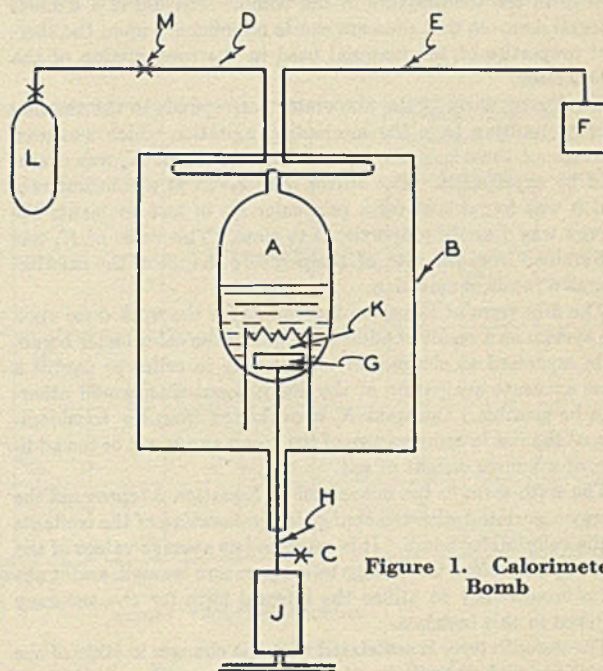
thermodynamic analysis is the same for the two procedures described but the relative magnitude of the various terms differs widely in the two cases.

Since the calorimeter may be considered an isochoric system, the analysis of the energy relations can best be made in terms of internal energy. From the first law of thermodynamics as applied to a binary system of variable weight in the case that the state of the system does not undergo great change during the course of a set of measurements, it may be shown that

$$[\bar{E}_{ii} - E_{i0}]_a = \frac{\int_A^B K_b(T_i - T_b)d\theta - \int_A^B C_b dT + Q_E + K_e(\theta_B - \theta_A) + \int_A^B P'V_1'K_f(dT_b/d\theta)d\theta}{\int_A^B [V_{10}/(V_{10} - \bar{V}_{1i})](dm_1/d\theta)d\theta + \int_A^B [m_{10}/(V_{10} - \bar{V}_{1i})](dV_{10}/d\theta)d\theta} + \frac{-[m_{0a}(C_{F0a} - b) + m_{1a}C_{P1a}](T_{bB} - T_{bA}) + \int_A^B m_e[T(\partial V_e/\partial T)_{P,Y_1} + P(\partial V_e/\partial P)_{T,Y_1}]dP}{\int_A^B [V_{10}/(V_{10} - \bar{V}_{1i})](dm_1/d\theta)d\theta + \int_A^B [m_{10}/(V_{10} - \bar{V}_{1i})](dV_{10}/d\theta)d\theta} \quad (2)$$

Space does not permit a presentation of the derivation of this special equation. It furnishes in terms of experimentally measurable quantities an expression for the average value of the change in the partial internal energy of a component in passing from a gas to a liquid phase. The equation was employed in the interpretation of the experimental results. It is believed that, under the conditions encountered in the experimental work, the uncertainties resulting from approximations employed in its derivation were less than the uncertainty of measurement in nearly all cases.

The first term in the numerator of Equation 2 represents the energy transferred between the jacket and the exterior surface of the calorimeter and assumes it to be directly proportional to the difference in temperature. This assumption was experimentally verified for the equipment used.





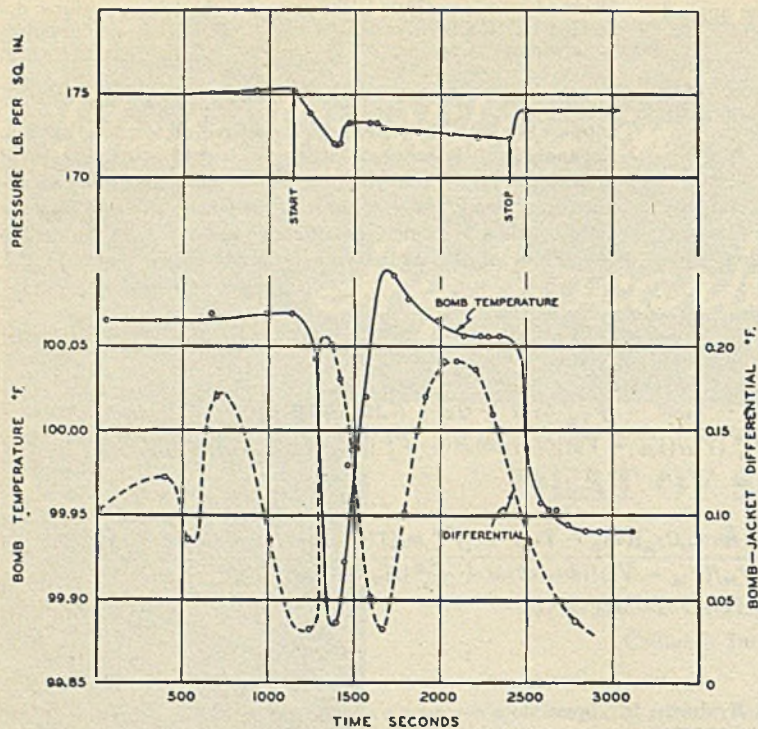


Figure 2. Typical Set of Experimental Results under Isothermal Conditions

To evaluate coefficient  $K_4$ , a convenient weight of material of known isochoric heat capacity was added to the calorimeter. The jacket was maintained at a constant temperature while the temperature of the bomb was raised somewhat above that of the jacket. Readings of the temperature of the bomb were made as a function of time and from this it was possible to evaluate the coefficient.

The second term accounts for the energy required as a result of change in the temperature of the bomb. The use of a definite integral assumes that pressure exerts no influence upon the thermal properties of the material used in the construction of the calorimeter.

The fourth term of the numerator corresponds to the thermal energy resulting from the mechanical agitation which was used throughout these measurements. The coefficient  $K_4$  was evaluated by experiment. The stirrer was driven at a constant rate and it was found that for a particular set of measurements the energy was directly proportional to time. The value of  $K_4$  was determined from the rate of temperature change of the calorimeter as a result of agitation.

The fifth term of Equation 2 accounts for the work done upon the system as a result of adding the gas to the calorimeter bomb. It is expressed as changes in temperature in order to permit a more accurate evaluation of the line integral than would otherwise be possible. Constant  $K_5$  is evaluated from the consideration of the rise in temperature of the bomb as a result of the addition of a known weight of gas.

The sixth term in the numerator of Equation 2 represents the energy associated with the change in temperature of the contents of the calorimeter bomb. It is expressed as average values of the heat capacity since the change in temperature is small, and it appears unnecessary to utilize the integral form for the accuracy required in this instance.

The seventh term is associated with the changes in state of the gas phase and may be considered as representing the energy

changes resulting from the pressure changes encountered during the process. The exact form of this term results from an attempt to express all of the changes in state in terms of pressure, temperature, time, and the weight of material added.

The two line integrals in the denominator of Equation 2 take into account the fact that the quantity of material added to or withdrawn from the calorimeter bomb was not equal to the quantity of material transferred from the liquid to the gas phase, or the reverse, within the bomb. Both of these quantities are expressed in terms of time in order to permit a direct evaluation from the experimental data.

#### PROCEDURE

The apparatus employed in the study of the propane-*n*-butane system in the critical region (7) was utilized in the measurement of the volumetric and phase behavior of the mixtures of propane and crystal oil reported as a part of this study. The experimental work was carried out with sufficiently accurate calibrations of the equipment used in the measurement of the primary quantities so that uncertainties in the reported bubble-point pressure of more than 0.1 pound per square inch are unlikely. The composition and weight of the samples investigated were ascertained from both gravimetric and volumetric measurements, giving agreement within 0.003 weight fraction of propane.

Furthermore, uncertainties in the composition do not enter directly into the calculation of the change of enthalpy upon solution.

The calorimeter employed for the direct measurements of the enthalpy change for the solution of ethane and propane was essentially that utilized in the measurement of the latent heat of vaporization of propane and *n*-pentane (9). However, the control equipment utilized in the approach to adiabatic conditions was improved by the use of electronic circuits permitting the continuous gradation in the current supplied to the heaters for the adiabatic jacket. This procedure decreased the correction for thermal energy losses from the calorimeter under both isothermal and "adiabatic" operation to about one fifth of that required earlier.

Precision control equipment for the temperature of the condenser was also installed. This permitted a much more uniform rate of withdrawal of the solute from the calorimeter. Some difficulties had been experienced originally from the condensation of small quantities of solute in the lines connecting the calorimeter with the several pieces of measuring equipment involved. This situation was obviated by the use of a more suitable oil circulating system in order to maintain the temperature of the connecting tubing at a constant value which was markedly in excess of the dew-point temperature for the pressures in question.

Rather violent mechanical agitation was provided within the calorimeter by means of a radial-throw impeller mounted between dual bearings. This impeller was driven by a wire (number 20, B. and S. gage) through a stainless steel tube. The temperature gradient along this tube was maintained at a negligible value by circulation of oil through a concentric jacket.

The nonvolatile liquid was added to the evacuated calorimeter and the quantity employed was determined gravimetrically. The amount of the gaseous hydrocarbon necessary to yield the desired initial composition was then added to the apparatus, and equilibrium was attained by the use of the mechanical agitator



located within the calorimeter. For the most part, measurements were made under isothermal conditions and the gaseous hydrocarbon was withdrawn from the calorimeter while electrical energy was added at such a rate as to maintain the temperature of the calorimeter and contents nearly constant. Upon leaving the calorimeter, the gaseous hydrocarbon passed through a motor-operated throttle valve which permitted convenient control of the rate of gas withdrawal. After passing through the control valve, the hydrocarbon was condensed in a small weighing bomb at such a temperature that a pressure differential of approximately 15 pounds per square inch was maintained across the main throttle valve. The weighing bomb was cooled to liquid air temperature after the completion of a set of measurements in order to avoid any appreciable loss of residual gas in the tubing connecting the weighing bomb to the motor-operated throttle valve.

Approximately 30 minutes were required for the completion of a set of measurements involving the withdrawal of a known weight of gaseous hydrocarbon, followed by the reattainment of equilibrium between the liquid and gas phases. In order to illustrate the nature of the experimental work, a typical set of measurements is shown in Figure 2.

Throughout the entire process the temperature of the calorimeter, the temperature of the gas leaving the instrument, the temperature difference between the calorimeter bomb and the adiabatic vacuum jacket, and the pressure within the calorimeter were determined periodically. In the instance shown there was a rather significant change in pressure at the beginning of the experimental measurements, but the changes in temperature were small and the difference in temperature between the calorimeter bomb and the jacket were of such a magnitude as to reduce the correction for energy losses from this source to less than 1 per cent of the total energy quantity involved.

In the early part of the experimental program measurements were made involving the addition of the gaseous hydrocarbon to the relatively nonvolatile liquid in the calorimeter. Under these circumstances the conditions were somewhat more difficult to control than in the case of the isothermal studies, but the results, within the uncertainty of measurement, were identical with those obtained for the withdrawal process. A typical set of results obtained from the measurements involving the addition of gaseous propane is given in Figure 3. Work of this type requires accurate information concerning the heat capacity of the calorimeter and these data were obtained by independent measurements under adiabatic conditions before and after each measurement of heat of solution.

The procedures followed in the case of both propane and ethane

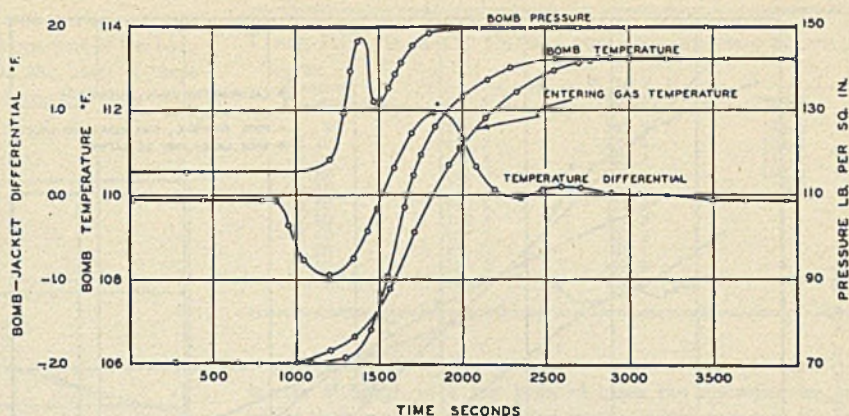


Figure 3. Typical Set of Experimental Results under Adiabatic Conditions

were essentially the same, although the higher pressures encountered in the case of ethane made the measurements somewhat more difficult. Furthermore, the correction terms were large, especially the value of the fifth term in the numerator of Equation 2, which was larger than all other terms in the equation with the exception of  $Q_B$ , which represents the electrical energy addition. The procedure outlined is somewhat time consuming and the calculations are tedious, and for this reason the method is not suitable for extended investigations. It serves rather to establish the consistency and applicability of the volumetric data in the prediction of the changes in internal energy or enthalpy as a result of the change in phase of a component of a hydrocarbon system.

#### MATERIALS

The nonvolatile oil used in this investigation was a paraffin-base, water-white oil refined from a Pennsylvania crude stock. Its specific gravity at 100° F. relative to water at its maximum density was 0.8244 and the average molecular weight as determined from the freezing point lowering of benzene, extrapolated to infinite dilution, was 342. The viscosity-gravity factor ( $\delta$ ) was found to be 0.7979. Its vapor pressure after deaeration was less than  $10^{-2}$  inch of mercury at 100° F. Throughout the remaining

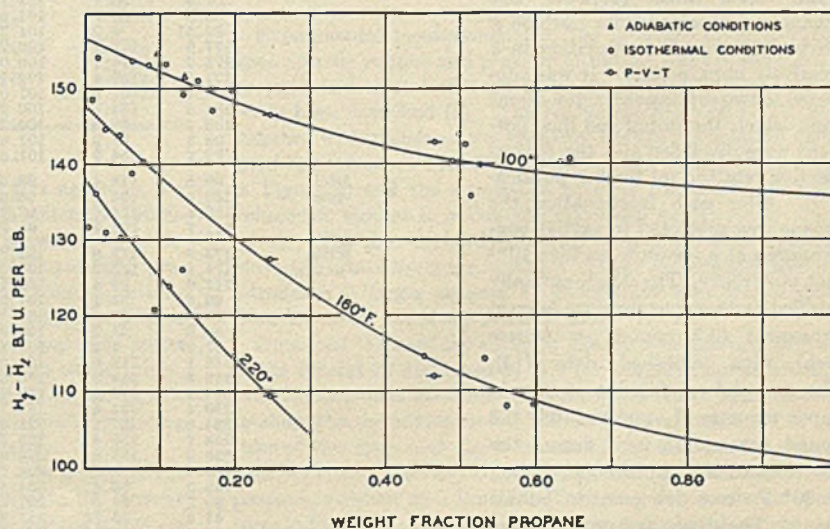


Figure 4. Enthalpy Change for Solution of Propane



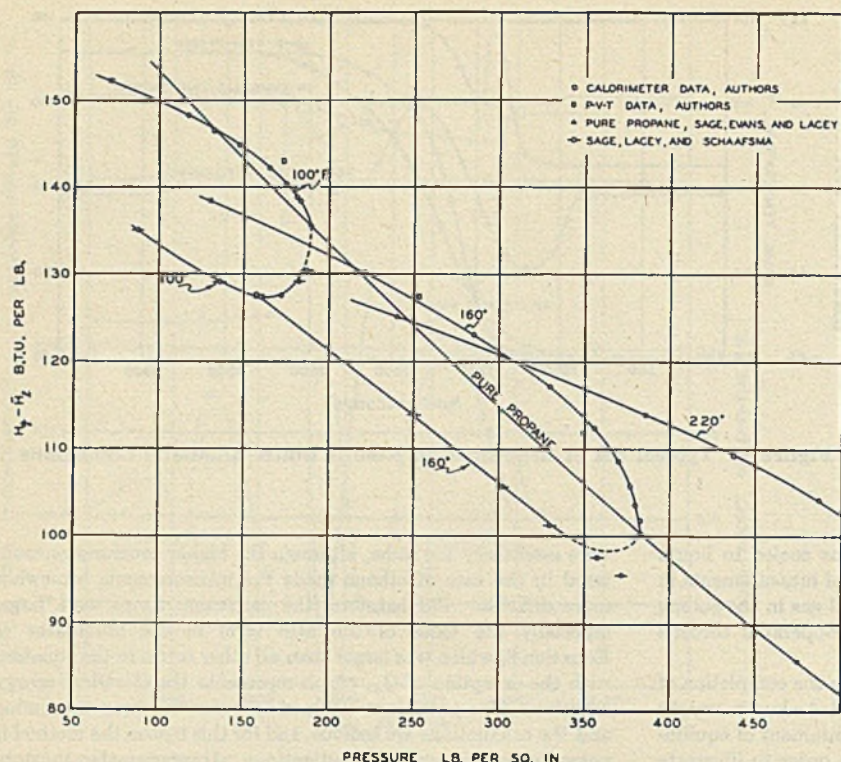


Figure 5. Comparison of Enthalpy Change Values for Propane

parts of this paper the oil will be called "crystal oil", but it was somewhat different in properties from the water-white oil used in other phase equilibrium studies by the authors. However, it was the same material as that employed in some viscosity measurements (10, 11).

The propane was obtained from the Phillips Petroleum Company, and the special analysis furnished with it indicated that the sample contained less than 0.01 mole per cent of material other than propane. The ethane was obtained from Carbide & Carbon Chemicals Corporation in a relatively impure state. It was subjected to two successive fractionations from which the initial and final portions were discarded and the central fraction retained for further purification. After each fractionation the ethane was subjected to partial condensation at a pressure less than  $10^{-3}$  inch of mercury. The ethane as finally purified had a vapor pressure in good agreement (0.2 pound per square inch) with published data (13). The material exhibited a change in vapor pressure of approximately 0.3 pound per square inch during the course of an isothermal condensation at 70° F. from dew point to bubble point. The ethane and propane were confined in steel weighing bombs permitting the quantity of material

added to or withdrawn from the calorimeter to be established gravimetrically with small uncertainty.

#### EXPERIMENTAL RESULTS

The experimental measurements relating to the propane-crystal oil system are given in Table I. The average conditions obtaining during each set of measurements as well as the variation in each of the pertinent variables are recorded. Although internal energy is the more fundamental thermodynamic property, enthalpy is of greater industrial interest and for this reason all of the results have been presented in terms of the latter quantity.

It is believed that the improvements made in the equipment have reduced its uncertainty in the evaluation of the heat associated with the operation of the calorimeter under isothermal conditions to less than 0.5 per cent of the electrical energy added to the calorimeter. The uncertainties in some of the measurements are as follows: variation in the temperature of the calorimeter and contents, 0.005° F.; weight of nonvolatile constituents and of solute added or withdrawn, 0.01 per cent; and electrical energy added, 0.01 per cent. The state of the gases withdrawn from the calorimeter was ascertained as a function of time, and it is believed that the integration of the relation be-

TABLE I. EXPERIMENTAL RESULTS FOR ENTHALPY CHANGE FOR SOLUTION OF PROPANE

Method of Measurement	Pressure, Lb./Sq. In. Abs.		Temperature, ° F.		Average Conditions		$H_0 - \bar{H}_1$ , B. T. U./Lb. <sup>a</sup>
	Initial	Final	Initial	Final	Temp., ° F.	Compn., wt. fraction	
With-drawal	89.1	79.3	101.102	100.999	101.05	0.1305	149.2
	79.6	66.5	101.021	100.842	100.93	0.1082	153.3
	67.5	53.4	101.169	101.155	101.16	0.0852	153.0
	53.5	38.70	101.048	101.075	101.06	0.0634	153.6
	26.51	4.25	101.254	101.249	101.25	0.0180	154.1
	177.9	177.1	100.784	100.480	100.63	0.6452	140.7
	175.2	174.1	100.065	99.940	100.00	0.6325	140.2
	171.0	169.4	100.999	101.021	101.01	0.5265	139.8
	169.4	167.9	101.026	101.075	101.05	0.5085	142.6
	184.5	184.3	100.208	100.369	100.29	1.0000	135.1
	188.9	188.8	100.297	100.261	100.28	1.0000	135.4
	96.3	81.9	101.683	101.620	101.65	0.1334	151.5
	82.1	54.9	101.611	101.548	101.58	0.0968	154.7
	Addition	99.5	113.4	98.641	102.782	100.71	0.1694
105.6		125.5	96.676	103.157	99.92	0.1953	149.7
160.5		174.6	97.150	103.095	100.12	0.4894	140.4
161.7		176.4	96.792	103.048	99.92	0.4688	135.8
175.9		173.8	102.755	102.626	102.69	0.4667	135.6
174.1		173.2	102.671	102.796	102.73	0.4682	144.0
117.0		99.6	161.116	161.078	161.10	0.0780	140.3
99.6		84.1	161.065	161.047	161.06	0.0638	138.7
84.9		56.2	161.112	160.970	161.04	0.0473	143.9
56.3		27.77	160.919	160.867	160.89	0.0272	144.6
27.97	4.15	161.116	161.035	161.08	0.0103	148.5	
354.1	348.6	160.653	160.640	160.65	0.5976	108.1	
349.3	344.3	160.691	160.597	160.64	0.5618	108.0	
344.2	340.7	160.550	160.528	160.54	0.5330	114.2	
330.4	324.4	161.142	161.155	161.15	0.4574	114.6	
284.6	257.1	222.416	222.172	222.79	0.1299	126.1	
258.7	226.4	224.318	224.380	224.35	0.1125	123.8	
226.9	183.9	224.447	224.380	224.41	0.0927	120.7	
183.4	138.3	224.267	224.176	224.22	0.0699	130.2	
138.3	90.8	224.163	224.280	224.22	0.0482	130.3	
89.7	51.5	221.868	221.918	221.89	0.0292	131.0	
51.5	26.22	221.985	221.822	221.90	0.0160	136.1	
26.20	3.51	221.747	221.772	221.76	0.0064	131.7	

<sup>a</sup> Change in the partial enthalpy of propane upon solution in crystal oil.



tween the enthalpy of this gas and the time was carried out with an over-all uncertainty of not more than 1.0 per cent of the electrical energy added to the calorimeter. On the basis of these facts taken with a number of other minor corrections normally

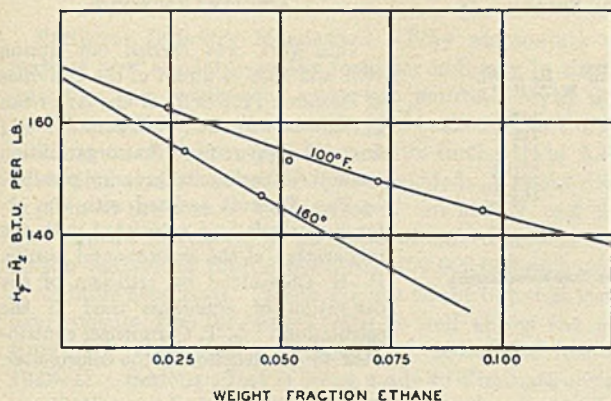


Figure 6. Enthalpy Change for Solution of Ethane

associated with calorimetric work of this type, it is estimated that the probable error in the reporting of the values of the change in enthalpy for solution is 1.5 per cent. On the basis of this analysis of the uncertainty of measurement, it is believed that the smoothed values are descriptive of fact within 2.0 B. t. u. per pound. This estimate is consistent with the fact that the values for the enthalpy change upon solution of propane agree with those computed from volumetric data within 2.0 per cent.

TABLE II. PROPERTIES OF PROPANE-CRYSTAL OIL MIXTURES

Temperature, ° F.	Bubble-Point State			$H_o - \bar{H}_l$ , B. T. U./ Lb.
	Pressure, lb./sq. in. abs.	Sp. vol., cu. ft./lb.	$(dP/dT)X$ , lb./sq. in./ ° F.	
Weight Fraction Propane, 0.2468				
70	88.0	0.02216	...	146.5
100	131.9	0.02254	1.656	127.4
130	185.2	0.02296	...	109.3
160	253.0	0.02339	2.528	...
190	337.5	0.02385	3.680	...
220	437.4	0.02437	...	...
Weight Fraction Propane, 0.4653				
100	173.2	0.02488	2.329	143.0
130	251.7	0.02552	...	...
160	349.6	0.02637	3.844	111.9
190	474.8	0.02749	...	...

The experimental uncertainty in a study of this nature is not readily expressed in terms of the precision with which the principle parameters were measured. Although the pressures, temperatures, weights, and energies involved were measured with precisions better than 0.1 per cent, the variation of these quantities in the course of an experiment and the finite intervals of time between observations introduced uncertainties somewhat larger than the precision of the individual measurements would imply. The foregoing estimates of the over-all accuracy of the experimental results are based upon the authors' experience in operating the equipment and are intended to be conservative.

The enthalpy change as a result of the solution of a unit weight of propane is presented in Figure 4 as a function of the average concentration of the liquid phase for the three temperatures experimentally investigated. The greater part of the experimental results are within the above-mentioned experimental uncer-

TABLE III. ENTHALPY CHANGE FOR PROPANE UPON SOLUTION

Wt. Fraction Propane	$H_o - \bar{H}_l$ , B. T. U./Lb.		
	100° F.	160° F.	220° F.
0	156.8	147.9	138.2
0.10	152.2	138.4	125.1
0.20	148.2	130.2	113.9
0.30	144.8	123.1	104.2
0.40	142.2	117.1	...
0.50	140.3	112.4	...
0.60	138.8	108.6	...
0.70	137.7	105.8	...
0.80	136.9	103.6	...
0.90	136.2	101.8	...
1.00	135.6	100.4	...

tainty, although in a few isolated cases the discrepancies are larger than would be anticipated from a consideration of the expected uncertainties in the primary variables. The results indicate a gradual decrease in the enthalpy change for solution of propane as the weight fraction of propane in the liquid phase increases. The change in enthalpy during solution is equal to the latent heat of vaporization when the composition corresponds to pure propane. A set of measurements of the latent heat of vaporization of this hydrocarbon at 100° F. was made and values are recorded in Table I. The results were in good agreement (0.2 per cent) with previously published data from the same laboratory (9).

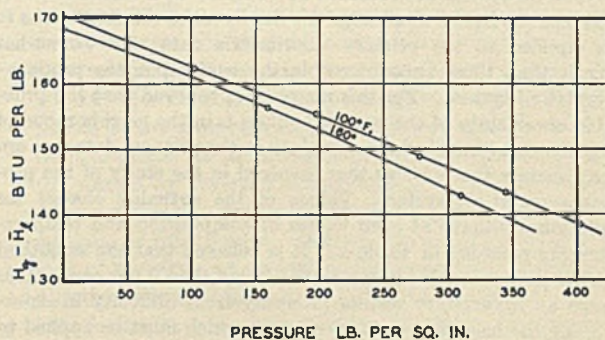


Figure 7. Enthalpy Change for Solution of Ethane as a Function of Pressure

Experimental measurements of the influence of temperature upon specific volume and pressure at bubble point of mixtures of propane and crystal oil were made by methods which have already been described (8). The results are recorded in Table II together with values of the enthalpy change for solution calculated in accordance with Equation 1. These values are included in Figure 4, and the agreement between the calorimetric and volumetric studies is within the maximum experimental uncertainty. The first derivatives of the volumetric data were employed in establishing the enthalpy change for solution, and this introduced a larger element of uncertainty than would result from the direct use of the primary data.

Smoothed values of the enthalpy change for solution of propane in the crystal oil employed in this investigation are recorded at even compositions for three temperatures in Table III. In order to show the deviations from ideal solutions encountered in systems of this type and the influence of the less volatile constituent upon the behavior, the enthalpy change for the solution of propane is shown as a function of pressure for several temperatures in Figure 5. Values are given from both the calorimetric and volumetric methods. For comparison the enthalpy change for vaporization of pure propane is included. These data indicate



satisfactory agreement between the calorimetric measurements and those derived from volumetric data for the materials used in the present investigation. There is a significant difference be-

be profitable to attempt to extend calorimetric measurements of this type to much higher pressures since the correction terms become much larger than the quantity of interest, and it becomes increasingly difficult to determine them with the necessary accuracy.

TABLE IV. EXPERIMENTAL RESULTS FOR THE ENTHALPY CHANGE FOR SOLUTION OF ETHANE<sup>a</sup>

Pressure, Lb./Sq. In. Abs.		Temperature, ° F.		Average Conditions		$H_g - \bar{H}_l$ , B. T. U./Lb. <sup>b</sup>
Initial	Final	Initial	Final	Temp., ° F.	Compn., wt. fraction	
331.9	230.4	160.811	160.719	160.77	0.0452	147.1
230.9	119.4	160.904	160.833	160.87	0.0278	155.1
367.2	299.8	100.860	100.849	100.86	0.0955	144.1
298.7	238.8	100.607	100.655	100.63	0.0720	149.6
239.5	162.3	100.744	100.704	100.72	0.0516	163.2
162.6	32.2	100.864	100.837	100.85	0.0243	162.7

<sup>a</sup> Method of measurement used, was withdrawal.

<sup>b</sup> Change in the partial enthalpy of ethane upon solution in crystal oil.

tween the enthalpy changes for the solution of propane in the water-white oil used in an earlier study (12). The earlier data were based upon volumetric measurements of much lower accuracy than those obtained in the present study. It appears, however, that the difference can be ascribed primarily to the difference in the compositions of the less volatile constituents in the two cases.

The calorimetric measurements obtained for the ethane-crystal oil system are recorded in Table IV as a function of the average conditions obtaining. In this instance the corrections to be applied to the primary calorimetric data were somewhat larger than those encountered in the work upon the propane-crystal oil system. For this reason it is believed that the probable uncertainty of the recorded values is in the neighborhood of 2 per cent, although the uncertainty in the primary data was approximately the same as that involved in the study of the propane-crystal oil system. Values of the enthalpy change for solution of ethane at even values of composition and temperature are recorded in Table V. It is believed that the smoothed values do not involve uncertainties larger than 3 per cent. This large an uncertainty results primarily from difficulty in determining the necessary correction terms which must be applied to the primary volumetric data in accordance with Equation 2. The variation in the enthalpy change for solution of ethane at 100° and 160° F. is presented in Figure 6, and the data show a rather rapid decrease in enthalpy change with an increase in the weight fraction of ethane in the liquid phase.

TABLE V. ENTHALPY CHANGE FOR SOLUTION OF ETHANE

Weight Fraction Ethane	$H_g - \bar{H}_l$ , B. T. U./Lb.	
	100° F.	160° F.
0	170.2	168.3
0.025	162.3	150.4
0.050	155.2	142.9
0.075	148.9	134.0
0.100	143.4	...
0.125	138.4	...

The enthalpy change for solution of ethane is shown in Figure 7 as a function of pressure for the temperatures investigated. No volumetric and phase equilibrium data were available for the particular less volatile components utilized in these calorimetric studies to permit a comparison to be made as was done in the case of the enthalpy change for solution of propane.

The pressure changes encountered in this experimental work were much higher than those obtaining in the study of the behavior of the propane-crystal oil system. It does not appear to

#### ACKNOWLEDGMENT

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#### NOMENCLATURE

- $b$  = specific gas constant, B. t. u. per lb./° R.
- $C_P$  = isobaric heat capacity, B. t. u. per lb./° R.
- $C_b$  = heat capacity of calorimeter bomb, B. t. u./° R.
- $E$  = internal energy, B. t. u./lb.
- $\bar{E}$  = partial internal energy of a component, B. t. u./lb.
- $H$  = enthalpy, B. t. u./lb.
- $\bar{H}$  = partial enthalpy of a component, B. t. u./lb.
- $K$  = coefficient
- $m$  = weight, lb.
- $P$  = pressure, lb./sq. in. abs.
- $Q_B$  = electrical energy added to calorimeter, B. t. u.
- $T$  = thermodynamic temperature, ° R. (° F. + 459.69)
- $t$  = time, sec.
- $V$  = specific volume, cu. ft./lb.
- $\bar{V}$  = partial volume of a component, cu. ft./lb.
- $X$  = weight fraction of a component in liquid phase
- $Y$  = weight fraction of a component in gas phase
- $f_A^B$  = line integral between states  $A$  and  $B$

#### Subscripts

- $a$  = average value
- $A$  = initial state
- $b$  = calorimeter bomb
- $B$  = final state
- $e$  = related to agitation process
- $f$  = related to addition process
- $g$  = gas phase
- $j$  = calorimeter jacket
- $l$  = liquid phase
- $1$  = more volatile component

Superscript ' = material being added to or withdrawn from system while at conditions prevailing outside system

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PAPER 40 in the series "Phase Equilibria in Hydrocarbon Systems". Previous articles appeared during 1934-40 (inclusive), 1942, and in July and August, 1943.



**Fertilizer Industry Headaches.** Why ammonium nitrate is now available to the fertilizer industry in sizable quantity was commented upon last month. Myth that the United States can become the food basket of the United Nations or of the world (as we move further into Axis-controlled areas) has been largely exploded. Yet our duty is plain to produce to the utmost of our ability, and this will require astronomical amounts of mixed fertilizer to obtain maximum results from our 400,000,000-odd acres of suitable crop land. There is little doubt but that fertilizer consumption for 1943-44 will be well above the all-time high consumption of more than 10,000,000 tons in 1942-43. Serious effort is being made to eliminate spring production peak, to distribute both production and distribution more evenly over the twelve-month period. The idea of doing away with sales of mixed fertilizer, and of having the farmer either do his own mixing or distribute the several ingredients separately, seems to be destined for complete discard. The average farmer has neither the time nor the equipment.

**Southwest Steel.** Industrialization of the Southwest, already proceeding at an amazing pace prior to Pearl Harbor, has accelerated still farther in the past eighteen months; in the van of this program have been the chemical, petroleum, and synthetic rubber industries. Yet that area has notably lacked a steel industry to complete a well-rounded industrial setup. Lone Star Steel, recently bringing some eighty coke ovens into production at Daingerfield, Texas, seems to be only part answer to date, for Washington has failed to give the green light for the establishment of a fully integrated steel center, estimated to cost 35 to 40 million dollars. Texas politicians in Washington limelight are reported putting on the heat. Ore deposits are located in Texas, and estimates run as high as 150,000,000 long tons or more, varying, of course, in quality.

**Corporate Earnings.** Watch for possible legislation designed to hold corporate earnings to a point where dividend payments will not exceed the interest rate on war bonds. It is a radical proposal and unlikely to get far, but there is an active element in Washington plugging hard for such a proposal. The alternate is said to be a drastic, Washington-dictated reduction in prices. To refute, the best argument is complete lack of money to initiate postwar plans for re-employment, but the more radical elements would welcome such a situation as definite proof that private industry is incapable of handling re-employment of 55,000,000, and that pump priming and government operation of many industries are the desirable and, indeed, the only answer.

**Trade Agreements.** The chemical industry is saying little now but is concerned about future policies on Reciprocal Trade Agreements in the postwar period. With wage scales the highest in the world, United States industry would be in a particularly vulnerable spot not only in export markets

*(Continued on page 128)*

but domestically as well. It is nonsense to plead greater efficiency in plant operations in this country over international competitors. If it exists at all, the difference is so slight as to be practically negligible in its over-all effect on production costs.

**Investors Are Active.** Wall Street is singing the praises of chemical industry loud and long. Of all groups with a postwar future the chemical industry and its ramifications are in the number one spot. Markets are most certain for chemicals, and although automotive and the airplane companies may stage a battle royal for the public's transportation dollars, fuels, paints, plywood, insulation, and plastics used in both will be products of the chemical industry. Whether present airplane plants turn out planes or houses or television sets, many of the materials used will be chemical in nature and certainly in manufacture. Investors' haven seems to be the chemical field.

**Freon at War.** Constant reminders to minimize operation of air conditioning apparatus irked many last summer. The reason for these warnings, that Freon, a preferred refrigerant for air conditioning, had gone to war, got new emphasis in the announcement of a 55 per cent increase to be built in plants for its production. Now Freon not only cools (or warms by reversed refrigeration cycle) submarines, but it carries death to insects in "health bombs" producing deadly aerosols of insecticides. Reason for using Freon is its own lack of toxicity and its high vapor pressure and solvency for pyrethrum-sesame insecticide. Figures on output are withheld for military reasons, but war on mosquitoes, gnats, and flies in remote camps is a sufficient reason for going light on air conditioning at home.

**Nylon Undies.** Release by the Army of nylon fabric rejected for parachutes gives the ladies hope of nylon underwear, but not stockings. That, perhaps, is less important than the fact implicit in this announcement that production of this valuable synthetic has reached a point of meeting demand. Only a short time ago nylon stockings which had served their original purpose went back to the plant to be reprocessed for their resin content. Clearly, much progress in production intervened to allow rejected fabric to be used for nonmilitary purposes.

**Domesticating Microbes.** Selmen A. Waksman, of the New Jersey Agricultural Experiment Station, coined a neat phrase when he recently described penicillin therapy as the "domestication of microorganisms", analogous to the domestication of animals and plants by primitive men. The further interesting, and probably important, fact was pointed out by Waksman that the production of an antibacterial substance by one fungus is ample reason to examine other members of this numerous class of microbes to learn whether they, too, may not yield useful products.





**T**HROUGH long custom this spying has been directed at emphasizing material to appear in our forthcoming INDUSTRIAL EDITION. Now, we believe, is a good time to break that rule and call attention to an especially important and timely paper in our November ANALYTICAL EDITION. Infrared spectroscopy has proved itself a potent tool for solving an increasing number of the vexing problems growing out of the swift advances of hydrocarbon chemistry. With pride the Editor urges us not to miss the comprehensive treatment of infrared spectroscopy and its applications in industry which will appear about November 15.

But to get back to December's offering!

Although automatic control has become the rule in most chemical processes, its full value can be realized only by the most careful design of process and integration of instruments with it. Thus the problem can seldom be solved by the mere installation of an automatic instrument simply to do what a human hand did before. There is much more to the matter than that, as we shall learn in December. Indeed, the whole subject will, we believe, take on new aspects from reading this able discussion of its many ramifications.

Emphasis placed by war on problems of hydrocarbon chemistry and engineering lend special significance to new data on absorption of low-boiling hydrocarbons in oils. This process is closely bound up with many current and prospective developments in this field but particularly with aviation gasoline production. Closely related is a new correlation of adsorption data required in the design of many diverse processes: air conditioning, solvent recovery, and others.

Borated resins have surprising properties which suggest a number of special applications for them in the widening field of plastic technology. An article about them will stimulate our thinking in new channels.

A new organic fungicide, 2,3-dichloro-1,4-naphthoquinone, has been shown to have remarkable effectiveness both in agricultural and in textile applications. At the same time it is safe to use on plants and seeds and possesses resistance to weathering. Obviously interesting is this new weapon against a superexpensive family of pests.

Chlorophosphates for fertilizer purposes are described as highly effective and of these we shall learn more.

The long familiar battle over soap builders continues. This time we shall be told of changes in pH of alkaline solutions with temperature.

Solubility of water in liquid carbon dioxide has become important with the increasing use of this compound in fire extinguishers. New data will be provided on this subject.

And, as always, there will be much more.

YOUR HUMBLE SPY







