Industrial and Engineering Chemistry

Volume 36 • Number 5

MAY, 1944

REPRINT EDITION
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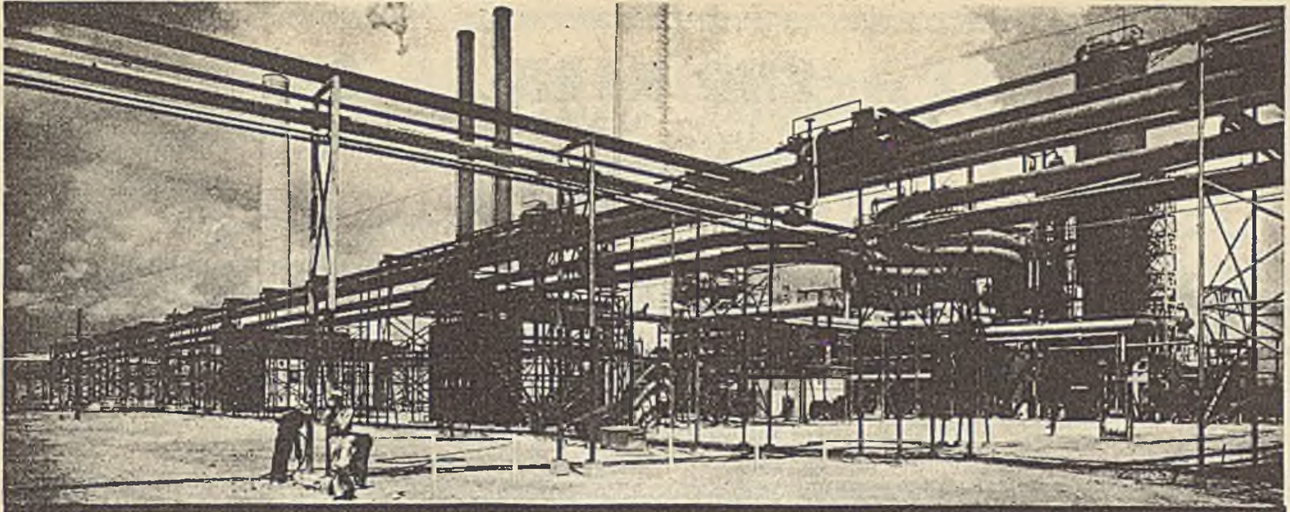


The photograph above shows a view in the plant of The Magnolia Petroleum Company, at Beaumont, Texas. The first commercial-scale Thermofor catalytic cracking unit was constructed there.

INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

EDITOR: WALTER J. MURPHY

Associate Editor: F. J. VAN ANTWERPEN

Assistant to Editor: N. A. PARKINSON

Manuscript Editor: HELEN K. NEWTON

Make-up Editor: BERTHA REYNOLDS

Manuscript Assistant: STELLA ANDERSON

30,000 copies of this issue printed

ISSUED MAY 6, 1944 ● VOL. 36, NO. 5 ● CONSECUTIVE NO. 9

THE POSTWAR CHEMICAL OUTLOOK:

UNIT PROCESSES:

Published by the American Chemical Society at Easton, Pa. Editorial Office: 1155 16th Street, N. W., Washington 6, D. C., telephone, Republic 5301, cable, Jiechem (Washington). Business Office: American Chemical Society, 1155 16th Street, N. W., Washington 6, D. C. Advertising Office: 332 West 42nd Street, New York 18, N. Y., telephone, Bryant 9-4430.

Entered as second-class matter at the Post Office at Easton, Pa., under the Act of March 3, 1879, as 24 times a year — Industrial Edition monthly on the 1st, Analytical Edition monthly on the 15th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

Remittances and orders for subscriptions and for single copies, notices of changes of address and new professional connections, and claims for missing numbers should be sent to the American Chemical Society, 1155 16th Street, N. W., Washington 6, D. C. Changes of address for the Industrial Edition must be received on or before the 18th of the preceding month and for the Analytical Edition not later than the 30th of the preceding month. Claims for missing numbers will not be allowed (1) if received more than 60 days from date of issue (owing to the hazards of wartime delivery, no claims can be honored from subscribers outside of North America), (2) if loss was due to failure of notice of change of address to be received before the dates specified in the preceding sentence, or (3) if the reason for claim is "missing from files".

Annual subscription — Industrial Edition and Analytical Edition sold only as a unit, members $3.00. nonmembers $4.00. Postage to countries not in the Pan-American Union $2.25; Canadian postage $0.75. Single copies — current issues, Industrial Edition $0.75, Analytical Edition $0.50; back numbers, Industrial Edition $0.80. Analytical Edition prices on request; special rates to members.

The American Chemical Society also publishes *Chemical and Engineering News*, *Chemical Abstracts*, and *Journal of the American Chemical Society*. Rates on request.

INDUSTRIAL AND ENGINEERING CHEMISTRY

REPORTS ON THE CHEMICAL WORLD TODAY

Technology

The Why of Rust Resistance. Herbert H. Uhlig, a metallurgist of General Electric, recently presented a novel explanation of why certain metals do not "rust". Speaking before the Electrochemical Society, he reported that vacant electron spaces in the atoms of nickel are responsible for its resistance to corrosion. In earlier researches he found that the stainlessness of stainless steel is not due primarily to the formation on the surface of a film of oxide, as formerly supposed. Instead it results from electronic arrangement in the atoms of the alloy. He finds the same to be true for two other widely used corrosion-resistant alloys—copper-nickel (Monel) and molybdenum-nickel-iron (Hastelloy).

Readers will find two innovations introduced in this issue: (1) the "Month's Headlines", events during the past month of interest to chemists, chemical engineers, and executives, as reviewed by the Editors, page 483; and (2) "Last-Minute Flashes from the Editor's Desk", on page 126 of the advertising section.

An atom may be thought of as a nucleus around which revolve, somewhat in the manner of planets around the sun, from 1 to 92 electrons. They move in one to seven different orbits or shells. Ordinarily one shell is filled with electrons before the next one begins, although in the case of certain "transition" elements there are vacancies in the shell next to the outer one. In nickel, for example, there are only 8 electrons in the third shell instead of the 10 it could hold, despite the fact that there are 2 electrons in the fourth and outermost shell. With inner shells completely filled, a metal is more subject to corrosion.

Because of the vacancies nickel is very resistant to corrosion, but it is too expensive for many applications and so is alloyed with copper which is lower in cost. The atom of copper has one more electron than that of nickel. In the alloy these extra electrons tend to fill the vacancies in the nickel atom. However, as long as any vacancies remain in the nickel, the alloy still resists corrosion as well as pure nickel. Finally, when the proportion of 60% copper–40% nickel is reached, all the nickel vacancies have been filled. Further increasing the proportion of copper makes the alloy less resistant until pure copper is reached, which corrodes much more than pure nickel. In the alloy of nickel with molybdenum and iron a similar effect occurs, says Uhlig.

Vast quantities of valuable metals are lost annually by corrosion. Such studies as these are highly important because knowledge of the exact way in which corrosion occurs may lead to more effective ways of overcoming it.

A True "Flash of Genius". It is no secret that heartbreaking days and even months were spent by the technical staff of Kaiser's Permanente magnesium plant in attempting to obtain the metal in the pure state and still prevent explosions and fires. One day it occurred to a chemist that, if the mixture was so difficult to control, it would probably be the ideal material for bombs. Chemical Warfare Service took up the idea, and the M76 or PT bomb, more familiarly known as the goop, is one of the later developments. It is a 500-pound bomb, containing the mixture of jellied oil, finely powdered magnesium produced in the Permanente process, and other ingredients. This bomb, which is the most recent type of incendiary to fall on German installations, is difficult to extinguish.

Three wholly unrelated but equally illuminating queries can be posed on this development: (1) Would Thurman Arnold, Wendell Berge *et al.*, consider the idea patentable? (2) Would the chemist serve the war effort better by driving a jeep? (3) Was not this chemist's "flash of genius" a rather novel way of solving a production headache? For the time being, Hitler has more cause to worry about why Permanente experienced difficulties in distilling off pure magnesium, than does Kaiser's technical staff, for quantities of goop bombs have been sold.

An interesting yarn came out in connection with the goop bomb publicity. The principle, a solidified or jellied oil ignited by a metal mixture, was perfected in World War I by Arthur Ray, then working in CWS. The chemical group kept it "hush-hush" until a Representative put it into *Congressional Record*. We looked it up, and on page 1023 of the *Record* for 1918 is the story of the bomb, called in those days "Mark II". The metal used was thermite and the contraption was set off by discharge of a service cartridge.

20th Century Alchemy. Methylolurea transmutes ordinary wood into a whole new range of usefulness, now available for war purposes and offering many postwar applications, according to a recent Du Pont announcement. It permits construction, for example, of doors, windows, and drawers that will not swell, stick,

(Continued on page 8)

An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries contract, or become loose. It reconstitutes wood to order, even makes it strong enough to substitute for steel in certain machinery parts. It enables industry to create in a few days woods harder than the ebony that takes a century to grow naturally. Poplar becomes harder than hard maple which, in turn, can be made harder than ebony. Transmutation of wood enables more available, cheaper species of woods to compete in fields hitherto open only to costlier, scarcer varieties from afar. Du Pont chemists developed this treatment from research that has paralleled studies conducted for years by Forest Products Laboratory.

Color also may be imparted permanently to the wood by mixing a dye with the impregnating chemical. Veneers sufficiently treated become self-bonding. They require no adhesive to be formed into plywoods, since heat and pressure fuse the product into a hard, dense substance. Even sawdust, shavings, and other wood wastes may be molded into articles, and dyes or pigments may be incorporated. Other cellulosic materials lend themselves to the treatment.

New Synthetic Rubber. Hope that the problem of heat build-up in tires made of synthetic products may be solved was indicated in the recent announcement by Mathieson Alkali Works of a new rubber that withstands elevated temperatures. Chief component is butadiene; but the copolymer is under secrecy orders, for the Germans apparently are still worrying about heat build-up in their tires, and revelation of the composition would be of definite comfort to the enemy. Details are scanty but officials of the company say that the copolymer can easily be made from available raw materials. The amount of copolymer added is about the same percentage as styrene in GR-S.

Tests reported by independent laboratories show that the new rubber has greater resistance to heat, moisture, oil, kerosene, and less permeability to gases than GR-S. Present capacity of the plant to produce the new polymer is reported to be about 25 tons per day by misinformed newspapers. Mathieson is now producing in small pilot-plant lots and hopes to get government approval for a plant to turn out 25 tons per day. Mathieson is now in two new fields—synthetic rubber and fertilizer.

Cotton Strip-Tease. Allocation of war-employed chemicals has postponed many ideas to our brave new world of tomorrow, but few plans we have listened to come closer to Utopia than the new scheme for causing King Cotton to lose its foliage at the will of the chemist. Fruition is postponed by chemical scarcities until war's end.

In action, the planter will decide that cotton is ready for picking. He will call the local airport, and a gently hovering helicopter will appear over the field to spread Aerodefoliant (manufactured by American Cyanamid) at the rate of 30–100 pounds per acre. In a few days the leaves will fall from the plant and expose the ripe bolls. Another advantage is gained through defoliation, because cotton bolls heretofore shaded by leaves are permitted to lose undesirable moisture. Then will come the mechanical picker, and, with clanging of gears and no sweat, the crop is picked.

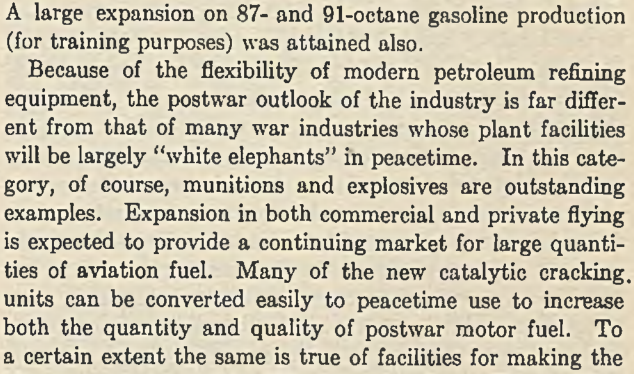
(*Continued on page 10*)

Future of 100-Octane Plants. Eighty-two per cent of the ultimate capacity of 100-octane plants in the United States will be privately owned. Probably no other major war industry has so small a proportion of government participation in plant construction. In terms of investment, private companies will have obligated approximately 550 million dollars of their own money in the expansion of 100-octane facilities between Pearl Harbor and the end of 1944. Government investment in the same period will come to approximately 210 million.

Three fourths of the government outlay, which came from Defense Plant Corporation, was for equipment for small refineries. Petroleum Administration for War has proceeded from the outset on the principle of apportioning responsibility for war production as far as possible among both large and small refiners. In all, 161 different companies are engaged in the present 100-octane program.

While production figures on 100-octane remain secret, it can be said that in the first two years after Pearl Harbor the output was multiplied several times; indeed, production is nearly nine times as great as it was in the pre-Pearl Harbor period and shortly will be twelve times as great. Sixty-five per cent of this increase came from such measures as converting prewar catalytic cracking equipment, employing new types of blending agents, increasing tetraethyllead content, and technological improvements which made for greater efficiency in the refineries. This was achieved without government financing. A large expansion on 87- and 91-octane gasoline production (for training purposes) was attained also.

Because of the flexibility of modern petroleum refining equipment, the postwar outlook of the industry is far different from that of many war industries whose plant facilities will be largely "white elephants" in peacetime. In this category, of course, munitions and explosives are outstanding examples. Expansion in both commercial and private flying is expected to provide a continuing market for large quantities of aviation fuel. Many of the new catalytic cracking units can be converted easily to peacetime use to increase both the quantity and quality of postwar motor fuel. To a certain extent the same is true of facilities for making the blending agents used in 100-octane gasoline. The problem will give a number of headaches, but the petroleum industry appears to have been on sound ground when it determined to finance a large part of the 100-octane production facilities.



Sources of Increased Production of 100-Octane Aviation Fuel (Jan. 1, 1942, to Dec. 31, 1943) According to PAW

(*Continued on page 14*)

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

War and Postwar

Swords into Plowshares. The U. S. Department of Agriculture is said to be making a determined bid to obtain permission to reconvert the ferrosilicon plant at Wenatchee, Wash., into production of triple superphosphate. Present operations are expected to end shortly as a result of the cutback in magnesium. Advocates of the plan insist that the huge electric furnaces are specially adapted for treatment of phosphate rock. They further present as arguments that the plant is located near phosphate rock deposits, and that West Coast farmers have been short of triple phosphate. One plan being discussed is to move the plant closer to raw material supplies (Idaho and Montana), but the question is, will enough power be available? In some quarters this bid of the Department of Agriculture is viewed as the forerunner of a major policy of seeking idle government-owned plants for production of agricultural products.

War Production Board is said to be against converting the Wenatchee plant during the war period; although sufficient ferrosilicon can now be turned out at eastern blast furnaces, the coal situation is so precarious that it is desirable to maintain the Wenatchee plant at least in standby condition. Those opposing the Department of Agriculture's plan point out that the furnaces at Wenatchee are not specially adaptable to volatilizing phosphorus, and that the principal value of the plant for such a purpose would be restricted largely to the electrical equipment up to, and including, the bus bars.

Veteran Employment. With discharges from the armed forces totaling some 100,000 a month, employment of veterans is an immediate problem—not one merely with postwar significance. Recognizing the moral and legal obligations of private industry, as well as other desirable economic angles tied to full employment for returning veterans, the National Association of Manufacturers' Committee on Veteran Employment, headed by Harry L. Derby, president of American Cyanamid & Chemical Corporation, has prepared a practical check list for management. It is intended solely for in-plant use by individual companies and, by the nature of the points it highlights, will serve to provoke the fullest consideration of ways and means by which industry may maximize veteran employment. Questions apply equally to ex-service men and women.

Marketing Surpluses. Easily understandable is the necessity for creating huge reserves while a global war is being fought. A nation which for months saw its armed forces go down to ignominious defeats solely because of "too little and too late" should in no way criticize the all-out production program requested by military officials. Few individuals had any comprehension of what America could turn out under the pressure of a war for survival. Now the specter of surplus stocks is beginning to plague industry.

Manufacturers of drugs and pharmaceuticals have only unhappy memories of what happened after World War I. There are differences of opinion as to how serious surpluses are at this point. National Wholesale Druggists Association has suggested a program based on

(*Continued on page 22*)

three principles: (1) Where feasible, surpluses should be turned over to Lend-Lease and to relief and rehabilitation agencies for distribution among populations in liberated areas; (2) supplies not so distributed should be offered to manufacturers of the products for marketing through regular distribution channels; (3) the Federal Food and Drug Administration should inspect all repackaged materials sold from surplus government stocks to protect the public health.

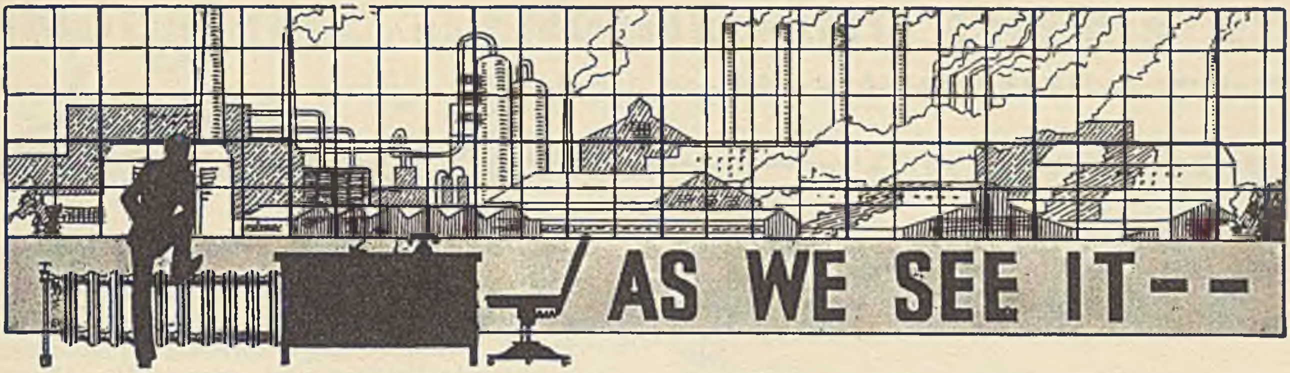
Several legislative proposals have been made to set up a federal administrator with the authority to determine how and when war-developed properties and surpluses should be sold. Attorney General Biddle stepped into this ring when he appeared last month before the Senate Military Affairs Committee. These proposals may lead to dangerous results, according to Biddle. He pointed out that some pending bills would have Congress stipulate that war properties may be sold only where such sales would not "unduly dislocate" markets or inflict "substantial injury" on industry. "The purpose of these declarations of policy," he testified, "is to prevent indiscriminate dumping of surplus war property on the market. That is doubtless a desirable objective. But the language I have quoted may lead to dangerous results."

The Attorney General made a countersuggestion that the administrator be instructed simply to dispose of property on the basis of a "fair return" to the Government. This "fair return" would be based not alone on original cost but on the value of property in the prevailing market, on the basis of its general usefulness.

At the moment, at least, there is little unanimity of thinking in Washington on the subject of ways and means of disposing of war plants and surpluses. Yet, unless such properties and materials are dealt with in a forthright manner, fair to Government, the public, and manufacturers, the present deluge of postwar planning is just so much talk and little else. The problem is fast being recognized as Washington's number one headache.

Ride for Life. This is in the "now it can be told" department. When A. L. Elder was appointed penicillin coordinator, an immediate task was to inspect, correlate, and report on the activities in the various establishments producing the drug. The Army, anxious to obtain action, asked Elder how long it would take him to complete the investigational trips to the producers. Apparently the estimate was too long, and Elder was asked what the Army could do to expedite matters. Upshot of the conference was a private plane for Elder, manned by the Army, which enabled the chief of the penicillin program to inspect, in various parts of the continent, sixteen plants in fourteen days. The time saved by this prompt action was invaluable in rushing output. No one who heard Robert D. Coghill at the A.C.S. meeting at Cleveland (*Chem. & Eng. News*, April 25, page 588) on the blessings conferred by this drug will doubt that any price in gasoline or planes can be too great in speeding this drug to mankind.

For our "department of inconsistencies", sadly are we forced to report that many of the important young scientists engaged in the penicillin program are now being drafted.



This Month

When this war reaches its agonized end, the rebuilding of a new world in which men can live and work will become the stupendous immediate task. That needs much planning in advance, and the profession and industry of chemistry must be prepared to perform important functions in accomplishing the necessary readjustments. Thus special interest and importance attaches to a broad view of prospects set before us in this issue in seven forward-looking papers by as many able thinkers in their several fields. Bass (page 387) introduces the subject and the series. Stevens (page 388) capably surveys trends in research against a background of long and intimate experience in this field. Rogers (page 391) with equal care goes into the probable effects of technical education on future events in our world. Badger (page 397) suggests the solution of some of the relatively elementary problems of engineering necessary to get us away from the present empirical phase and into a more logical and fundamentally sound engineering tomorrow. Financial and accounting phases of the future of chemical operations are discussed by Sheehan (page 401) to supply an obvious gap in customary chemical thinking. Glenn (page 394) integrates the problems of foreign markets and their postwar needs with American chemical industry and presents significant facts on this prospect. Problems of management are discussed by Flanders (page 400) to round out the picture.

Unit processes, the fundamental chemistry of manufacture, are carried farther in a symposium presented in this issue. The development of this phase of chemistry and chemical production has been particularly fostered by R. Norris Shreve (page 411), who introduces the eighth symposium on the subject, held under his chairmanship. Particular emphasis is placed on inorganic unit processes, typified by base reactions as applied to the recovery of potassium salts in usable form wyomingite. The three phases covered are base exchange between wyomingite and sodium carbonate by Green and McCarthy (page 412), separation of chloride and sulfate from the resulting alkaline brines by Ervin and McCarthy (page 415), and removal of dissolved silica from the alkaline brines by Meyer and McCarthy (page 420). These processes, simple in the laboratory, become important when their economy is emphasized by large-scale operation. Fused salts provide convenient media for chemical reactions under some conditions encountered in industry, according to Johnstone and Winsche (page 435), who describe this technique as applied to several high-temperature reactions in fused baths of sodium chloride–ferric chloride. Organic processes are represented by production of aminoguanidine by Shreve and Carter (page 423), its elaboration to dyes by Shreve, Carter, and Willis (page 426), and a continuous partial-pressure process for nitration of toluene by Othmer and Kleinhans (page 447).

Radio power offers advantages in many chemical process applications and is sufficiently new to need fuller explanation at this time. Robertson (page 440) describes characteristics of the several systems for applying heat directly to the reaction zone by high-frequency electrical circuits. He views this technique as one of growing importance in the field.

Ammonium ferrous phosphate is suggested by Erskine, Grimm, and Horning (page 456) as a new pigment for metal protective paints. Test results of the use of the new pigment in primer coats as compared with other familiar pigments are given.

Lactic acid offers advantages as a raw material in a number of syntheses; and since the acid itself can be readily produced by fermentation, these become of timely interest. Methyl acetoxypropionate is derived from lactic acid and methyl acetate by Rehberg, Faucette, and Fisher (page 469) and from methanol and lactic and acetic acids by Filachione and Fisher (page 472). The importance of the ester lies in its easy conversion to methyl acrylate, valuable in synthetic elastomers and resins.

DHKilleffer

Next Month

Agitation and mixing are to be featured for the month of roses when we print most of the 10th Annual Chemical Engineering Symposium, held this past Christmas at the University of Pennsylvania by the A.C.S. Division of Industrial and Engineering Chemistry. There will be a review of the state of the mixing art by Hixson of Columbia University. He has been investigating the phenomena of agitation and mixing for many years and sums up progress to this eleventh hour. This particular phase of chemical engineering art was thought by many to be a sadly neglected subject. The Philadelphia meeting, however, brought out that many first class investigations were underway, and the future seems to hold great promise that much of the unknown in mixing will be soon unmixed. For those contemplating setting up a research program in mixing, there will be an important message on the basic problems involved. Rushton and co-workers gave a mass velocity theory which was well received by the engineers, and we suggest that the engineering fraternity will soon be well acquainted with what he proposes.

Of interest to those in the drug and pharmaceutical industries will be the paper from the Eastern Regional Research Laboratory on the catalytic oxidation of nicotine, picoline, and quinoline to nicotinic acid; the latter material is one of the required additives to enriched flour. Not many years ago this vitamin, the antipellagra factor, was a laboratory curiosity, the total production amounting to only grams. Today the manufacturers will make about 300 tons during the course of the year. Not much when considered on the usual scale of chemical production, but only a few milligrams are needed to fortify a loaf of bread.

This column has lost its originator, D. H. Killeffer, who started this page back in 1932. He has now entered the advertising business, recently becoming associated with Hazard Advertising Company. The mantle of interpreter descends upon the shoulders of the Associate Editor, and I know it will be years before I fill all the folds of my inheritance which now fits me so swimmingly. If Goldsmith will pardon:

And still I gaze, and still my wonder grows
How one small body filled out all these clothes.

INDUSTRIAL AND ENGINEERING CHEMISTRY
PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY

Editorials

WALTER J. MURPHY, EDITOR

Deferment Confusion Compounded

OUR military officials and those directing or currently misdirecting Selective Service policies respectfully are referred to page 148 of H. L. Mencken's "A New Dictionary of Quotations" where they will discover in "Outlandish Proverbs" by George Herbert (1640) the following: "For the want of a nail . . . the kingdom is lost."

Deferments for chemists, chemical engineers, physicists, other scientists, and skilled chemical operators in the 22 to 26-year-old age bracket engaged in essential research and production would mean in terms of military effectiveness less than one division of infantry. Is our high command ready to trade inevitable decline in production of vital matériel and the dissipation of America's irreplaceable development organizations for a paltry few thousand foot soldiers? If it is, it not only is gambling unnecessarily with the successful prosecution of the war, but is bartering away our birthright for a mess of pottage.

England in World War I permitted patriotic, but nevertheless misguided, youthful scientists to die on the fields of Flanders and has never ceased to regret such folly. She is not making the same fatal mistake in World War II, but we are!

The most recent Selective Service expediency—"Critical List of Activities for Occupational Deferment of Men under 26", issued by the War Manpower Commission Inter-Agency Committee on Occupational Deferments—is so restricted as to be nearly useless in holding adequate numbers of chemists, chemical engineers, and other essential chemical manpower in the Production Army. True, it does provide for the necessary needs of the Office of the Rubber Director, the Petroleum Administration for War, and a few other selected favored activities. But it fails to recognize that back of such a highly selected group of end-point occupations must come full support from numerous process industries.

It ignores the irrefutable logic of maintaining a "reserve" of educated young scientists and engineers with specialized training in new technical fields, imbued with a young point of view and physical stamina, able to cope instantly with new technological problems that may confront us at any moment. Our leaders may choose to ignore such logic, but our enemies and allies alike are holding their technical reserves in readiness for any emergency.

One cannot turn research on and off like the spigot of a barrel. We cannot train technologists as we do welders in 60 or 90 days; indeed, we cannot turn them out fully trained in less than four to seven years.

No other reasoning can be read into the latest decrees of so-called "Selective" Service but that the high command is ready to accept the doctrine that we can win this holocaust without any new contributions from science. In so far as America is concerned our scientific knowledge largely has been "frozen" as of April 11, 1944!

We have served notice that the United States, the "arsenal of democracy" whose production has turned the tide of battle, has deliberately and knowingly stripped its laboratories of its young and mentally virile scientists in order to add a division or so of infantry to the invasion forces.

The most recent directives of Selective Service not only will cripple output and seriously impede research, but will curtail most effectively the training of future technologists badly needed in industry should the war continue for another year or two, and most certainly will destroy the life blood of the postwar period.

The Selective Service has cancelled all deferments for students in chemistry, chemical engineering, physics, etc., effective July 1. In strange contrast is its action of deferring students enrolled in schools of medicine. We presume the same privileges are being extended to future dentists, osteopaths, theologians, and veterinarians.

All such medical students who normally would have registered on October 1, 1944, will be permitted to remain until they graduate, even though three or four years are necessary to complete such courses. To add still further mystery to this compounded confusion, we are reliably informed that General Hershey has given his approval to the deferment of future doctors, provided the medical schools arrange for matriculation of students on or before June 30, 1944, to meet the letter of the law!

God help us if our enemies suddenly surprise us with some new and terrible weapon.

A Distorted Picture

CHEMICAL production as measured by the Federal Reserve Board Index is declining. The unadjusted index, recently revised, stood at 356, compared with 360 in January, and 362 in February 1943. Peak production was reached in August and October when the index registered 400. Taken alone, this gives a very distorted picture of what is happening along the chemical production front. Not properly analyzed, it gives the impression that we are over the peak in chemical production. It may be used as a forceful argument against further deferment of technologists. The picture is not only a distorted one, but a dangerous half truth in the hands of the uninformed.

The Government, it is true, is slashing production at ordnance and munition plants, and a few cutbacks in other products have been placed in effect in the past few months. However, "total" chemical production figures have been swollen tremendously for the past two years or more by explosives, their various ingredients, etc. Actually the "industrial" chemicals production index is still rising and is far above the point reached two years ago. In February it reached a peak of 399, as against 322 in the same period a year ago. This, then, is the true barometer to watch. Misinformed individuals have pointed out that the manpower situation is not critical in chemical plants, for the reasons that comparatively small working forces are employed, are highly efficient, and greatly assisted by liberal use of automatic control devices. It is true the chemical industry is not a large employer of help, when comparison is made with some other industries—for example, textiles—but those employed in chemical plants are among the most highly skilled in the world. Furthermore, skilled help is necessary in any setup where automatic controls are widely used. If only a small fraction of the total of such help is taken in the draft, production will decline drastically. Few realize that cutbacks in munitions and explosives do not release large numbers of chemists and chemical engineers, for the simple reason that relatively few graduate chemists and chemical engineers were required except at the start of such operations.

Every indication points to the likelihood that the over-all need for chemists, chemical engineers, and skilled operators will grow rather than diminish. Not only is "industrial" chemical production likely to increase, but here and there sudden heavy demands will occur for certain old and new products. Unless an adequate staff is maintained, these demands will not be met, nor will it be possible to staff new projects. There is little doubt that many such new programs will develop in a technological war. Chemists and chemical engineers are not completely interchangeable parts in the chemical production scheme. A rubber chemist with 15 years' experience cannot be converted overnight to a food chemist, and vice versa. The need of holding chemists and chemical engineers in the Production Army was never greater than it is right now. Tomorrow that need will be even more pronounced than it is today!

Scientific Curbs on the Reich

LORD CHERWELL, British Paymaster General and close friend of Winston Churchill, told the House of Lords on April 18 that science will be called upon to render Germany impotent to wage another war of aggression and that His Majesty's Government had decided to invite a large number of scientists to consider ways and means of achieving this end.

This action raises two interesting points: (1) Will United States scientists have a voice in any such setup? (2) What means will scientists employ to control Germany?

I. & E. C. Editors commented at length on this question in the January issue (see I. & E. C. Reports, January, page 5) and offered a specific amendment to the Sherman Antitrust Law of 1890 which would make it lawful for this country's technologists to participate in such international action. We cannot hope to do anything of a constructive nature, unless, and until, this or a similar amendment is passed. The time for action by Congress is now!

Control of science in Germany will entail utmost watchfulness. Unless Germany and, indeed, most of Europe is to be purposely permitted to revert to the dark ages, chemists, chemical engineers, scientists of all kinds, must be allowed to function. Water, sanitation, medicine, electricity, fuel, clothing, transportation are just a few of the many services and materials which require technical direction. Only well-informed technologists will distinguish between acts strictly economic in their intent and those that are primarily directed toward rearmament. Indeed, such men will have one of the most ticklish assignments ever devised. They must not only be highly skilled in a scientific sense, but strong in character, and must have the support of the political leaders of the United Nations. Let us not forget that hundreds of the most prominent technologists here and in England sounded warnings in the early thirties, but to no avail.

Re-employment of Veterans

THE Selective Service Act requires that employers provide jobs for former employees following discharge from military service. Returning veterans must be given positions of like seniority, status, and pay to those they held prior to enlistment or induction into the Armed Services. There is, however, a proviso that an employee must apply for reinstatement within 40 days following his or her discharge from military service.

Few service men and women are aware, however, that they must act within a 40-day period, and no machinery has been set up by Selective Service to advise employers of military discharges of former employees.

A great many employers are learning of such releases by mere chance. Meanwhile, employers have maintained on their records definite commitments to these men and women and have gaged employment plans and procedures with such commitments in mind. Uncertainties of this nature are unfair to former employees, present employees, and to employers, and play havoc with postwar planning.

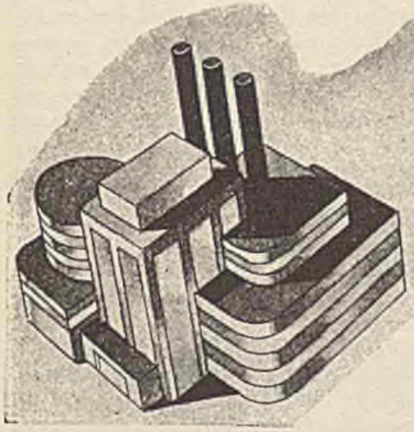
A uniform procedure should be established without further delay so that employers will be automatically informed of military discharges of former employees, thus permitting full compliance with terms of the Selective Service Act without jeopardizing the interests of other employees and employers.

The present statute on re-employment of veterans is badly in need of clarification. No official rules or regulations have been promulgated to guide employers. O. C. Cool, director of the Labor Relations Institute, succinctly summarized the dangers attending the present state of uncertainty when he told the Steel Founders Society:

"There is more dynamite in the returning veteran problem than in any other which has confronted business since the war began. It is filled with heartbreak for all concerned. It is a 'hot potato' that even Selective Service apparently deems too hot to handle."

The postwar chemical outlook

Papers on pages 387 to 403 were presented before the Division of Industrial and Engineering Chemistry at the 107th meeting of the American Chemical Society which was held in Cleveland, Ohio. Lawrence W. Bass, director of the New England Industrial Research Foundation, Boston, Mass., introduced the symposium with the remarks which follow.



AN EYE to the future is second nature to both the chemical profession and the chemical industry. Their parallel development during the past two centuries is based on the concept that it is always possible to do things better, and that advances in science and its applications should not be left to chance but should be systematically encouraged. In brief, then, forward planning—today usually called "postwar planning"—is nothing new to us; now we are merely placing greater emphasis on a basic philosophy to which we all subscribe.

The chemical industry in its many branches is and will continue to be at the heart of the war effort. The munitions program, the gigantic synthetic rubber industry, the expansion of aviation gasoline production, and the development of a host of wartime substitutes for other essentials leave no doubt that chemicals are the lifeblood of our approaching victory over the Axis. These contributions are absorbing all our attention, technical manpower, and facilities.

The Nation, however, is convinced that industry must take serious account of the problems to be faced when the war is won. Victory will be hollow if management has not made preparations to the best of its ability for the readjustment of our economy to a peacetime basis.

The manufacture of chemicals will play a vital part during the transition and postwar periods. Our improved products will be the focus of new developments in other industries. During the transition we will have to provide alternate materials to keep national production machinery turning. Our technical advice will be an indispensable help to small business. And, in the longer range future, we must spearhead the imagination which leads to better satisfaction of the consumer and hence to more jobs throughout the nation.

We are experiencing a critical shortage of chemists and chemical engineers in war production, and the situation is growing worse. It is therefore particularly fitting that we should, through such discussions as this symposium, search for the best paths toward a rapid reconversion of this key industry when scientific and engineering manpower is available.

Because chemical manufacturing hinges on research, the nub of factual advance planning, we can well start our look into the future in the laboratory. All agree there will be more and better research. Our experience in wartime emergencies should enable us to make a keener selection of problems, a more discriminating attack, and a more aggressive program of commercialization.

There will be an increased demand for chemists and chemical engineers, even after demobilization. These jobs will be found not only in the process industries but throughout the manufacturing world. The war has shown clearly the importance of the technical man in all fields of business and the lesson will not be forgotten. We should therefore examine the educational developments which will make our profession still more useful in the world of the future. The implementation of new chemical discoveries to commercial scale will make increased demands on the talents of our chemical engineers. What have we learned from the war that will help in the transition and postwar periods? Chemical manufacturing involves large investment in equipment and heavy depreciation. What are the financial problems we will face in reconversion? We must remember that postwar readjustments are a world problem. What are the opportunities for the chemical industry in international trade? We must be leaders.

Finally, the war has drawn management and technical men even closer together. The more intimate this cooperation, the more we can expect in the way of a concerted, aggressive effort toward a better tomorrow.

Lawrence W. Bass

SOME TRENDS in RESEARCH

RAYMOND STEVENS

ARTHUR D. LITTLE, INC., CAMBRIDGE, MASS.

AN INDUSTRIALIST once asked Arthur D. Little to name a text on creative thinking, for he wished to convert his engineers to research workers. Doctor Little smiled and then suggested "The Road to Xanadu". It appears on investigation that "The Road to Xanadu", of John Livingston Lowes, discusses the source material from which Coleridge synthesized the "Rhyme of the Ancient Mariner". To a degree it displays the working of the poet's creative mind.

There are no texts on research. Describing research is like describing religion. Everyone knows roughly what is meant, but there are no satisfactory and universally accepted definitions. Certainly there is no universal acceptance of what is meant by fundamental research. The head of a great industrial laboratory once objected strenuously that, unless research is fundamental, it is not research. In the absence of satisfactory terminology, we may assume that fundamental research seeks primarily to extend the knowledge of natural law without other direct objectives. Applied research, on the other hand, is aimed primarily at a specific objective of improved health, wealth, or happiness.

WORLD RESEARCH

Some factors bearing on the future of research lend themselves to present examination. The first over-all view is one of complexity and confusion, but of great activity. Instead of a calm fog in the gazing crystal we find a mass of whirling, intercepting clouds—and the greatest cloud takes the shape of Russia. It is possible that the unorthodox, uninhibited research policies of the U.S.S.R. and the support of research there on an astronomical scale may have more effect on postwar research than any other single factor. It has been reported that in some of their first laboratories able scientists were given splendid facilities and large staffs, and then shared with the staffs the choice and conduct of their research programs. Awkward initially they may have been, but reports emphasize widespread interest and support of science and conduct of investigations on a scale that may dwarf that of other countries. Russian scientists are able; and with a multitude of science-minded and science-trained youth to draw from, with almost fanatical public interest in scientific work, and with unbounded physical facilities, they may set a furious pace for the rest of the world to follow. Technical schools may well start teaching Russian to scientists who would keep abreast of future progress!

In England Sir Harold Hartley, vice president of London, Midland and Scottish Railway Company, and others continue successfully to urge increased support and more widespread use of research (*2*). Germany may be expected to continue research activity on a scale large in proportion to her means. She was once the leader in the volume of applied research, although she lost that leadership to the United States well before the present war, for which we should all give daily thanks. Japan's interest has been aroused and laboratories have been established. Much of her technical literature has been hard to comprehend even in translation, but there are those who refuse to subscribe to the copycat thesis. There are many indications of original Japanese discovery of significance. Some of the most brilliant scientists in our technical institutions have been Chinese, and we may be certain that once they throw off the threat of Japanese domination, research in fundamental and applied science will be well established in China. Where once serious research was confined to a very few geographical areas, the trend toward world-wide adoption continues (*9*).

CHEMISTRY, PHYSICS, AND BIOLOGY

All branches of physical science are active. Chemistry and research were once almost synonomous, so much so that one of our earliest and greatest industrial laboratories was organized and directed by a chemist, even though the field was entirely electrical. Research chemists still outnumber other research scientists (*8*). The field of chemistry is still expanding, with the chemistry of many of the elements awaiting investigation and exploitation. But physics has at last taken its proper place and is currently so active that this war has been called a physicists' war. It is easy to assume that physics will draw the limelight when censorship is removed, but there is one broad hint of possible surprise. The head of our largest applied physics laboratory, the dean of American applied science, stated recently that peacetime applications of war biological developments will outshine those based on creation of instruments and instrumentalities of destruction (*4*).

In the face of the current emphasis on applied physics this prophecy for biology seems startling; but nutritional and medicinal advances, for example, have been significant, and recent biological work has expanded rather than exhausted the fundamental science on which it is based. We find similar activity in biophysics and in many other fringes between various scientific and engineering disciplines. Classical mechanical engineering feels the impact of physics and the research method. The metallurgy of light metals and of rare metals and new alloys is under persistent scrutiny. Atomic energy will some day have application. There is great laboratory activity and plenty of new opportunity. There will continue to be drama in research.

SOME HAZARDS

But some of the dense clouds in our crystal are storm clouds. Possible misunderstanding between the research world and government in particular constitutes a hazard to the public benefit from research. Science could become a political football with frightening possibilities. Patent law might be so revised as to force greatly increased secrecy, a lack of incentive, and other harm. Attempts at coordination of various types might permit support of mediocre research. The inadequacy of such "coordinated" research might not become apparent or its lethargy be shaken by comparison with progress under competitive auspices. Simultaneous work in an active field in several laboratories is not necessarily an economic waste; the reverse is usually true.

Frank B. Jewett notes almost complete stagnation of progress in fundamental science during active warfare. He predicts a dearth of highly trained men for fundamental science immediately thereafter (*4*). There may, then, be a period in which fundamental research is being reformed, when the atmosphere in the universities becomes cleared. It has been suggested that four years will elapse after the war before a normal freshman class will be received, even if the faculties and research groups could become established more quickly.

A FEW RESEARCH NEEDS

Wartime stagnation in fundamental research must be offset, and more than a casual return to prewar policy seems indicated, for some of the sources of support have been weakened. The stream of scientific youth should be exposed to fundamental research thought, activity, and method; according to one leader in science, this inoculation can be accomplished only in the university. With university endowment sources lessened, industry should increase its sponsorship of fundamental research in its own interest. There are signs from the sugar and other food groups and from the coal industry and other sources that some of this support is forthcoming.

Willis R. Whitney once told his associates how to choose between the pronunciation of re-*search* and *re*-search. R*esearch* is done in laboratories, and *r*esearch is done in libraries. With increasing frequence, however, as investigations extend and overlap, re*search* can and must be based on a foundation of previous work. Otherwise it merely duplicates and does not advance. Properly compiled, indexed, and redistributed, the vast volume of technical literature of our great scientific libraries becomes a prolific source of new exploration. It is probable that scientific libraries will have increased significance in the postwar period. Technical library staffs will include increasing numbers of specialists in scientific literature. They may well increase the efficiency of utilization of our great storehouse of scientific data and accelerate the rate of postwar accomplishment in research.

Raymond Stevens

SCIENTIFIC AND TECHNICAL LITERATURE

The volume and diversity of publication is such that more survey types of publications are needed. More attention, better organized procedure, and greater support will have to be given the publication, indexing, abstracting, distribution, and re-use of all scientific and technical literature. If Russia fulfills her promise of science on an astronomical scale and other countries attempt to keep pace, the mere mechanical handling of the consequent publications will become a stupendous problem. Even now we need the mechanical literature catalog and reference mechanism once proposed by Vannevar Bush (*10*). He visualized a research worker simply pressing keys, operating electronic selections at a thousand per second. Within one minute he would obtain a card catalog of every article bearing on any given subject.

Above all, we could use talented men who have been trained specifically for research, as contrasted with a training in past science. There is a need for more study of methods in science, better knowledge of how the mind works and how to use it properly. The "Road to Xanadu" should not be the best available text on creative thinking for research men. The psychologists, philosophers, and educators may yet find improved means of developing talent for it and preparing more men who can truly be called research scientists.

RESEARCH AND WAR

Research in the United States has followed the wars. The Civil War saw the National Academy of Sciences established by Lincoln to enlist the organized help of scientists. The Spanish War immediately preceded the establishment of organized research laboratories in industry. The first World War was immediately followed by relatively great increase in the number and size of research laboratories and in the recognition and use of the research method by industry, particularly those industries in which chemistry and physics were of dominant importance. The progress of fundamental research is less readily measured, but there are some indications that its growth and sponsorship parallel applied industrial research in this country, that with applied research it has surged forward after war periods. Many factors are now present that caused great increase in research after previous wars, and some that are new or more significant. We may expect precedent to be followed.

During the present war many uncataloged industrial research laboratories have come to light. After the last war there were three hundred industrial laboratories; in 1940, twenty-two hundred were known and cataloged by the National Research Council (*6*). There are now estimated to be some twenty-seven hundred recognized laboratories. There will be more research workers and many more skilled technicians available for these and for new laboratories. From the National Roster of Scientific Personnel we find that one in every two hundred Americans has some specialized technical or scientific training. Not only have increasing numbers of men become experienced in research practice, but during the war scientifically trained women obtained full recognition and for the first time laboratory demand exceeded the supply. There may soon be many to match Madame Curie's singleness of purpose, persistence, and trained ability.

MORE CAPACITY AND ACCELERATED PACE

New laboratories and more research workers mean a greater volume of research, but we may also expect an accelerated pace. During the war applied science research has been under great pressure for speedy attainment of objectives. There have been many instances of new and constructive contact with other laboratory staffs. Some laboratory directors have learned how increased capacity and pace is possible, and this experience may have permanent result.

We are now much better equipped physically for both fundamental and applied research. In recent years scientists have conceived, created, and refined many effective research mechanisms and research procedures. Two dozen great atom-smashing cyclotrons are working night and day on war assignments. They and their skilled crews are now available, and their tagged atoms are solving mysteries in many branches of science. The cyclotron, the electroencephalograph, the electron microscope and other high-magnification equipment, the newer great integrating machines, and many other mechanisms are so recent that they became available only immediately prior to the war. They have been used to capacity during the war. On the release of laboratory men and equipment from war tasks, the extended application of these tools will have potent effect in accelerating research.

More extended and more skillful use of applied mathematics also contributes to acceleration of research pace. As men with training in advanced engineering, physical chemistry, physics, and even special courses in applied mathematics filter into laboratories, there is increased means of eliminating many tedious empirical investigations. Where mathematicians can produce a generalized law, the capacity of many research workers is increased automatically. The use of mathematics in research may be expected to accelerate and with it, correspondingly, research itself. Mathematicians, physicists and other research workers will be helped by mechanical calculation methods, which save the time of able scientists and free them for other problems. These methods enable attack on problems involving such mountains of mathematical calculation as to be impossible without mechanical aid. Recently, for example, the atomic structures of several molecules and crystals were determined from electron-diffraction patterns, and spectrum data by office accounting-machine methods. These mathematical analyses would have taken years by hand.

REDUCTION OF LAG BETWEEN INVENTION AND APPLICATION

Discovery and invention must be followed by many steps before general public application. The consequent lapse of time, or lag, between creative research and the consumer often represents a serious public loss. Fifty-one years lapsed between Faraday's discovery of electric induction and Edison's first central power station in 1882 at Appleton (*3*), fifty-one years from theory to taxation. On the other hand, Roentgen's x-rays were used by surgeons and by welders a year after his epochal discovery. Haber proposed high-pressure ammonia synthesis in 1908, and the first commercial plant operated only five years later. Penicillin was known nine years before it was tested on human diseases, and that was five years ago. Back in 1928 Lawrence V. Redman found that a usual birth-and-infancy period of directed product research was seven to eight years (*7*). More recently Vannevar Bush estimated that this hiatus had narrowed to five years (*1*).

Research and engineering executives are developing various means of reducing the hazard, the cost, and the time of this lag between anticipation and realization. The well-known principle of similitude, for example, has been applied in model ship basins, wind tunnels, and photoelastic structure design, generally with increasing frequence. Such small-scale trials hasten transition from theory and design to practice. More and more pilot plants are used with increasing frequence in the process industries. Statistical methods are being employed increasingly, especially in biological work. Even taste and other organoleptic characteristics are being subjected to improved test procedures. Accelerated age testing methods, still usually unsatisfactory, have been further developed under war pressure, as have been many other methods of screening and evaluating new products and processes.

Some of industry is becoming more flexible, and greater flexibility reduces the research to application lag by decreasing resistance to change. Many chemical companies have had flexibility forced upon them. New and improved chemicals appear with such rapidity and continuity that chemical industry policy with both production and sales is necessarily one of continuous flux. With such a policy comes increasing stability and insurance against product and company obsolescence. Continuous change makes the rapid introduction of new products easy. There are indications that this policy of flux, of continuous introduction of new laboratory products, is spreading from the diversified chemical companies to many others. The public will benefit by more rapid availability of new and improved articles of trade.

LIAISON BETWEEN MANAGEMENT AND TECHNOLOGY

One of the most potent lag-reducing factors lies in the realm of administrative personnel. In the normal course of advancement, many able technical men have now been promoted to high administrative positions, and have established effective liaison between the laboratory and the directors' board room. In 1927 it could be said: "Even today it is extremely difficult for the sponsors of a new chemical process to find, in adequate amount, money with the vision to recognize its potentialities and the courage and tenacity to carry through the necessary stages of development", and "While every chemist will admit he needs a banker, the fact that every banker needs a chemist is not yet recognized in financial circles" (*5*). Ten years later in 1937 the situation had already changed, and now we have available plenty of "educated money". The graduates of our technical schools sit high in many managerial circles. There they can bridge the serious gap between the creative, but abstruse and inarticulate, field of science and the busy practical field of mass production and sale.

During the war this liaison between management and technology necessarily has been strengthened. Many manufacturers have been forced into rapid production of new materials and products of highly technical nature. They have learned to include technical counsel with that of their lawyers and bankers. The wartime experience will stand them in good stead in profiting quickly from continuing technical advances in their various industries.

CONCLUSION

As we lift our eyes from this overpopular and overrated gazing crystal, we recall a general impression of size and quantity: First of Russia and its mass of research workers with a fresh and zealous approach; then, of the mechanical and almost mass production treatment of great quantities of mathematical calculations; and again of an enormous amount of scientific literature pouring forth in English, Russian, German, Japanese, Chinese, and other languages. We have visualized a much greater volume of research, probably conducted at an accelerated pace and possibly more speedily applied to public benefit. It is rather an exciting picture.

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The FUTURE of TECHNICAL EDUCATION

H. S. ROGERS

POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.

IN APPROACHING an inquiry into the future of technical education (using the term broadly to include physical sciences and engineering), it is well to bear in mind that historically such education has been designed to serve the broad social and economic functions of industry and public works in organized society. From the early period of the great development under the Morrill Act to support "liberal and practical" education, its ultimate purpose has been to provide better clothing, housing, sanitation, transportation, and communications—to lay the foundations for a broader distribution of the fruits of civilization and a higher culture. In the accomplishment of such broad purposes, educators have associated themselves with technical and professional groups outside the college in the active service of industry and public works.

Together the educators and professional groups have accumulated knowledge and developed a mode of thought fundamental to economic progress and to the resultant level of living, also fundamental to power warfare. This fund of knowledge of materials and products, of forces and power, of machines and processes, and of methods and practices and "know-how" has grown rapidly in peacetime and at an accelerated rate under wartime pressures. The mode of thought which nourishes this growth has been focused upon the improvement of efficiency, the elimination of waste, the reduction of costs, and the development of new materials, new sources of power, new machines, new processes, and new products.

In any examination of the future of technical education per se we must, therefore, attempt to understand the challenge of industrial and public needs; to appraise the significance of this fund of cumulated knowledge; to judge the strength and weakness, uses and limitations of this mode of thought; and to project the avenues and direction of growth of educational programs. In an examination of technical education at the immediate time we should also review wartime developments to see if they offer anything of value to peacetime needs and objectives.

TECHNICAL TRAINING

Too often technical training has been confused with technical education. The training of skilled workers for repetitive operations in industry or for certain military tasks, which may be organized as job training in the manual arts, is vastly different from the intellectual development sought in technical education. Under wartime pressure certain jobs for skilled workers have been more critically and thoroughly analyzed and further subdivided. New and unusual training methods for them have been utilized, and highly satisfactory results have been obtained. Some of these achievements will undoubtedly affect all manual arts training in the future, but they have little significance for technical education.

The new training of army personnel in the language fields has produced results most astounding to those of us who plowed through years of grammar and practice reading. Men have been taught to speak new languages, not too fluently and not too correctly, but rapidly in the period of a few months. This training in linguistic arts has a direct analogy to training in the manual arts. It may, however, have more influence upon the future objectives and methods in language programs at the college level than new methods in the manual arts.

Perhaps the most striking achievement in training methods is found in the pilot schools of the military forces. Here there has been a comprehensive and critical study of psycho-physiological aptitudes, psychological abilities, emotional reactions, and instructional methods. This study has given astounding results in the selection and training of pilots. Such training is, in many respects, more analagous to training in the manual and linguistic arts than to technical education even though it requires the operating integration of a vastly greater number of factors. What the psychological studies will yield of value to technical education cannot now be determined. In the main it may be concluded, however, that such developments offer little which may be transferred with value to the methodology of technical education.

Subprofessional Courses. The defense and war training programs of the United States Office of Education (now called the Engineering, Science and Management War Training courses) have effectively met certain needs of industry for young men and women trained at the subprofessional and technological level. More than a million and a half have taken these courses throughout the country, and many have found their way into industry or into technical jobs in the military services. In the industrial centers these courses have been directed toward technical applications such as jig, tool, fixture, die, and mold design, such as aircraft and ship lofting, productions scheduling, and powder chemistry. In the rural sections they have more often been abbreviated college courses in surveying, drafting, and other aspects of technology.

The experience of wartime has indicated a great need for training at this level. If American industry is to operate under a postwar schedule of full production, there will certainly be a continuing need for such training. The State Department of Education of New York is now planning for a group of technical institutes which will provide training in a wide range of business, agricultural, and industrial fields. Other agencies are also surveying the need for such institutes.

Army and Navy Programs. The experience of operating the Army and Navy college programs has hardly been long enough to provide results which may be appraised as related to peacetime objectives and methods. These programs are essentially curtailed and compressed scientific and engineering programs. The Army program has been much more curtailed and compressed than the Navy. They are scheduled on a continuous calendar and operated under heavy pressure. Little time has been given in them for reflection and maturation of scientific thought. The morale of the boys enlisted in them has, however, been generally high, and their application to assigned studies has been strongly motivated.

The Army program was framed within certain limiting conditions of time. Subject matter was necessarily prescribed with no experience to indicate the time required for mastery. It placed the schools under compulsions that were entirely new to them, but it has not continued long enough to determine what accomplishments could be made within the prescribed limitations. It is doubtful, therefore, whether any continuing influence in

Harry S. Rogers

instructional methods or program planning will derive from this experience.

The segregation of men from widely distributed geographical areas and with diversified interests and former pursuits presented a task of classification which was both difficult and new, but in which much progress was being made. One of the principal conclusions of the schools from this classifying program has been that general intelligence is no substitute for prerequisites in scientific and mathematical courses. This judgment will strengthen the insistence of the technical schools on admission requirements.

A phase of the Army program which gave considerable promise was the subject matter testing program. Because it was necessary to measure the achievement of men from widely scattered institutions who were thrown into classes together and because the directors of the Army Specialized Training Program desired some means of appraising the work of the institutions, the Army had undertaken a program of developing achievement tests in which many educators were participating. Whether this work has gone far enough to yield conclusive results is not yet known. The programs of classification and of testing, however, will undoubtedly stimulate the colleges to further developments along the same lines.

TECHNICAL EDUCATION

Returning to the primary question, "What is the future of technical education", let us review the principal features which have characterized it in the past and attempt an appraisal of their adequacy as evidenced both in peacetime and wartime experience. The judgments which are made concerning the merits and limitations of these features will determine the revisions and developments in the postwar period.

Technical education at the college level has developed into a type of career training which, although differentiated by the broad fields of scientific applications and of engineering practice, is characterized by programs and standards so universally adopted that recently created accrediting agencies have been able to approve a large majority of the institutions offering such programs. This career training has been geared to the needs of industry and public works, and has been molded by professional objectives, standards, and ideals. It has been planned to articulate with a postcollegiate apprenticeship leading to the attainment of full professional stature or to administrative and managerial responsibilities. The professionalized programs which colleges have offered in the technical fields have prepared graduates for some junior or subprofessional tasks immediately after graduation and have laid a foundation in the mastery of basic principles upon which professional growth could be built.

Among the objectives sought in terms of student development, the following have had general or partial recognition: (1) a mastery of that knowledge basic to applied science and engineering but differentiated by the specific applications of major professional groups; (2) a discipline in scientific and engineering methods of thought and in the skills and habits of work associated therewith; (3) some indoctrination in the attitudes, obligations, and loyalties common to all professional groups or characteristic of engineers in particular; and (4) some preparation for the exercise of worthy citizenship and for participation in the cultural interests of life.

MASTERY OF KNOWLEDGE AND METHOD OF THOUGHT

The first two objectives traditionally have received greater emphasis because they have counterparts in the curriculum and the methods of instruction. How satisfactory our technical programs have been and how well students have been trained in the method of scientific thought can be gaged by the fact that in peacetime technical schools are almost the sole source of junior professional personnel employed in industry and public work.

The schools and the colleges have maintained a close liaison with the professional societies, and by this means have kept the college programs well tuned to the needs of industry and public works. There has been general agreement that the programs presented by the schools and the mastery of knowledge sought by the students should be planned around basic principles and fundamental applications of science in the broadly differentiated fields of technology and engineering. It has also been commonly agreed that throughout these programs and pursuits attention should be focused upon the methods of scientific thought and the habits and skills of industry, thoroughness, orderliness, and accuracy. It has further been recognized that the mastery of principles should be carried to a level that would develop facility in the solution of new problems. How well these purposes have been attained is indicated by statistics published in "Who's Who in America", which show that almost 100% of those engineers recorded in the publication are graduates from recognized technical institutions.

In wartime, moreover, other evidences of the strength of this fundamental training have been presented in a large number of widely diversified fields. Henry Kaiser's shipbuilding program has been directed by engineers who originally knew little about ships. The engineers of Firestone Tire & Rubber Company have built and are operating an efficient plant for the manufacture of anti-aircraft guns. Innumerable examples of such achievement indicate the constructive character and particular value of technical education.

While these and similar demonstrations of the ability of American engineers and scientists may be judged to stem from their technical education, it must not be assumed that the colleges are smug about their attainments. They recognize, on the other hand, a great need for relating the curricula more closely to their objectives and for a better understanding of and discipline in the method of constructive scientific thought—in other words, a great need for the strengthening of technical education.

CHEMISTRY PROGRAMS

Wartime conditions have also emphasized certain needs in industry that in recent years have been becoming more apparent. When the demand for chemists began to accelerate at the beginning of the war, it was evident that industry preferred to recruit those graduates from four-year programs who had completed a professionalized curriculum in chemistry rather than those who had pursued undergraduate work in the elective system of the liberal arts college. While the latter may be adequate as a foundation for graduate work and subsequent professional growth, the former provides a better training for immediate entry into industrial service. The choice between the two cannot, however, be made on the basis of technical training alone. Education for citizenship and for cultural living is also deserving of important consideration. These problems will receive better consideration when education in chemistry has the immediate interest, cooperation, and support of a professional society in a measure equivalent to that extended by the engineering societies in their respective fields. Development toward this end seems now to be in progress within this SOCIETY.

EDUCATION FOR MANAGEMENT

Another need bearing upon the four-year programs which has received increasing emphasis is for men directed by their training more particularly toward the responsibilities of supervision in the processes of production and operation. Prior to the war there had been a growing demand for training in the field of engineering management. The schools have not responded to this demand too hastily because it was not immediately possible effectively to present programs in this field with specific knowledge and disciplinary goals equivalent to those directed toward design and research. Wartime experiences have emphasized this need. Peacetime operations requiring reconversion and full employment will bring a similar demand.

With so large a percentage of engineering graduates finding their ultimate careers in management, administration, and other related fields, it seems quite certain that the pressure for programs along these lines will continue. A number of institutions have inaugurated courses of study which still preserve training in the basic engineering sciences and discipline in the scientific manner of thought, yet at the same time provide those special techniques in the arts of production which will prepare young men for entrance into the managerial field. These programs give promise of growing in number and importance. The future development will be one of evolution, however, rather than of revolution.

GRADUATE AND POSTCOLLEGIATE STUDY

Perhaps the field of technical education which will be influenced most by war experiences is that area beyond the undergraduate program in the graduate and postcollegiate years. The expansion of research and the development of new techniques in all fields has exceeded the imagination, but particularly has this been so in chemistry and in chemical, electrical, and aeronautical engineering. While much of this development has been in the fields of application rather than in basic theory, the technology involved has been upon such a high level that graduate work is becoming increasingly more necessary and supplemental training of scientists and engineers in industry more desirable.

These developments will bring more formal course organization into the programs at the master-degree level; they will undoubtedly push downward into the undergraduate program and will more closely relate the methods and objectives of work of the last year to the graduate school programs for those who expect to go into design and research. They will also stimulate the expansion of work for the doctorate degree. Short courses and seminars for men in industry are increasingly important, and many institutions in industrial centers are looking forward to the expansion of such service.

PROFESSIONAL INDOCTRINATION

The indoctrination of students in the attitudes, loyalties, obligations, and purposes of the technical professions has received little organized attention since the war began. The programs normally sponsored by the student branches of the professional societies have been practically abandoned, and the efforts of the Engineers' Council for Professional Development in cooperation with the Society for the Promotion of Engineering Education, just begun in this field, have been able to command little attention. After the war it is certain that there will be not only a rebirth but also a rapid development in the understanding of the goals sought and in methods of their achievement.

CITIZENSHIP

It is doubtful, however, whether the studies which are collateral with the scientific and technological programs, directed toward worthy citizenship and cultural life, will be materially changed. In the past these programs have been built by selecting a few courses here and there in economics, English, history, and psychology without any coordination or direction toward recognized and unifying goals. In a few institutions unified sequences are under development, but no general recognition of the need has been given throughout the country. Perhaps the war will throw emphasis upon the need for a better understanding of citizenship and of the contributions of culture among technical graduates, and a wider recognition of the role which they must play in a representative democracy.

It is certainly to be hoped that a revision of technical curricula in the interest of saving time which may be allocated to the humanistic-social studies can be made. In addition to the need for time, moreover, there is need for creative and vigorous leadership in this field. Adequate preparation cannot be provided by fragmentary courses. Programs equal in vigor to those in the scientific-technological field must be designed and directed by competent and inspired teachers and administrators. This is one of the big jobs ahead. Leadership is not immediately available, however, for the fulfillment of large expectations.

OPERATING MATTERS

As far as the educational programs and objectives of our technical institutions are concerned, the above seem to represent the major evolutionary forces. When we come to the problems of projecting enrollments in college attendance and of estimating the supply of technical personnel needed in industry, no one but a clairvoyant can see their answers clearly in the crystal ball. If we are to operate a yearly national economy above 100 billion dollars, the demand for technically educated men will be greater than ever before. The gaps in the normal flow of technically trained men into industry caused by the manpower demands of the war must be filled.

Many men who would not otherwise have become interested in technical education have been inducted into it under the Army and Navy programs. Many who have not carried their programs of education to desired terminals will return to them after the war, undoubtedly under some aid from the state or national government. Transition programs to articulate the work of the veteran with the regular schedule will be necessary. Cooperation with industry in the placing of these men after graduation will be increasingly important.

All of these facts indicate that the technical schools will be extended to the utmost in the post war period. How they will be held together in the interim or how they will be rehabilitated after the war are matters which each institution must solve individually. Of this I am certain, the future presents technical education with the greatest challenge of a long era of distinguished service to society.

OUTLOOK for FOREIGN TRADE

JOHN B. GLENN

PAN AMERICAN TRUST COMPANY, NEW YORK, N. Y.

FORTY years ago this country was primarily an agricultural nation, with over half of the people deriving their support from farms and with industry providing only a minor part of our total income. American chemical industries were in the late stages of their long infancy, and Europe was the dominating factor in world trade. Before World War I we were dependent on Germany for fine chemicals, pharmaceuticals, dyes, potash, chemical glassware, lenses, and fine instruments, and we were a debtor nation. Almost overnight we were to become a creditor nation and to attain world leadership in industry, research, finance, and trade, so that at the outbreak of World War II our national income was greater than that of Germany, France, and Great Britain combined, even though their total population was much larger than our own.

This tremendous progress was due mainly to private enterprise, which deserves full credit for our leadership in every field and has made us the greatest producing nation of all time. It is due to private enterprises, which have cooperated wholeheartedly and efficiently, as well as to the spirit of a free nation among our courageous armed forces, that we may expect to come out of this war victoriously to sustain our principles of freedom and democracy and the right to plan and build for a better world.

When victory comes, we shall find that we possess greater manufacturing facilities, more new materials, and more skilled labor than ever before. We shall also be faced with a public debt of some 300 billion dollars, with government holdings of surplus materials worth probably 75 to 80 billion dollars, with the cancellation of large government war contracts, and with the disposal of land and government-owned factories acquired during the war, amounting to another 50 billion.

It will then be our great problem to swing industry back to a peace basis, and promptly and efficiently to create minimum unemployment and maximum opportunity to supply the world's markets with the products of our manufacturing plants. These will be greatly in demand, particularly to build up the standards of living of other nations. Government and industry should work closely together to create a well arranged distribution of war materials through proper trade channels and to avoid the dumping of supplies, which would greatly upset local and foreign markets and, at the same time, prevent the Government from obtaining the best prices for its surplus materials.

OF ALL our industries, the chemical industry has the least problem of conversion; its products required for war are essentially those used in peacetime trade. The problem of the chemical industry becomes one of adjusting quantity rather than of changing type. Sulfuric acid, soda ash, hydrocarbons, synthetic resins, now required for war, are identical with those consumed in peaceful pursuits. Nylon yarn for parachutes is not fundamentally different from nylon yarn for hosiery. Dyes for army and navy uniforms are very much the same as dyes for civilian goods. This is even more true of basic chemicals. With the splendid wartime cooperation of all chemical industries and the exchange of research knowledge between highly competitive groups, a vast production has been attained which will be of great peacetime value; chemical products will be available in new abundance at prices beyond foreign competition. The great future of the chemical industry obviously lies in quantity production at lower cost and the sale of surplus in foreign markets.

American business must show an aggressive spirit of expansion and fight for the conquest of those economic frontiers which were previously lost to us through foreign competition. During World War I we did considerable postwar planning for foreign trade, but our inexperience as world traders and financiers led to many mistakes. We lost vast sums of money and the opportunity to be the world's greatest financial center. Although nothing is more difficult than postwar planning, let us hope that this time we shall have learned by experience.

First we must obtain the unconditional surrender of the Axis powers, to be followed by the military policing of enemy countries. Immediately we must help to provide relief, rehabilitation, and economic stability. This applies principally to Europe and the Far East. Western Hemisphere postwar planning will be much easier; in fact, it presents primarily the problem of materials.

All countries will be desirous of purchasing the goods they need, and, at least for the first phase of the postwar period, we will have little competition. We will have a larger amount of goods to sell after the war for, with our industries intact, we should have the greatest abundance of merchandise ever known in history. We must keep this huge new production in full operation for our own best interests. With replacements in our own country, the immediate demands from our Allies in former Axis-occupied countries, and orders from the nations of this hemisphere, we may be severely taxed to furnish all the goods required, even allowing for the large government-owned war surpluses which we will undoubtedly have on hand.

THE question before all of us is: How can some of these countries pay? Some of our Allies may receive further assistance on Lend-Lease to aid in the rehabilitation period, since many of their plants have been moved to Germany or destroyed during the war. Others have largely increased their cash reserves with us until this amounts to well over 4 billion dollars. Of this, 2 billion belongs to Europe and an equal, if not larger amount, to this hemisphere. European deposits consist of escape money, the use of foreign ships by our Government, and local expenditures in countries occupied by us. Large Latin American balances have been built up by the excess of their exports to us to fill our war needs and their present inability to purchase goods from us.

Just how large our foreign trade may grow is difficult at present to surmise. The Bureau of Foreign and Domestic Commerce has prepared a study of "Foreign Trade after the War" in which our imports as calculated may exceed 6 billion dollars in 1948 or two and one half times the average of 1935–39. Our foreign payments for services as estimated should reach 4 billion. This forecast would make the total annual amount available to foreign customers 10 billion dollars.

The Bureau estimates our potential export value for 1948 at 7 billion dollars, which is double the amount of our exports in 1937, the largest volume of any year immediately prior to World War II. This presents an exceptionally favorable outlook for the future sales of American goods to foreign countries and one worth keeping in mind.

In the past we have sold approximately 10% of our production abroad, and this has represented in great measure the difference between prosperity and hard times. In the future we may be called upon to sell as high as 20% to keep our workmen employed, to cover increased taxation due to the war, and to produce profits commensurate with our capital investment. The 20% is based on our greatly increased production now and hence is much larger in money value than twice the prewar figure.

We have all heard of the desirability of establishing a world bank and the Keynes and White plans for currency stabilization. We should be somewhat reluctant to enter into any international currency arrangements whereby funds supplied by this country would be subject to foreign control. Undoubtedly the need for currency stabilization could best be met through the medium of our Export-Import Bank. This has already been of efficient help during a trying period in making large dollar exchange loans to foreign central banks. This bank has also issued special export letters of credit, and given important assistance to the American exporter in handling long-term credits and in purchasing of a large percentage of foreign bills without recourse.

Unquestionably the monetary standard of the future should be international in scope and free from political control. Gold is the only medium which offers any reasonable prospect of becoming international on a large scale. We fully realize that an international unit of value cannot be maintained perfectly stable and that some management may be essential. Obviously no kind of monetary standard could have functioned satisfactorily under the conditions prevailing during the last thirty years.

Countries are linked closely to those with which they trade and establish balances in these foreign currencies, depending upon the volume of sales and purchases which, in turn, affect the rate of exchange. No medium of settlement of balances has yet been found which is freer from political domination or more satisfactory internationally than gold. That this point is well recognized is proved by the fact that for the year 1943 the United States lost gold to the rest of the world either by physical shipment or by earmarking to the extent of about 750 million dollars. During the same period wherever free markets have existed in any part of the world, gold has commanded a premium in terms of currency ranging anywhere from 10 to 100%.

In our postwar world we will find an ever increasing need that trade and finance be permitted to move with a minimum of restrictions across political borders. Foreign trade must of necessity be a two-way street. Over-all trade must ultimately balance. We cannot expect to sell to foreign countries unless we, in turn, purchase from them, whether our purchases be in the form of merchandise, services such as freight or insurance, foreign travel, or immigrants' remittances. We can, of course, make loans abroad and extend our capital investments, but these will aid the purchasing power of the foreign country only to the extent that these funds remain abroad; all remittances to us as interest or dividends must serve as a deduction.

WHILE we may not expect a great deal of foreign competition in the immediate postwar period, we would do well to lay a solid foundation for the future; for as economic conditions become more stabilized, the needs of our European competitors will become less and the production greater. Great Britain, of course, with her factories only slightly damaged, will promptly resume her contest for world trade, vital to the life of the nation. She will be followed by a resurgent Russia which bids fair to become a great country, not only agriculturally but industrially. We may expect increased activities of France, Belgium, Holland, Sweden, and Italy; finally Germany will again lift her head along industrial lines.

In the Far East, Japan will have lost her prestige and power both militarily and as a trading nation. China, which has lost so much both in capital and industry, will be a fertile field for American trade, but she can pay for goods only in raw products. She will need large supplies and, above all, capital for industries. We would do well to consider the erection of small plants in that country to supply the needs of the potential buyers among her 450 million inhabitants.

Our own Hemisphere has been the only section of the world where nations are at peace with one another. All of the countries have broken relations with the Axis powers and are democracies bound together by ties of respect and mutual cooperation. They have always purchased a substantial volume of our exports, and this should be considerably increased during the postwar period. Canada is one of our best markets, not only through the sale of our merchandise north of the border, but also through the many industries which have been established by American capital there, greatly to the benefit of both nations.

LATIN America is composed of twenty countries and 130 million inhabitants, and is about two and a half times larger than the United States. Today it offers the most promising field for immediate development in all the world. With a diversity of climate varying from the tropics to perpetual snow, it produces every type of vegetation from coffee, cocoa, rubber, and tropical fruits to corn, beans, and wheat. Brazil, which is larger than the United States excluding Alaska, exports 57% of the world's coffee; Cuba supplies 50% of the world's sugar; and the Argentine is the largest exporter of grain and meats in the world. Nearly all of these countries are rich in oil, minerals, and precious stones. Mexico is the world's largest producer of silver; Chile is a substantial producer of copper; Bolivia, of tin; Brazil, of manganese; and Venezuela is the world's greatest exporter of oil.

Latin Americans really discovered us after 1914 when the European markets were closed to them on account of that war. If we go back to 1913, we will find that Great Britain supplied 24.4% of Latin American imports, Germany, 16.6%, France, 8.3%; our sales, amounting to 25%, were the largest of any individual country. These three European nations thus controlled 49.3% of total sales to Latin America. This was almost double our share in this trade, in spite of our proximity to Mexico and the West Indies, and our natural zone of influence extending through Central America to the northern part of South America, particularly to Colombia and Venezuela.

KAIDEN-KEYSTONE

John B. Glenn

By 1938 Great Britain's exports to Latin America had dropped to 12.2%, Germany's had increased to 17.1%, and France's had fallen to 3.5%. Our sales had at the same time gone up to 35.8%, or 3% greater than those of Great Britain, France, and Germany combined. In 1941 our sales had increased to over a billion dollars, and I see no reason why we cannot keep them constantly in excess of this amount, provided we continue our purchases and make our shipments to them as required by the conditions and trade of each country.

TO ENCOURAGE reciprocal Latin American trade, and to protect ourselves against any future shortage of strategic materials, we should do everything in our power to continue our present purchases of all types of materials, as well as to assist in the cultivation of those tropical products which are most needed by us. In the past we have committed the grave error of purchasing 94% of our essential tropical crops from the Far East, and bringing them a distance of 10 to 12 thousand miles; some of these plants are native to the Americas and all can be produced on this hemisphere, many within 500–1000 miles of our southern border.

Many of our important companies are convinced of the opportunity which presents itself. Active plantings of these tropical crops are now being made in Mexico, Central America, Haiti, Brazil, Ecuador, and Peru, in anticipation of large future sales to the United States and, in any event, to fill the local needs of commerce and industry of each producing country and its intra-American trade. Some of these products now being grown to advantage are rubber, abaca hemp, roselle (an important jute substitute), tea, and a number of others important to the drug and chemical trade, derris root (consumed annually to the extent of 6.5 million pounds in the manufacture of rotenone), cinchona (from which we obtain quinine), camphor, pyrethrum, and menthol.

Those of us who have been doing business with Latin America for many years are convinced of the honesty and integrity of the well established firms. We know that they are proud of their position and reputation which, once lost below the border, can never be regained. That our Latin American business has been profitable has been substantiated by the Foreign Credit Interchange Bureau, which reported on January 31, 1944, all Latin American countries as "good" both as to credits and collections. Dun & Bradstreet's Survey, covering a period of more than ten years, shows that credit losses amounted to only 0.4% which is as good as or better than our own. We would also do well to consider that these countries, through increased exports to us and reduced imports, have now built up large balances to their credit in the United States which, in gold and bank balances, amount to approximately $1,700,000,000.

Whether a world bank is established or not, it seems certain that Latin American exchange will be tied closely to the dollar, that these countries will emerge from the war in a stronger economic and commercial position than at any time in their history, and that we will become the clearing house of all the Americas, provided we realize and act upon the opportunity which now presents itself.

WHAT we will now find in Latin America is a strong trend towards nationalism and industrialization. The larger countries are anxious to establish new industries and look forward not only to supplying their own needs, but to selling their manufactured products in inter-American trade. Mexico and Brazil present golden opportunities with abundant raw products and cheap labor and little, if any, competition; for until now, our southern neighbors have specialized chiefly on the products of agriculture, mining, and oil. New factories are constantly being built, and within the last few months a number of our idle plants have been shipped and transplanted to Latin America, where the wheels of industry will turn in new fields for higher profits.

Development of national industries abroad is viewed by many as reducing opportunities for the export of our products. This view is obviously fallacious. Raising the standard of living of a people, by whatever means, inevitably increases both their purchasing power and their desire for more goods. Furthermore, the peculiar position of the chemical industry as a supplier of producers' goods makes the development of some national industries necessary to create demand for its bulk goods. Thus the sale of dyes in an export market requires a textile industry there if quantities involved are to be more than the barest minimum. Production of most chemical products will always be cheaper when large quantities are made. Thus, so long as the needs of any export market are relatively small it will be clearly advantageous to meet them by imports rather than by attempting home manufacture.

Chemical industry as now developed in the United States produces an extensive list of the thousands of products necessary to self-sufficiency. This was not reached at a single bound but rather was achieved by slow degrees. The same will necessarily hold true in other countries as they strive to build up self-sufficient industries, and the result will obviously be a long period of partial diversification. This provides specially valuable opportunity and a useful service for American chemical manufacturers.

American capital is needed and welcome in all of the Americas and will pay splendid dividends, provided it is invested in conjunction with local capital and not in wholly foreign-owned enterprises. Today the average profits for industry in Mexico and Brazil are estimated to be around 15%, the average profits from commercial enterprises from 15 to 20%, and bank profits at a minimum of 10%.

This is an exceptionally opportune time for drug and chemical companies to study the Latin American field. Some of our leading chemical executives have lately visited many of these countries. Various American companies have already established laboratories and plants, and all would do well to consider that the future policy of Latin America will be to keep the chemical trade on this side of the Atlantic. Drug and chemical companies will not return to the former German control so powerful before the war, but will be held and operated as local companies.

IN SUMMING up our opportunities for postwar world trade, I should like to emphasize that our ability to hold and increase our future business against normal European competition will depend largely upon the facilities of credit we are willing to grant and our willingness to meet keen competition in shipping, packing, and complying with the customs and needs of each country. In any event, our relations in world trade will be greatly facilitated in the future through better and faster transportation and communications, and improved banking facilities. In the final analysis we will find that markets are built and maintained principally by the worth of the product, ability of the sales agent, and amount in advertising dollars we spend.

Let us keep before us the fact that the restoration of world economy after the war will offer a tremendous opportunity to American production; and that industrial development and construction in China, Russia, and Latin America will open vast new markets by raising the standard of living abroad and by increasing per capita wealth and purchasing power. This will create a constantly expanding market for American products, and nothing is more conducive to international friendship and enduring peace than satisfactory trade relations.

This war has taught us that we cannot isolate ourselves from the rest of the world, that as a nation we face a new era in international relations, and that the future of our country depends on our ability to accept this challenge of world leadership. We must maintain our private enterprise, keep our workmen employed, increase our national income, and reduce our government debt. By so doing, we shall have made the greatest contribution possible towards the development of world trade.

PROSPECTS for ENGINEERING DEVELOPMENTS

W. L. BADGER
DOW CHEMICAL COMPANY, ANN ARBOR, MICH.

TO PREDICT what will happen in the field of engineering is difficult unless we look at how things have happened in the past. By calling attention to the methods by which most of the equipment for unit operations has developed, we can make some kind of guess as to how it will develop in the future.

In the earlier days of most unit operations, the equipment was more or less makeshift; then in almost every case rather suddenly a piece of real engineering equipment appeared which was designed by an engineer and which radically changed the aspect of that unit operation. The next step was the appearance of a wide variety of equipment, produced partly by the inveterate inventor who always wants to build something different, and partly by engineers who were beginning to understand the principles back of that unit operation. During this period the variety of equipment available for that operation multiplied tremendously, and it was often difficult to decide which piece to use for a particular application. Gradually, as the understanding of the principles underlying that unit operation became better understood and particularly as quantitative rather than qualitative data began to be gathered we find that the number and variety of equipment available began to decrease. The industry then standardized on a rather small number of pieces of equipment. The further development of that unit operation has always been a refinement of the understanding of, and accumulation of quantitative information regarding, the design of the equipment. That is the usual cycle. Once in a while a radically different piece of equipment comes into the picture from some industry, which at first is not considered germane to the subject. Sometimes this completely upsets our knowledge of what should be done in the field; sometimes it is merely an addition. By examining the various unit operations and comparing them with this cycle, a guess can be made as to what developments we may expect in the near future. No one can predict the radical and brilliant introduction of something totally different from what we have been accustomed to. All I can hope to predict are those developments that follow the ordinary pattern. To illustrate, I will discuss that unit operation with which I am most familiar.

EVAPORATION

In the earliest days of the development of this unit operation the equipment was crude; it consisted usually of a kettle borrowed directly from the chemist's beaker or from the kitchen stove. When it was decided to heat these with steam, they were simply set inside another kettle, and so we had jacketed kettles; they were then refined and altered in detail but not in principle.

In 1812 Howard put a vacuum on the kettle and boiled at a lower temperature, but still nothing particular was done about the design. Then came the radical introduction which changed the picture: In the sugar campaign of 1843–44 Rillieux built in Louisiana the first multiple-effect evaporator. And he did one other thing for which he is not usually given credit; he made the first evaporator with a tubular heating surface instead of simply a jacketed bottom. That made it possible for us to build equipment of any desired size.

Thus the second period in the development of evaporation was marked by radically new equipment designed by an engineer. Then followed a period of multiplication of design; from Rillieux' first evaporator in 1844 up to about 1910, there was a bewildering succession of designs of multiple-effect evaporators, as shown by the patent literature of this country and Germany. During the latter part of this period, there began to be an understanding of principles and a collection of inaccurate and totally qualitative data but, nevertheless, a real understanding of the principles of heat transfer. The later part of this development was motivated by an attempt to apply those qualitative ideas to the performance of these multiple-effect evaporators.

About 1910–12 the first quantitative experimental work was done on heat transfer coefficients in evaporators. Following that came the period of the refinement of past designs and a quantitative understanding of what was going on. The result was that at present we have settled down to two or three, or at most four, different types of evaporators which are universally recognized and used for all applications. The wide variety of evaporators invented in the past have all disappeared. Barring the brilliant introduction of something radically new, usually by someone outside of the field who comes to it with a new point of view, what we can look for is a refinement, a better understanding, a more completely available set of data on performance and design which will enable us to fit these standard types more perfectly to the particular operations involved.

RADICAL INNOVATIONS

This brilliant introduction of something new is illustrated in the field of filtration. For many years, both in the standard literature and in practice, in this country and abroad, filtration was always carried out with a sand filter, with the overgrown Büchner funnel called a Nutsche, or with the filter press. Then suddenly out of a foreign industry (the cyanidation of gold ores) came the rotary continuous vacuum filter which completely revolutionized the field. Nowadays the filter press is relegated to a relatively minor position, and the first thing that anyone thinks of in connection with a filtration problem is whether or not the rotary continuous filter can be applied to it.

Such brilliant and radical introductions are totally unpredictable. However if a certain unit operation has a relatively small number of types of equipment that are fairly well standardized, and if there is beginning to be a volume of information on quantitative design, we should not look for immediate radical changes in that field but rather a continuation of detailed improvement. On the other hand, in those unit operations where there is still a bewildering variety of designs, where the field of each design is poorly outlined, and where there is poor understanding of why a certain machine is used for a given job, then the prospects are that there will be a great reduction in the number of available designs and a continued effort to standardize on a relatively small number. In any field where a wide variety of designs and a poor definition of their functions exist, that unit operation is by that very token not well understood. We may expect in that particular field a considerable advance in the next few years in the understanding of the fundamental principles and particularly in the development of quantitative performance data.

You must not be misled by my saying that some of the unit operations are well understood. In those cases where we know most, we have only scratched the surface. One who is concerned with the actual design of machinery knows only too well how fragmentary our knowledge is, and how much still is to come from future research.

CORRELATION OF RESEARCH

From what source may we expect those answers? Largely from the research laboratories of the various universities. The unfortunate thing is that these various research programs, on which the industry must depend for its future fund of information, are in no way correlated. In many instances the research, though well done and reliable, is directed by men who have not had practical experience and, consequently, have not much idea of which are important problems. The position of engineering research and development in this country (that is, the engineering of equipment for unit operations) would be greatly advanced by some sort of clearing house operated by a national society. This society would not direct such work (that would be calamitous) but would assemble the problems. Then some of the young men in research laboratories with not too much practical experience, with graduate students available, could draw on that information to find out which problems are pressing and which are not. Such a program might direct the many scattered research programs to a more coherent and systematic end than has been done in the past.

To give an idea of what I mean, when I speak of the gaps in our information, I will discuss some of the questions that have arisen in one of my latest jobs. I have just finished building and am trying to start the operation of an evaporator installation that has cost about 700,000 dollars. Now, an installation that costs that much justifies a lot of investigation; for if we had more accurate information on some questions, it is conceivable that we might have been able to cut 100,000 dollars from the cost.

For certain reasons I decided to use the old fashioned, standard, short-tube, vertical evaporator with external salt settlers and with propellers in the body to promote agitation. The salt to be crystallized has an inverted solubility curve and will form scale. Thanks to a paper published by Warren L. McCabe, we know that, for a true scaling solution, the rate at which the coefficient falls off is obtained by plotting $1/U^2$ (where U is the heat transfer coefficient) against time; from the slope of the straight line obtained, the rate at which the coefficient will decrease can be predicted.

In this particular problem I had a pilot plant with a fair-sized evaporator. We made a great many runs and got some slopes for those $1/U^2$ curves. However, it is one thing to work on clean pilot plant solutions and totally different to work on our commercial solutions which bring along calcium sulfate and calcium carbonate.

QUESTIONS TO BE ANSWERED

How fast is the calcium sulfate scale going to form? How fast will the coefficient decrease due to salting? We can tell something about how fast the salt scale will form, but in addition we have the phenomenon of salting. In other words, any solution that is boiled with crystals in suspension will sooner or later build those crystals on the heating surface to such an extent that the evaporator has to be boiled out.

How fast is it going to salt? What is the relation between the smoothness of the tubes and the rate at which the salt begins to build up on it? What can we do about the fact that masses of salt collect on the sides of the evaporator, fall down into the salt offtake, and plug it? How do we design pipe lines for handling salt slurries to and from the settlers and to and from the filters so that they will not plug with salt? That always happens in the most inconvenient points.

How do we guess how high the vapor space should be? This comes back to the question, with a liquid boiling under certain circumstances, what are the sizes and quantity of droplets ejected into the vapor stream? What is the terminal velocity of fall of the largest and the smallest drops? With a certain vapor velocity up through the vapor space, how high should that space be to precipitate most of the drops inside the evaporator? For the fine ones that we cannot settle out by any means inside the evaporator, what type of entrainment separator are we going to use?

The entrainment separator is a subject about which absolutely nothing is known. In the Patent Office there are hundreds of designs of entrainment separators and not a bit of data on any of them.

When we begin to put this evaporator on paper, almost every line the draftsman draws raises questions. Let us suppose that we have determined the number of tubes and the proportions of those tubes we want for the heating surface. How thick should the tube sheets be? There is no method for analyzing the thickness of a tube sheet. With our "by-guess and by-gosh methods" we have had no failures; but on the other hand, we do not know whether our factor of safety in the thickness of tube sheets is 20 or 100%.

What should the slope of the bottom be in order that the salt shall not stick to it? What should be the size and speed of the propeller, and what horsepower will it take? We went to marine engineers and they said, "We can tell you exactly what power the propeller is going to take." They looked at the problem, and the longer they looked, the less they knew about it; finally they said, "We have not the slightest idea about how much power this propeller will take because the conditions in this evaporator are totally different from ship propulsion."

We do not even know what the proper design of that propeller should be. We do not know what the pitch should be, what the speed should be, or anything else about it for best performance on this service. As a matter of fact, based on the most accurate information we could get both from the makers of propellers and from marine engineers, we used 35 horsepower motors, ran the propellers up to 120 r.p.m. and found that, when we got them to that speed, 85 horsepower was being consumed. And now after two or three months of operation (stepped down to 80 r.p.m. to get within the range of our 35-horsepower motors) we have tried speeding them up to 110 r.p.m. and find they take only 50 horsepower. What is the answer? I do not know. Neither do I know how one decides what the displacement of such a propeller should be in order to give a certain minimum desired velocity up through the tubes.

There are more questions even simpler than the preceding. The draftsman starts out to design the rings that the body is made of, and the first question he asks is, "How wide and how thick should these flanges be?" You cannot analyze a flange. Attempts have been made to do so by considering a section of the flange as a beam with the bolt pressure on one end and the gasket pressure on the other. That is all right if you are concerned merely with how thick the flange should be to resist the bending moment where it joins the body. But in vacuum apparatus we have other problems. How wide a gasket should you use on a big ring to make it vacuum-tight? We know that gaskets of a certain width hold, but we do not know whether that is wide enough or twice as wide as we need.

The analysis of a flange, assuming it to be a beam between the bolt and the body, does not take into consideration the distortion of the flange between bolts, and a heavy cast-iron flange can spring between two bolts if those bolts are too widely spaced. We say we will put them "about so close together" and that is about all we know. For instance, my own rule is that the center-to-center distance of the bolts along the flange should not be over $3^1/_2$ inches, but I do not know how safe that is. I know that if they are $3^1/_2$ inches on centers, I can keep that flange tight to vacuum but I do not know whether $4^1/_2$ inches would be safe or not. I know that 8 inches is not safe, and that a heavy cast-iron flange will distort enough between bolts on 8-inch centers to cause leak between the bolts.

If you are designing pressure apparatus, there are elaborate formulas for determining the weight of the flange, the weight of the bolting, etc. You will find that all those formulas involve the coefficient of friction between the gasket and the metal surface. What is that coefficient? The handbook will say, "Assume that coefficient is 0.2." But who knows? And fifty-seven different varieties of gaskets are used in the chemical industry.

Many of these problems can be answered only by experience on full-scale equipment. On the other hand, many of them can be handled by research programs in industrial laboratories. The principal reason why more of this work has not been done in the past is that so few of the young men who are directing research in university laboratories have had contact with these practical problems.

PROBLEMS FOR RESEARCH

One of the things that we should be able to look forward to in the near future is plastic tubing that will leave us free from fittings, will be soft enough to bend around corners, and will give a smooth inside surface so as to reduce friction to the minimum. A start has been made along those lines, but we are a long way from substituting plastics for ordinary iron pipe.

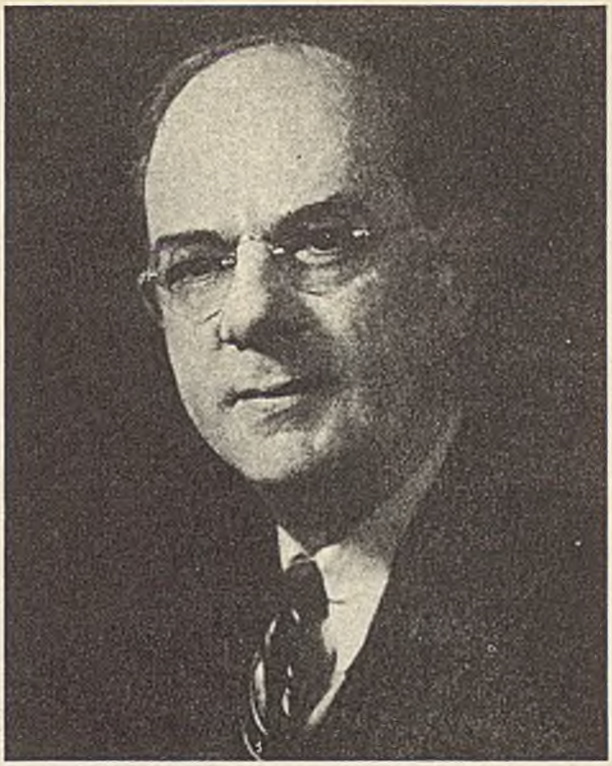
A valve for special materials is needed. The chemical engineer has to use all kinds of construction material. It is true that the great bulk of the equipment we use is made with iron and steel, or some modifications of iron, but there is a great number of places where we have to use plastic or rubber, stoneware, etc. Those who have not been in contact with the engineering side of these problems probably do not realize that except for those cases where we can use iron or steel or brass, there is no such thing as a valve—no good way of controlling the flow of liquids. There are constructions that can be used, but they are not engineering solutions.

Another continual problem is the stuffing box of pumps. If you are pumping clear water, with no particular abrasive or corrosive material, there is not much difficulty. But when you consider the wide range of corrosive materials, of abrasive materials, the wide range of temperatures and pressures under which we have to work nowadays, pump stuffing boxes are a problem.

When will somebody build a pump in which the rotor of a squirrel cage motor is on the rotor of the pump, the stator is on the outside of the pump, and the casing comes in between so that we have no stuffing boxes? Somebody will do it some day. Such a pump will give very poor efficiency; but in some cases where we are pumping difficult liquids and the corrosion problems are extreme, we would be glad to sacrifice efficiency for tightness.

A much wider use of high-temperature heat transfer of fluids is to be expected. In the case of heat flow in general, one of the problems to be worked out is the rate of condensation of steam inside pipes. We have various formulas for the condensation of steam on the outside of pipes; but nobody has ever tackled, experimentally or theoretically, the problem of steam condensation inside pipes. I know just enough about it to realize that any heating coil ever designed was probably too long, and the steam is condensed before it reaches the end. But there is not a scrap of information in the literature on that point.

Another question is the condition of surfaces and their relation to rates of heat transfer. How far are we justified in trying to get exceedingly smooth surfaces? And how smooth is a smooth surface? Methods are available by which the profile of surfaces can be determined accurately; but nobody has tried to correlate the readings of that instrument with rates of heat transfer to predict whether highly polished, smooth surfaces would have any advantages. We do know that tremendous advantage would accrue if we could get dropwise condensation of steam, but except in a few isolated instances we do not know how to control even that. It is probable that most heat transfer equipment would be improved from 10 to 100% in capacity if we could always assure only dropwise condensation on the surface.



W. L. Badger

Why does salt stick to a surface? Is there any relation between the rate at which the salt is formed, the temperature gradient to the surface of the metal, the smoothness of the metal, the shape of the solubility curve of the salt, and the rate at which it grows on the surface?

We know very little about the entrainment problem. We know nothing about the amount of liquid that is ejected from a boiling surface, the relative size of the drops, or the relation of the size of those drops to the properties of the liquid, its velocity, and the distance below the surface at which the bubble forms. When you realize that in many evaporation operations we must keep the solid content of the condensate down to a few parts per million, this problem amounts to a good deal. For instance, in a certain caustic evaporator with which I am familiar, if we let the caustic in the condensate go above 40 p.p.m. the loss is altogether too great.

CONCLUSION

I have tried to put across two ideas: First, from a historical analysis of the way progress in unit operations has gone on, you can make some kind of a guess as to what sort of progress we may expect in the near future. Secondly, I have tried to ask a lot of questions to illustrate how full of holes our present knowledge of even well understood unit operations is, and how much is left to be done by the research laboratories that should be working on such problems.

TECHNOLOGY and INDUSTRIAL MANAGEMENT

RALPH E. FLANDERS

JONES & LAMSON MACHINE COMPANY, SPRINGFIELD, VT.

HAVING had a lifetime of experience in the field of mechanical engineering, I cannot speak with assurance in the field of chemical engineering and research. I can only hope that there is enough similarity between the two fields to make such observations as I can offer suggestive, if not directly informative.

The progress of invention and commercial exploitation has been steadily from rule-of-thumb and empirical methods to a greater dependence on rigorous scientific investigation. This is particularly true of the older fields. No industry with a century or so of history (for example, the making of rubber products, dyes, or prime movers of any sort) can maintain itself competitively without the best scientific foundation and continuous research.

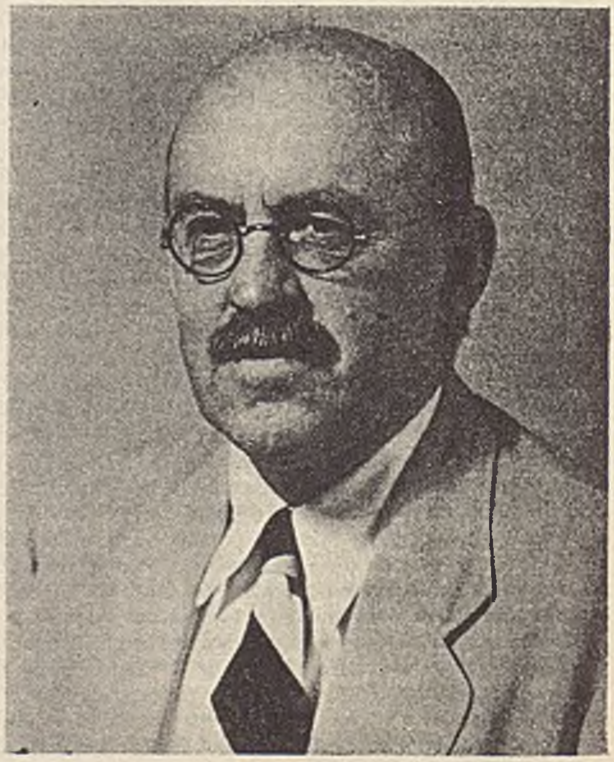
This does not mean that the garret inventor is out of date. In the fields with which I am best acquainted, new ideas of apparent value are still coming from the brain of the individual. Without doubt it is still true that in the older fields brilliant new ideas are born in the minds of brilliant individuals. In general, however, the mature field is best cultivated for new developments with the tools of organized scientific research. As a result, it is natural, inevitable, and even, probably, socially desirable that these mature fields should be occupied by larger organizations, while younger and more restricted areas still offer rich rewards for individual initiative.

For large-scale research we have new tools and new opportunities. We have more trained men and women than ever before. We have new calculating mechanisms for mathematical analysis which make both the impossible and the impracticably possible, practicably possible. The whole science of applied mathematics has made leaps ahead in the past few years; the pure mathematician who disdains those branches of his science which have practical application long ago heard the baying of the engineering hounds on his trail and, of late, has felt their hot breath on the back of his neck. Is there still left any large area of mathematics of which we can say that it has no possibility of practical application?

The very accumulation of literature and the organization of libraries facilitate the progress of research, whether organized or individual; the war with its throwing together of large numbers of men in the attack on common problems has furnished a stimulus of personal contact which works to the same end of accelerating the pace of research. For the time being, at least, the results obtained in the last few years are not appearing in their end results of products for public use. The restrictions put on production for other than war purposes in this time of war are, of course, the controlling factor, but much is being dammed up for postwar release.

Even after the war, the placing on the market of spectacular new products may not meet the public expectation. In many products, notably in the case of automobiles, the requirements are going to be so large and so pressing that there will be no time to revise plants and invest in new facilities for radically new products. The public demand will be overwhelmingly for large production in quantities of satisfactory goods, and that can be met only by producing the best type of prewar goods in heavy volume. The existence of this pent-up demand for immediate production will be a fortunate circumstance, since it will allow a breathing spell in which new designs, based on new discoveries, can be made and put into marketable form; in which pilot plants can be built, and the products tested in service before large-scale manufacture is undertaken. We may look, therefore, for a postwar lag in the introduction of the radically new in most lines of manufacture. This necessity for lag is often misunderstood by the public. There may have been some cases in which inventions were held back from public offering for a longer time than the public interest required, because the manufacture and sale of the old have represented a highly profitable return on a heavy investment. This factor must, however, be taken into account in any business which expects to survive. Without knowing whether a parallel holds between my own business of machine tools and that of the wide variety of chemical products, I venture to state the case of machine tool improvements, nevertheless.

A machine design being brought to completion on the drafting board never arrives at its absolutely finished form. Day by day, week by week, month after month, new and good ideas can be incorporated in it. Yet the time comes when, almost brutally, the process of improvement must be shut off if purchasers are to get the benefit of the new ideas and the producer is to realize any profit from the new undertaking. Inability to close off and



Ralph E. Flanders

button up a line of development and research has ruined more than one hopeful undertaking.

After the machine is on the market and has come into general use, it is necessary to make some changes from time to time, and the temptation continuously exists to make these improvements continuously and on a large scale. Here again, business judgment requires that these changes be not so large or so many as to imperil the possibility of profit in the production of the machine. Good management requires that the improvements be incorporated, in general, in a series of accumulated changes in design, each series of which is brought onto the market after its predecessor has brought in enough profit to finance the change.

A company which does not keep the improvements resulting from invention and research under control in this way in their commercial application is almost sure to get into financial difficulties. Occasions do occur, however, in which competing companies have brought out machines or products so far in advance that changes are insistently required before they are financially warranted. Such conditions represent an emergency, of a frequent sort, indeed, but outside of the steady course of good business management. These holdings-back of new ideas and their release in accumulations at infrequent periods may give to the public the appearance of holding inventions arbitrarily out of use. Such practice is not censurable in the long run, whether from the interest of manufacturer or general public.

In general, when management faces the problem of research, it must keep the following points in mind: First, it must be willing to have only the occasional research project turn up commercial possibilities; there will be many duds. Second, it must be prepared to look at the results with imagination. Frequently something new and valuable has turned up which is a little outside of the result being sought; a shift of viewpoint is required for proper appreciation. Third, the results of successful research must be put into commercial exploitation at the proper time. This time will be neither too early to allow a satisfactory product to be put on the market, nor so late that markets have been lost and large sums spent in the endeavor to reach an unattainable perfection.

ACCOUNTING and FINANCIAL PROBLEMS

DANIEL M. SHEEHAN

MONSANTO CHEMICAL COMPANY, ST. LOUIS, MO.

THE technical, production, and research problems of the postwar period are closely related to, and will directly affect, many of the accounting and financial problems with which the chemical industry will be faced in that period of postwar adjustment. Those problems, which are now in the making, affect the industry as a whole as well as individual companies. In many respects they are similar to problems to be faced by all business, but this discussion will touch particularly on their relation to the chemical industry.

The problems of business after the war will, to a considerable extent, be dependent upon the type of economic system then prevailing. Notwithstanding the rigid restrictions under which we have been placed as a result of the war and the socialistic leanings of some of the officials in power in Washington, most of us feel confident that our democratic form of government and system of free enterprise will continue with the return of peace. There seems to be a trend in national politics toward more conservative ideas and to a greater recognition of the necessity for a system of free enterprise with the profit motive necessary to cultivate initiative and sustain ambition on the part of business men generally. The country's experience with production for war purposes has clearly demonstrated the superiority of organizations developed under the American system of private enterprise. On the other hand, it is probably true that business as a whole may expect certain types of government regulation after the war.

Great opportunities should be presented to many types of business, and the chemical industry is well up on the list of those which will benefit from the technical developments made during the war. In the coming period of keen competition for markets there will be a greater need for, and realization of, the importance of good accounting practices and procedures and sound financing. Accounting is said to be the language of business in that it is the means of expressing the results of its operations and financial position, and of effecting means of executive control over various types of operation. As technicians and business men, each of us should be vitally interested in accounting problems as they affect our particular activity as well as that of the company as a whole.

Although the problems of reconversion to peacetime activities will not be so great in the chemical industry as in many others, we shall nevertheless be faced with the necessity of finding uses for, and working capital with which to operate, temporarily overexpanded plants and plants to be acquired from the Government. In some instances funds must be provided for repairing and rebuilding worn out plants which, because of the exigencies of war, have not been fully maintained. The construction of plants and the working capital needed for the manufacture of new products will also require funds. Some of the additional money needed for working capital probably will be supplied by bank loans; but those which may be required for investment in plant should not be so temporary in nature and will probably be obtained from the sale of stock or other public financing. The experience of the chemical industry is that an exceptionally high investment in plant is required for each dollar of sales, an indication of the desirability of permanent financing. The selection of the type of permanent financing as between common or preferred stock will depend to a great extent on the present corporate structure of the individual company.

ACCOUNTING PROBLEMS

RECONVERSION. One of the important problems which will arise in the postwar period is connected with the reconversion of plants used for war purposes, many of which have been constructed and operated for the Government. Aside from the matter of valuation of such plants as may be acquired by the companies which have been operating them, there will be problems occasioned by temporary inability to use productively all facilities which may be acquired or which are owned. Obviously,

Daniel M. Sheehan

costs should be charged only with depreciation and other fixed expenses applicable to facilities used in production. The cost of carrying plant and equipment not so used must be charged against income, and therefore in considering margins of profit an effort must be made to provide sufficient income to absorb such charges.

Costs of Products from Amortized Plants. During the war period certain plant facilities have been constructed under so-called Certificates of Necessity, which permit amortization of the cost of these facilities over the war or emergency period. Thus facilities of considerable value will be available for production; but as a result of amortization of their cost over the war period, they may be carried in the accounts at little or no value. The calculation of costs used in the determination of selling prices must necessarily include provision for depreciation of the cost or fair value of such facilities. From an accounting viewpoint this probably will entail the charging to operations of a proper provision for depreciation of such facilities, with an offsetting credit to income so as to nullify the effect on net income of the provision for depreciation of this fully depreciated property.

Capital Expenditures. Substantial additions to property have been made during the war period, and in many cases little consideration has been given to these costs; the primary consideration has been to construct productive facilities in the quickest possible time. General wage levels and other items also have tended to increase such costs unduly. With the return of normal conditions, good management will require that careful consideration be given to expenditures for plant property to be assured that they are in amounts which will permit adequate return on the investment. It also will be important that careful control be exercised over expenditures for additions or betterments to property to be assured that actual performance is in line with estimates on which authority for the work was based, or to be satisfied that there are good reasons for variations of consequential amount. Records should be maintained showing not only the accumulated cost of the various additions and betterments to property, but also a comparison of the cost with estimates previously prepared. These records should be the basis of monthly reports to the management and to operating officials.

Receivables. Under present conditions losses from uncollectible accounts of customers are relatively small, and the delinquent accounts are less than usual. Notwithstanding this fact, it is sound policy to continue to make provisions for uncollectible accounts by charges to current income so as to build up reserves adequate to provide for losses, which may result after cessation of hostilities, from accounts originating during that period. Even though credit departments carefully watch the extension of credit, it is probable that losses from uncollectible accounts will be suffered during the postwar period which are properly chargeable against reserves now being provided. The extension of credit during the postwar period undoubtedly will require greater diligence on the part of credit departments, because for a time at least, the financial condition of some companies may make them poor credit risks.

INVENTORIES

Inventories are one of the largest of current assets of the average chemical company. Their size alone makes it important that every reasonable control be exercised to keep them properly balanced so that losses due to decline in values, which may occur at the end of the war, will be as small as possible. After the war many companies will be faced with problems arising from the disposition of products useful only in the prosecution of the war. There will also be the problem of disposing of inventories which, by reason of the discovery of processes for improvement in old products or in the development of new ones, will have become obsolete and must be sold at less than usual prices. A company should anticipate such a situation in the postwar period and pursue policies of inventory valuation which will place it in a position at the end of the emergency of having made adequate provision for such losses. With a view to minimizing losses which might occur by reason of decline in market prices, two methods of accounting suggest themselves. Reserves may be provided by charges to current income, or the "last-in first-out" method of valuing all or a portion of the inventories may be adopted. Generally speaking, the latter permits the charging against current production of materials at their most recent purchase cost and thus tends to keep the inventory value low. Unlike the reserve method of keeping inventories conservatively valued, the last-in first-out method is acceptable for income tax purposes and thus is a great advantage at present in view of the exceedingly high tax rates.

RESERVES

Recognition is being given to the creation of reserves for extraordinary expenses and contingencies arising as a result of present conditions and those likely to follow. The necessity for creating such reserves presents a problem which is ably discussed in an Accounting Research Bulletin of the American Institute of Accountants, from which I quote:

> The existing situation presents in acute form the problem of reconciling two basic accounting objectives; first, that of bringing charges as nearly as may be into the same accounting period as the revenue against which they are fairly applicable, and secondly, that of basing accounting entries as far as possible on objective evidence or on estimates of a reasonably definite character. In general, the committee believes that the first of these objectives should be regarded as the more essential; but this conclusion does not warrant the presentation of figures in which amounts determined with a reasonable degree of accuracy, and in accordance with accepted accounting principles, are combined indistinguishably with others representing mere conjecture.
>
> While no attempt is made in this bulletin to classify specific reserves, they fall, for accounting purposes, into two groups: (*a*) those reserves or parts of reserves which must be provided in order to conform to accepted principles of accounting, and (*b*) those additional reserves or parts of reserves which are created in the discretion of

management as a matter of conservative business administration, but are not presently determinable within the limits necessary for definitive accounting statements. It has long been established in accounting that reserves may not be used for the purpose of arbitrarily equalizing the reported income of different accounting periods.

Among the reserves for postwar purposes, listed in this Accounting Research Bulletin, are:

> Accelerated depreciation of facilities as a result of intensive use and of operation by less experienced personnel.
>
> Accelerated obsolescence of facilities due to intensive research during the war in an effort to increase productive efficiency.
>
> Amortization of the cost of rearrangement and alteration of existing facilities which will probably be rearranged in the postwar period.
>
> Amortization of the cost of additional facilities acquired, the usefulness of which is expected to be substantially reduced at the termination of the war.
>
> Losses which may be sustained at the end of the war in the disposal of inventories useful only for war purposes, or in the adjustment of purchase commitments then open, including any amounts which may be paid for the cancellation of such commitments.
>
> Losses which may be sustained in the disposal of inventories not necessarily applicable to war production, due to decline in the price level, which, on the basis of past experience, usually follows a pronounced rise in prices.
>
> Repairs and maintenance deferred as a result of pressure for war production.
>
> Separation allowances which may be paid to employees who are discharged at the termination of the war.

It is important that both business and government recognize the necessity for such reserves. The Government should make a provision in the tax laws to allow as deductions, provisions for reserves of this kind. Certainly some method should be devised to allow charging against war income, costs which are related to and result from the creation of such income. Personally, I am opposed to contingency reserves unless there are definite reasons for their creation, and believe that in such instances the reserves should be charged only with expenses or losses of the nature for which they were provided.

BUDGETS AND CONTROL OF EXPENSES

As a means of controlling all types of costs, budgets will come into even more general use in the postwar period. They will be used, not only in measuring the effectiveness of the sales force, but in controlling production, research, and general expenses. Such budgets should be prepared on a departmental basis and monthly comparisons should be made with actual expenses.

One of the most difficult tasks, and probably one of the most important, which will confront businessmen generally in the postwar period will be the return of expense consciousness. During the war economy has, in many instances, been subordinated to expediency in the conduct of business, with the result that expenses have spiraled. High taxes also have been a contributing factor to this disregard of the cost of doing business. The strong competition which probably will result in the scramble for markets after the return of peace will make it more important than ever that costs be carefully controlled. The effectiveness of the control may mean the difference between profit and loss from operation of the business, particularly in instances where the margin of profit is small.

Sales managers should review more closely the expenses of their sales forces with a view to determining those which are essential and those which may be curtailed without affecting the volume of business secured. Selling costs will have to be considered more carefully in the determination of market prices of goods to be sold.

Production costs, both those of a direct and indirect nature, must receive careful scrutiny by those in charge of production, and variations from standard costs must be promptly investigated with a view to correcting conditions due to inefficiency or extravagant expenditures. One source of high costs, which should disappear to a great extent with the return of peace (and before if possible), is that occasioned by the payment of considerable amounts of overtime premiums for work in excess of 40 hours weekly. In addition to the extra cash outlays required, which in themselves increase the cost of production, there is little doubt that the productivity of the individual is adversely affected by longer working hours. Both of these factors increase unit costs of production. In connection with production, cost departments will be faced early in the postwar period with the determination of costs of new products and revision of those of old products by reason of new processes developed as a result of research, both during and after the war. Administrative and general expenses will be subject to the same type of control and scrutiny as those of other departments of the business.

Because of the large amount normally expended for research by chemical companies, and of the probable additional expenditures which will be made in developing products and processes as a result of development during the war period and of the effort to secure new markets, it will be necessary to exercise careful control over expenditures for research. Such control is not intended as a restriction upon the initiative or resourcefulness of research departments, but will be for the purpose of ascertaining that the proper amount is expended on each project in the program commensurate with its importance to all other projects. It is not my intention to imply that such controls shall be carried to unreasonable extremes or that they be such as to restrict necessary activities. I do want to emphasize that expense control in the postwar period will be essential to successful business management.

TERMINATION OF WAR CONTRACTS

In addition to renegotiation of war contracts, we will be faced with many problems arising from the cancellation of contracts by the Government. This problem is already receiving considerable attention. It will be to the advantage of companies having war contracts to give serious consideration to problems which are likely to develop as a result of termination. Proper planning should do much to facilitate satisfactory and prompt settlements.

The cancellation of important contracts, either before or upon cessation of hostilities, may leave some companies with large inventories which cannot be liquidated for some time. To meet this situation, consideration should be given to the advisability of negotiation with banks for VT loans. Such loans would provide additional working capital to tide the company over what might otherwise be a critical period, occasioned either by delay in settlement with the Government or liquidation of inventories.

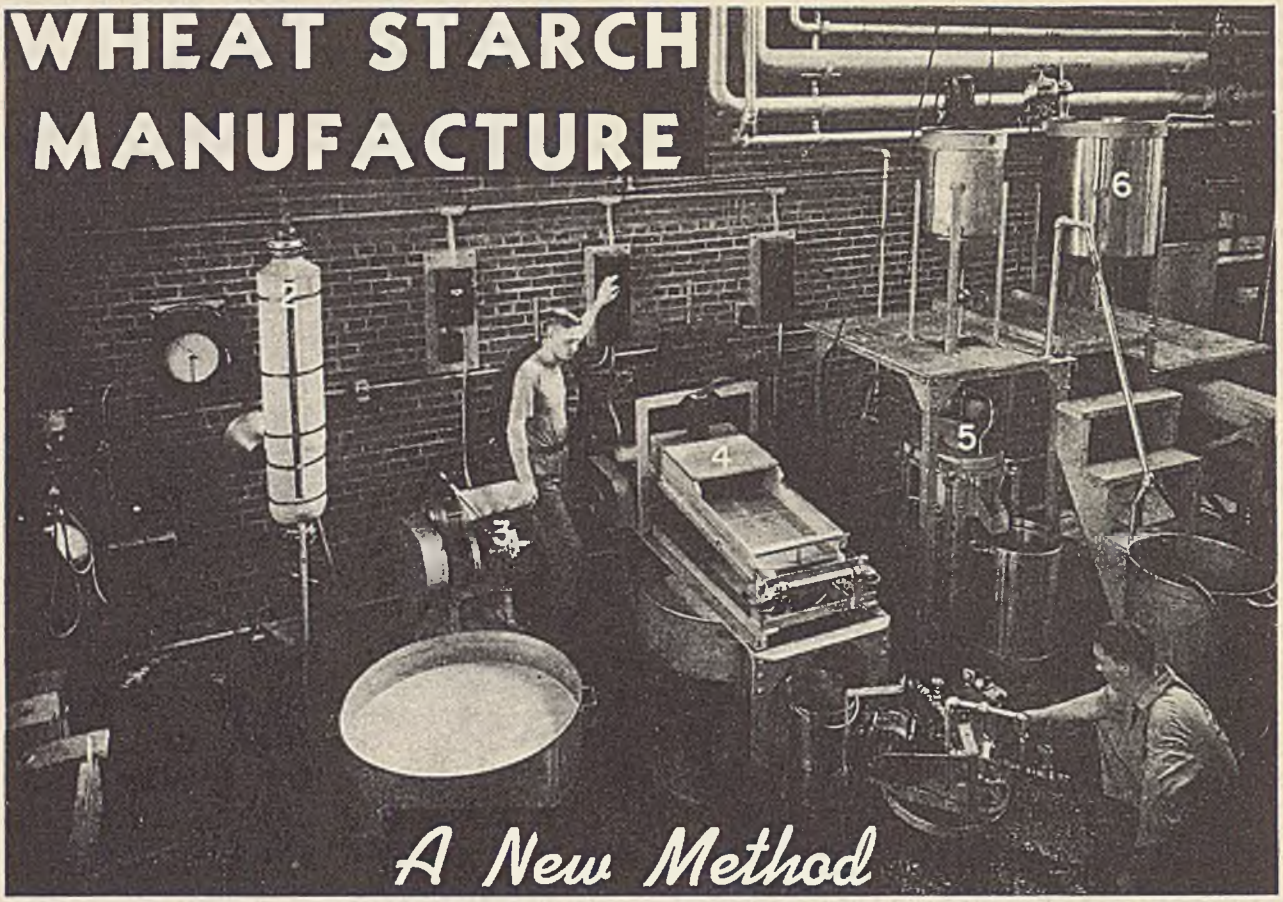
CONCLUSION

Because of the continued growth of chemical industry, the forecasting of financial requirements will be of vital importance to the management of chemical companies. The effect of the present high taxes on income is a serious problem to business and financial management. These taxes leave little for distribution to stockholders and for building up a surplus which may be needed to meet unforeseen contingencies of the postwar period and possible temporary reduction in the volume or profitableness of business. That such taxes are necessary to meet the tremendous cost of the war cannot be questioned, but all of us should be alert to impress upon those with whom we come in contact the importance of strict control of government expenditures and waste. It is also appropriate to stress the need for simplification of tax laws.

Some of the postwar problems cannot be foreseen but a great many can be anticipated. To that extent every action necessary should be taken at this time to provide for them and to place business in a strong position to meet the uncertainties of that period.

WHEAT STARCH MANUFACTURE

A New Method



THE STARCH PILOT PLANT (ABOVE) SHOWS THE FOLLOWING, FROM LEFT TO RIGHT: (1) HEAD OF STARCH TABLE, 46 FEET LONG; (2) STEEP TANK; (3) ATTRITION MILL; (4) VIBRATING SCREENS; (5) BUHRSTONE MILL; (6) A TANK FOR MILL STARCH; AND ACCESSORY EQUIPMENT.

Richard L. Slotter and
Cecil T. Langford
NORTHERN REGIONAL RESEARCH LABORATORY,
U. S. DEPARTMENT OF AGRICULTURE, PEORIA, ILL.

AS THIS is written, there is a surplus of wheat in the United States, but the quantity of corn reaching the market is rapidly becoming restricted. Both of these grains are used principally as food and feed, but corn has several important industrial uses, notably in the manufacture of starch and its conversion products, sirup and sugar. Owing to the shortage of molasses and to the increased demand for alcohol, corn and wheat are now being used for the production of industrial alcohol. Any further substitution of wheat for corn in industry is therefore of considerable importance at this time.

The new method of wheat processing developed at the Northern Regional Research Laboratory is of interest because it may be carried out with practically the same equipment as that regularly used in the wet milling of corn. If the present shortage of corn should deplete the supply available to starch manufacturers, they could, with only a slight additional investment and minor changes in plant equipment, utilize wheat for the production of starch. Furthermore, wheat which has been stored for some time, or is unsuitable for flour, can be utilized for the manufacture of starch and other products by this new method.

Through the ages several methods of manufacturing wheat starch have been evolved. According to Eynon and Lane (*1*) these methods differ chiefly in the processes employed for obtaining the raw starch; in respect to the purification of the starch they have much in common. The oldest method for extracting the starch is the so-called Halle or fermentation process in which the grain, softened by steeping in water, is crushed between rollers and then made into a mash with water and allowed to ferment for a week or two. This so modifies the properties of the gluten that it no longer interferes seriously with the washing out of the starch. A second method, known as the Alsatian process, consists in steeping and grinding the grain and washing out the starch without previous fermentation. A third and now the most important method, Martin's process, employs wheat flour instead of whole wheat and involves essentially the washing out of starch from a dough made up of flour and the proper quantity of water. Another method which employs wheat flour as raw material is Fesca's thin-mash process. The flour is not formed into dough but is mixed with water, and at once treated in a centrifuge to separate the starch from the other constituents of the flour.

Inasmuch as soft white wheats are normally high in starch content, it was concluded that such a type would be more readily amenable to processing for the extraction of starch. The critical temperatures at which the starch granules from such wheat will disintegrate and the degree of disintegration were determined by microscopic examination. A portion of the floury endosperm was scraped from a number of kernels of Dawson variety soft white winter wheat (1941 crop) into a test tube containing water. The resulting suspension was heated slowly in a water bath; samples were removed periodically and examined under the microscope. The following observations, made at increasing temperatures, show that processing temperatures should not exceed a maximum of 103° F. if gelatinization is to be avoided:

First indications of gelatinization	104° F.
Gelatinization definitely initiated	108
Structural detail very distinct in large granules	129
Few of largest granules completely gelatinized and showing incipient folding	131
Folding or denting common on large granules	135
All but smallest granules gelatinized	142
Gelatinization complete	146

LABORATORY EXPERIMENTS

Experiments were carried out to determine if the whole wheat kernel can be processed for the extraction of starch in a manner somewhat analogous to that for corn. Processing was conducted as outlined in the laboratory-scale flow diagram shown in Figure 1. A charge of 908 grams of soft white winter wheat, Dawson variety, was placed in the steep tank of the steeping system shown in Figure 2. Distilled water was added to about twice the height of the wheat in the steep tank. The water was circulated by a pump through the coils in the thermoregulated heating bath and back to the steep tank. Sulfur dioxide was added to the water until its odor was detected at the vent. After the wheat had been steeped in this system for 24 hours at 100° F., the steep water was drained off and the wheat was ground several times in a power-driven, laboratory, chemical and drug mill, using distilled water as a grinding lubricant. The pulpy mass was then screened through a perforated copper plate, the openings in which had a diameter of 0.0394 inch. Coarse fibers were retained on the copper plate, and the slurry which passed through it was screened over No. 17 standard silk bolting cloth. Fine fibers were retained on the silk. The fiber fractions were thoroughly washed with distilled water for the purpose of removing starch and gluten. The washings were combined with the suspension of starch and gluten which had passed through both screens. The resulting liquor, known as mill starch, was then allowed to flow down an inclined trough or table, where the starch settled out on the bottom of the trough and the gluten suspension flowed off at the lower end. The gluten exhibited no dough-forming characteristics. The starch table used in the initial experiments was a wooden trough, 12 feet long, 4 inches wide, and 4 inches deep. This was later replaced by a table 16 feet long, 2.5 inches wide, and 2.5 inches deep. The starch was flushed from the table with distilled water, and the suspension was screened through No. 17 standard silk bolting cloth and filtered. The starch was washed and dried. The finished starch was excellent in color, and had a total protein content of 0.28%.

Since a good separation of starch was obtained, the experiment was repeated with the same wheat. Complete initial separation was again effected on the starch table. The experiment was repeated a third time with Rex, another variety of soft white wheat. Again there was complete separation on the table, and the yield of starch was greater than in the two previous runs. From 908 grams of wheat charged to the steep, 400 grams of starch were recovered, a yield equivalent to 26.5 pounds of starch per bushel of wheat. Companies manufacturing wheat starch in the United States use wheat flour as a raw material. According to the U. S. Tariff Commission (*3*), the yield obtained by them is equivalent to 22 pounds of starch per bushel of wheat, assuming that 42.5 pounds of flour are obtained from a bushel. Therefore the laboratory yield was well above industrial yields.

EFFECT OF SULFUR DIOXIDE. A series of experiments was conducted with the small-scale laboratory apparatus to study the effect of sulfur dioxide on the ease of processing and on the quality of the finished starch. All samples were steeped 24 hours at approximately 101° F. but with varying concentrations of sulfur dioxide. Since the steeping period was relatively short, the temperature was increased to a value just below the gelatinization temperature of wheat starch. In these experiments the steep water was introduced into the tank and circulated through the heating coils until a temperature of 101° F. was reached. Sulfur dioxide was then added until the desired concentration was obtained. The sample of grain was introduced and steeped for 24 hours. The experimental procedure was essentially the same as that previously described for the small-scale laboratory processing. In all cases the steeped grain was ground twice, and the fiber fractions were washed with the same amounts of water. The gravity of the mill starch liquor was adjusted in all experiments to 2° Baumé at 100° F. and was tabled at 100° F. The results of these experiments are shown in Table I.

It is obvious that the process may be conducted with varying concentrations of sulfur dioxide in the steep water. However, at a very low concentration of sulfur dioxide many difficulties in processing and separations are encountered. It is conceivable that at high concentrations—namely, 0.5 gram sulfur dioxide per 100 cc. or above, which are economically and practically unsound—a modification of the starch due to acid hydrolysis with a consequent decrease in viscosity probably would result. Therefore, it is apparent that the optimum operating conditions will lie well within the range of concentrations covered by these data.

PILOT-PLANT EXPERIMENTS

Pilot-plant experiments have been carried out on 60-pound batches of wheat. A photograph of the plant is shown on page 404. The steep tank is a large glass vessel with a capacity of slightly more than one bushel of grain; and the steeping procedure is similar to that used in the small-scale laboratory apparatus. The wheat is steeped for approximately 24 hours at about 100° F.; then it is ground in a 16-inch buhrstone mill with the addition of distilled water for a grinding lubricant.

In the initial pilot-plant runs the steeped wheat was ground in an attrition mill which is normally used for grinding steeped corn, but the mill could not be adjusted properly for grinding wheat; hence the results were not entirely satisfactory. However, an attempt was made to separate the germs from the ground wheat by gently agitating the slurry in a germ separator which had been used with fair success in the analogous operation with corn. Less than half of the germs, together with some of the fiber, was separated by flotation. The density of the germ after steeping was found to be less than that of water; hence, the poor separation of the wheat germs was due principally to poor grinding and to the inadequacy of the germ separator. A new separator, more nearly like those used in the wet milling industry, is being constructed. However, it is difficult to assimilate a continuous industrial germ separator and utilize it in a batch operation. In an industrial plant optimum conditions for floating the wheat germ can probably be attained in continuous processing. Kaffir grain has been successfully processed in wet milling equipment, and wheat germs are about the same size as kaffir germs. In subsequent experiments with wheat the attrition mill was not used, but the steeped wheat was ground in the buhrstone mill and no effort was made to separate the germs.

The slurry from the buhrstone mill is screened over a 26-mesh stainless steel wire gauze, and the material which passes through is screened over No. 17 standard silk bolting cloth in a Rotex screener. The fractions retained on these screens are washed twice with distilled water. The suspension of starch and gluten from the original screening is combined with the wash waters and the resulting mill starch is allowed to flow over a starch table 46 feet long. Starch settles out satisfactorily and the gluten suspension flows over the end of the table. A thin layer of gluten is removed from the surface of the settled starch by playing a stream of air carefully over the table. Some starch is removed at the same time. This fraction is known as squeegee starch and would be returned to the mill starch for retabling in continuous plant operation. The starch is removed, suspended in water, and screened over No. 17 standard silk bolting cloth

A process is developed for extracting starch and other products from the whole wheat kernel which is analogous to the process used in the wet milling of corn. The quality of the starch from sound wheat is excellent. The starch may be converted to sirups and sugar by methods used in the conversion of cornstarch. Good starch can be extracted from damaged wheat which is otherwise unsuitable for food or feed. Pilot-plant operating data are given for typical runs using wheat; similar data are presented for processing corn.

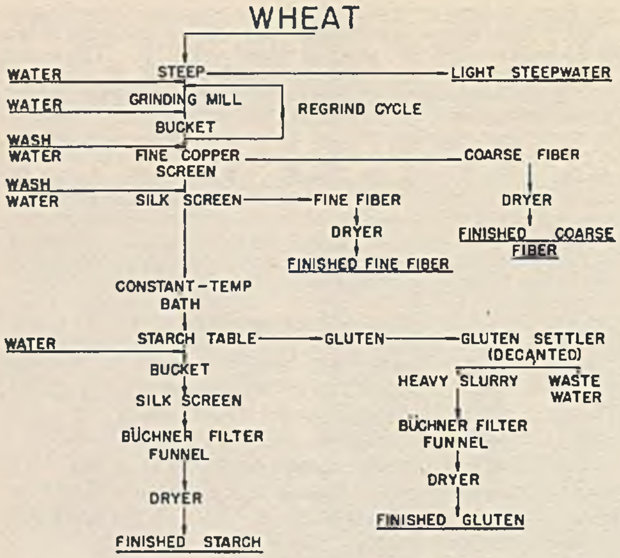


Figure 1. Flow Sheet for Wet Milling of Wheat on a Laboratory Scale

to remove small quantities of fiber and dirt. The slurry is centrifuged and the starch, after being washed, is dried at 165° F. in a Proctor & Schwartz convection oven.

The gluten is allowed to settle and the clear supernatant liquid is decanted. The thick gluten slurry is centrifuged, and the cake is placed in pans and dried in a Hurricane convection dryer at 180° F. The coarse and fine fiber fractions, retained on the wire screen and silk bolting cloth, respectively, are combined and dried at 180° F. in the Hurricane dryer. The gluten settler water and the wash water from the starch are combined and sampled before being discarded as waste water. The steep water is also sampled before it is discarded.

Although many samples of both wheat and corn have been processed in the pilot plant, representative data for four wheat runs are given in Table II, together with data for one of the best corn runs for purposes of comparison. Thatcher wheat is a hard red variety, while Dawson is soft white. Three runs on the soft variety are included because of differences in processing conditions, notably in the sulfur dioxide concentration in the steep water, in the mill starch, and in the pH of the latter. Corn processing differs from wheat processing chiefly in the time and temperature of steeping. The 46-hour steeping period at 125° F. conforms with usual industrial practice for corn. Even though the steeping temperature must be reduced for wheat to avoid gelatinization of the starch, the time required is only approximately half that necessary for steeping corn.

Compositions and amounts of products are given on a dry basis which is the usual practice in the starch industry. Moisture determinations on the wheat grain were made by utilizing the Brabender moisture tester for 1.5 hours at 130° C. The moisture tests on the fiber fractions were also made in the Brabender apparatus but by heating for 1 hour at 130° C. Moisture in the starch was determined by drying the samples in a vacuum oven at 105° C. for 20 hours. Gluten samples were dried in a vacuum oven at 105° C. for 6 hours.

The Kjeldahl-Gunning-Arnold method was used for determining nitrogen, and in the case of wheat the results were multiplied by 5.7 in order to calculate the wheat protein content of various samples. In the case of corn the factor 6.25 was used.

Starch in the wheat was determined polarimetrically by the method suggested by Hopkins (*2*). The viscosities reported in Table I were measured by the Stormer viscometer. Starch was suspended in the calculated amount of distilled water to give a suspension containing 2% of dry starch. Allowance was made for evaporation. This suspension was heated in a water bath for ten minutes and then transferred at once to the viscometer cup and brought to 90° C. A reading was taken immediately and at one minute intervals thereafter for ten minutes, giving a total of eleven readings. The average of the eleven readings was used as the viscosity.

Aside from the processing data given, the points of chief interest shown in Table II are the recoveries and quality of the starch. In the run using corn, for which data are given, 87.2% of the starch contained in the grain was recovered as dry starch. This is the highest recovery of starch from corn obtained in the pilot plant. Average recoveries amount to 82–84%. The recoveries of starch from wheat are somewhat lower; however, yields as high as 80% have been obtained. It is felt that the low pilot-plant yields of starch are the result of the comparatively

Table I. Laboratory Starch Extractions from Dawson Soft White Wheat, 1941 Crop, Containing 12.81% Moisture and 60.60% Starch

Run Number	8	9	13	7	11	12
Grams of wheat used	908	908	908	908	908	908
Steeping time, hr.	24	24	24	24	24	24
Steeping temperature, ° F.	102	101	101	103	102	102
Gr. of steep water at 60° F., °Bé.	1.31	1.47	1.59	1.61	1.57	1.71
Grams SO_2/100 cc. steep water						
Beginning	0.056	0.098	0.195	0.296	0.401	0.493
End	0.025	0.036	0.105	0.182	0.261	0.342
pH at beginning	2.50	2.05	2.10	1.95	1.70	1.80
pH at end	5.45	4.65	3.80	3.30	2.81	2.60
Products accounted for, dry basis, grams						
Steep water solids	31	45	45	44	47	49
Coarse fiber	88	78	73	86	76	62
Fine fiber	22	30	32	22	29	35
Starch	395	403	403	401	406	407
Gluten	177	169	157	174	193	197
Total	713	725	710	727	751	750
Total in wheat	792	792	792	792	792	792
Products accounted for, %	90.0	91.5	89.6	91.8	94.6	94.6
Starch						
Extd., dry basis, grams	395	403	403	401	406	407
In wheat, dry basis, grams	550	550	550	550	550	550
Recovery, %	71.9	73.3	73.3	73.0	73.9	74.0
Drying temp., ° F.	100	100	100	100	100	100
Protein, dry basis, %	0.458	0.254	0.260	0.289	0.235	0.218
Stormer viscosity, sec. (H_2O = 5.1)	6.7	6.6	6.5	6.4	6.5	6.6
Color[a]	Good	Good	Very good	Very good	Excellent	Excellent
Protein in gluten, dry basis, %	24.00	24.85	30.30	30.40	30.60	30.60

[a] The color of a commercial wheat starch (Martin process) was graded basically as fair. This same starch gave a Stormer viscosity of 6.1 seconds and contained 0.255% protein.

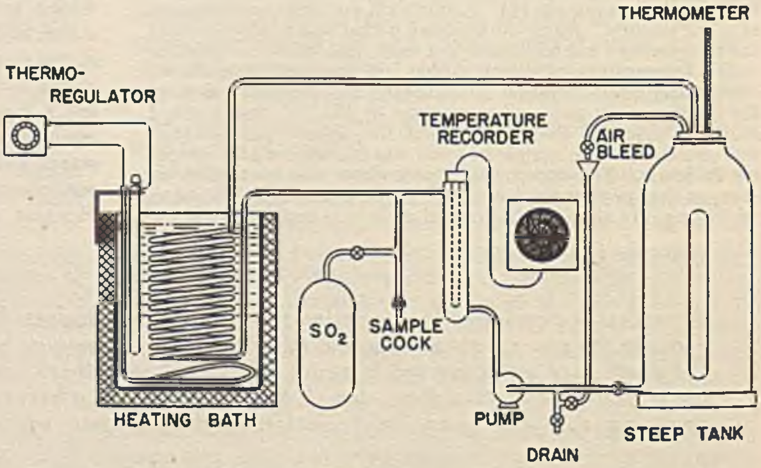


Figure 2. Steeping System for Wet Milling of Wheat on a Laboratory Scale

Table II. Wet Milling of Grain in the Pilot Plant

Run No.	2-P	22-P	23-P	25-P	14-P
Kind of grain	Wheat	Wheat	Wheat	Wheat	Corn
Variety of grain	Thatcher	Dawson	Dawson	Dawson	Ill. 972
Commercial grade	2 Dark Northern Spring	2 Soft White Winter			1 Yellow
Grain analysis, commercial basis, %					
Moisture	12.35	12.52	12.52	12.52	9.55
Starch	52.9	59.0	59.0	59.0	65.2
Protein	14.9	10.45	10.45	10.45	9.32
Oil	1.68	1.74	1.74	1.74	4.28
Grain processed, lb.	59.5	60.0	60.0	60.0	55.75
Processing data					
Steeping					
Time, hr.	22.0	21.0	23.0	22.75	46.0
Temperature, ° F.	98.0	99.0	99.0	100.0	125.0
Gram SO_2/100 cc.					
At beginning	0.425	0.293	0.262	0.259	0.290
At end	0.248	0.202	0.163	0.172	0.206
pH at beginning	1.53	1.63	1.63	1.78	1.62
pH at end	4.42	4.50	4.08	4.67	4.22
Vol. dist. water used, gal.	8.73	8.73	8.73	8.73	8.73
Vol. S.W.[a] withdrawn, gal.	2.51	4.10	4.00	4.06	5.00
Gr. at 60° F. of S.W. withdrawn, °Bé.	3.68	3.38	3.45	3.45	3.40
Mill starch to table					
Temperature, ° F.	97.0	95.0	97.0	97.0	99.0
Gravity, °Bé.	2.4	3.3	3.7	3.8	3.0
pH	4.59	4.82	2.47	5.08	3.28
SO_2, gram/100 cc.	...	0.012	0.135	0.007	0.035
Starch recovery					
Starch extd., D.B.[b], lb.	20.30	26.50	25.60	26.85	31.60
Starch in grain, D.B., lb.	31.50	35.40	35.40	35.40	36.30
Recovery, %	64.5	75.0	72.3	76.0	87.2
Products accounted for, D.B.					
S.W. solids, lb.	1.00	1.53	1.52	1.52	1.77
Fiber, lb.	6.56	6.25	6.35	6.47	5.75
Starch, lb.	20.30	26.50	25.60	26.85	31.60
Gluten, lb.	13.10	10.20	12.08	11.75	7.22
Squeegee starch, lb.	2.32	0.80	1.32	0.24	0.49
Waste water solids, lb.	6.24	4.92	5.26	4.94	2.19
Total, lb.	49.52	50.20	52.13	51.77	49.02
Total in grain, lb.	52.2	52.4	52.4	52.4	50.3
Accounted for, %	95.0	95.8	99.5	98.9	97.5
Protein distribution, D.B., %					
In S.W.	23.80	23.65	27.20	26.90	35.90
In fiber	14.20	10.00	11.30	11.30	16.15
In starch	0.27	0.25	0.23	0.22	0.29
In gluten	37.40	29.60	25.70	28.80	38.70
In squeegee starch	9.10	23.65	20.45	7.67	11.20
In waste water	33.80	33.80	29.30	35.25	33.80
Protein accounted for, D.B., lb.					
In S.W.	0.238	0.362	0.414	0.409	0.635
In fiber	0.930	0.625	0.717	0.730	0.927
In starch	0.054	0.065	0.059	0.060	0.092
In gluten	4.900	3.040	3.100	3.390	2.790
In squeegee starch	0.209	0.189	0.270	0.018	0.055
In waste water	2.110	1.660	1.540	1.740	0.740
Total	8.441	5.941	6.100	6.347	5.239
Total in grain	8.87	6.27	6.27	6.27	5.20
Protein accounted for, %	95.2	94.8	97.3	101.3	100.1

[a] S.W. = steepwater. [b] D.B. = dry basis

small-scale batch operations. The nature of the processing also probably accounts for the inadequate over-all material balance, although in this case a part of the discrepancy may result from difficulties involved in moisture determinations. The quality of the starch is excellent. Industrial cornstarch should not contain protein in excess of 0.35 per cent. It will be observed that the cornstarch prepared in run 14-P meets this requirement, and that the wheat starches contain even less protein.

The protein content of the gluten obtained in the pilot plant is invariably much lower than that in commercially prepared gluten. In the wet milling of corn the gluten normally produced in an industrial plant contains approximately 50% protein. The lower values obtained in the pilot plant are probably due to batch operation which gives a lower concentration of dissolved materials in the mill starch. Distilled water is used in preparing the mill starch in the pilot plant, whereas in a commercial plant mill starch is prepared with "process water" which contains considerable quantities of soluble material derived from other steps in the operation. This point was tested recently by procuring a 100-gallon batch of commercially prepared mill starch from a corn processing plant and subjecting it to the tabling, washing, centrifuging, and drying operations as usually performed in the pilot plant. The resulting dry gluten fraction contained 51% protein, as compared to 38.7% obtained in pilot-plant run 14-P (Table II) on corn, in which distilled water was used.

It is believed that a steeping time of 24 hours at 100° F. is the maximum required in the particular steeping installation described. It is possible that a shorter period will suffice with an estimated possible minimum of 8 hours at 100° F. Lower temperatures should require longer periods of steeping, while increased temperatures should require less steeping time; however, a temperature in excess of 103° F. is to be avoided because of the gelatinization of wheat starch at a temperature slightly above this.

Additional experimental runs have been conducted for the purpose of extracting starch in this manner from different varieties of wheat, both sound and damaged. All were successful, but lower yields of starch were obtained from damaged wheats. These experiments included the processing of Durum, Red Durum, Hard Red Winter, Hard Red Spring, and Soft Red wheats. Thus far, soft wheats have given the greatest yields of starch because of their higher starch content, but any variety of wheat is amenable to processing by the new method, including those that are unsuitable for use in making flour.

A few pilot-plant runs have been made with the Dawson variety of wheat to ascertain whether process water can be reused as it would be in continuous operation in an industrial plant (Table III). In this series, waters from the fiber squeezing, the gluten settling, and the starch filtering were combined in each experiment and retained as process water for the next run. The recovery of starch is greatly increased by using the so-called closed system and increasing the density of the mill starch to the tables. On the basis of these runs, the average yield of marketable starch, containing 12% moisture, amounts to 33 pounds per 60-pound bushel of wheat; that in the commercial wet milling of corn averages 34 pounds per 56-pound bushel.

In runs 47-P and 48-P the steep water was mixed with the fiber and gluten fractions for the production of by-product feed of excellent quality. From these experiments and from the amounts of fiber and gluten obtained in the other runs, the yield of commercial feed, containing 12% moisture, was found to be approximately 21 pounds per 60-pound bushel of wheat. This is considerably higher than the average yield of 16.75 pounds per 56-pound bushel of corn. This type of feed is selling currently for approximately 2 cents per pound.

Except as an emergency measure, the wet milling of wheat would not be considered in the corn belt where the price of wheat exceeds that of corn. However, in the Pacific Northwest, where the price of soft white wheat is relatively low and invariably less than that of corn in Chicago, the process is economically feasible. For a small plant with a capacity of 10,000 bushels per day, the total cost of processing is estimated to be 23 cents per bushel. Assuming a price of $1.00 per bushel for soft wheat, the cost of raw material and processing amounts to $1.23. With no credit for oil the only by-product credit is that for feed, amounting to 42 cents per bushel. Thus, the net production cost for 33 pounds of marketable starch is 81 cents, or an average cost of 2.46 cents per pound. While this figure probably ex-

Table III. Effect of Process Water on Recovery of Wheat Starch

Pilot-Plant Run No.	No. of Times Process Water Used Previously	Gr. of Mill Starch at 100° F., °Bé.	Starch Recovery, %
42-P	4	2.2	79.0
44-P	6	2.65	80.8
45-P	7	2.8	80.9
46-P	8	3.3	81.9
47-P	9	3.7	82.6
48-P	10	3.7	83.0
49-P	11	4.0	86.0

ceeds the cost of cornstarch, it is very much lower than the current market price of wheat starch (5 cents per pound) and is considerably less than the price of cornstarch (3.46 cents per pound).

The starch produced from wheat by this process is of better color, contains less protein, and gives more viscous pastes than the average commercial wheat starch now available on the market. One large industrial processor has found it to be excellent raw material for the production of sirups and sugars. While the wheat germ is not extracted in the pilot-plant procedure, there is no reason to believe that it could not be recovered in continuous-plant operation and used for the production of wheat oil and oil meal. The fiber and oil meal, along with some gluten, could be used as feed. The gluten recovered in this process has lost its dough-forming characteristic as a result of the sulfur dioxide treatment but still remains a source of protein. An industrial producer of monosodium glutamate has found that the protein present in the gluten fraction gives the usual yield of glutamate, but that its low protein content makes it an unsatisfactory raw material for the commercial process.

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PRESENTED before the Division of Agricultural and Food Chemistry at the 106th Meeting of the AMERICAN CHEMICAL SOCIETY, Pittsburgh, Pa.

TERNARY SOLVENTS FOR ZEIN

CYRIL D. EVANS AND RALPH H. MANLEY[1]
Northern Regional Research Laboratory,
U. S. Department of Agriculture, Peoria, Ill.

IN THE commercial utilization of zein for coating purposes, the solvents are usually blends of two or more components formulated to meet the requirements of particular operating conditions. A study of ternary solvent systems for zein is, therefore, of practical interest because it affords data which can be used in controlling the rate of evaporation of solvent mixtures; it also provides a means of improving the compatibility of other resinous materials and plasticizers with zein-solvent systems, and offers opportunities to reduce the cost of binary solvents by the addition of low-cost diluents.

Primary and binary solvents for zein have been investigated by the authors (*2*, *6*) and by Swallen (*10*). There is little to be found in the literature, however, on ternary solvents for zein, with the exception of some observations reported by Galeotti and Giampalmo in 1908 (*4*) on the solubility of zein in five ternary mixtures, all of which included ethyl alcohol and water as the binary zein solvent. The present work was undertaken to supplement earlier studies on primary and binary zein solvents in order that the general characteristics of ternary solvents for this protein might be available. The zein was from the batch used in earlier studies on primary and binary solvents (*2*, *6*). In all instances the protein was dried to constant weight in vacuum at 55° C. before use. The method of measuring its "critical peptization temperature", or the temperature above which the zein is soluble in all proportions and below which it is soluble only to the extent of 2 or 3%, was previously described. Since small amounts of impurities in the solvents used were found to have a marked effect on their peptizing capacity, great care was exercised in their purification. Peptization temperatures were readily reproducible to within 1° C.

IN BROADEST terms, solvents for zein may be classified as primary solvents, which are capable in themselves of dispersing zein; secondary solvents, which are not solvents for zein but may contribute to the solvent power of primary solvents in binary systems; and diluents, which have no solvent power for zein and are not capable of contributing to the solvent power of primary solvents when used in binary or more complex mixtures.

Primary organic solvents for zein are either acids, amides, amines, or hydroxides, although not all compounds of these types are zein solvents (*2*). Propylene glycol is a good zein solvent at room temperature, but ethyl alcohol and glycerol are primary solvents only when heated to elevated temperatures (*7*, *8*), and amyl alcohol and sorbitol will not peptize zein at any temperature. Likewise, water is not a primary solvent for zein, possibly because it denatures the protein at temperatures below those required to peptize it.

The authors classified secondary solvents for zein (*6*) as active-hydrogen compounds and showed that there is a positive correlation between the effectiveness of certain of these compounds as zein solvents and their capacity to act as electron acceptors in forming hydrogen bridges. Chloroform, nitromethane, formaldehyde, and acetoacetic ester are good solvents of this type. Somewhat anomalously, because their hydrogens are so weakly active, benzene, toluene, and similar aromatic compounds are also secondary zein solvents.

Compounds which do not contain the carboxyl, amide, amino, or hydroxyl group necessary to form primary solvents, and do not contain any sufficiently active hydrogen to make them act as secondary solvents, may be classed as diluents. Hexane, diethyl ether, and ethyl acetate are representatives of this group.

While the classification of ternary organic solvent systems for zein seems simple and clearly defined from the above outline, it is considerably more complicated. As previously indicated, the line of demarcation between primary solvents and nonsolvents is not sharp, as illustrated by the wide differences in solvent powers of propylene glycol, glycerol, and sorbitol. Likewise, the dividing line between primary solvents and secondary solvents is indefinite. Zein denatures so rapidly in water at elevated temperatures that water must be considered a nonsolvent despite its being a hydroxide. Water, however, has sufficiently active hydrogen to make it an excellent secondary solvent. A mixture of 75% ethyl alcohol and 25% water is a good zein solvent at temperatures above 0° C.; the alcohol alone must be heated to 120° C. or higher to peptize the protein. To complicate the picture further, acetone, which is not a primary solvent at any temperature and is a fair secondary solvent when used with the lower aliphatic alcohols, is a good solvent in binary mixtures with water. Furthermore, the borderline between compounds which have sufficiently active hydrogen to make them secondary solvents and those which are simply diluents is not sharply defined. Dichloropentane is a little better than hexane as a diluent, whereas 2,2,4-trichloroethane is a very good secondary solvent.

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[1] Present address, General Mills Inc., Minneapolis, Minn.

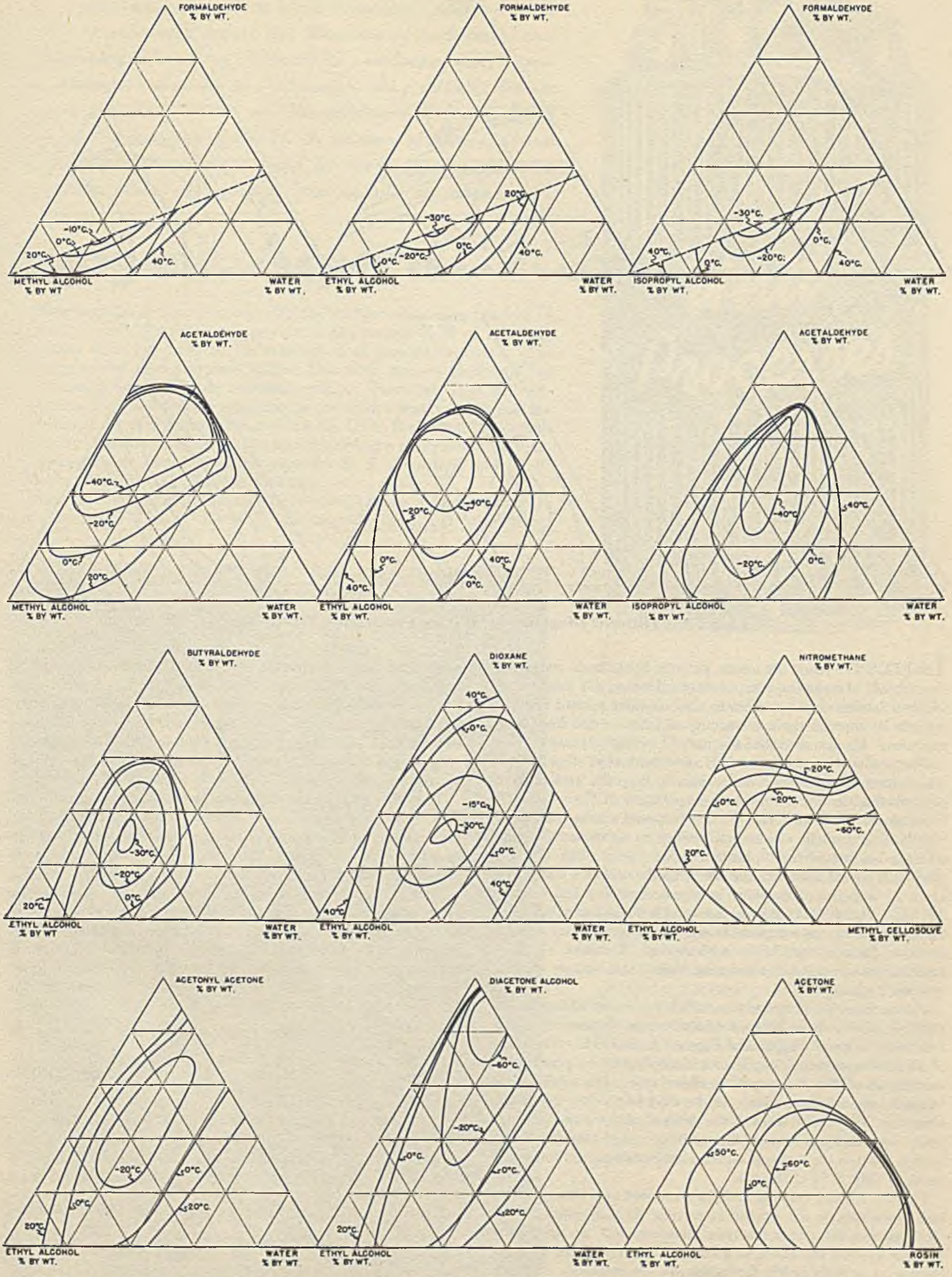

Figure 1. Trilinear Diagrams for Critical Peptization Temperatures

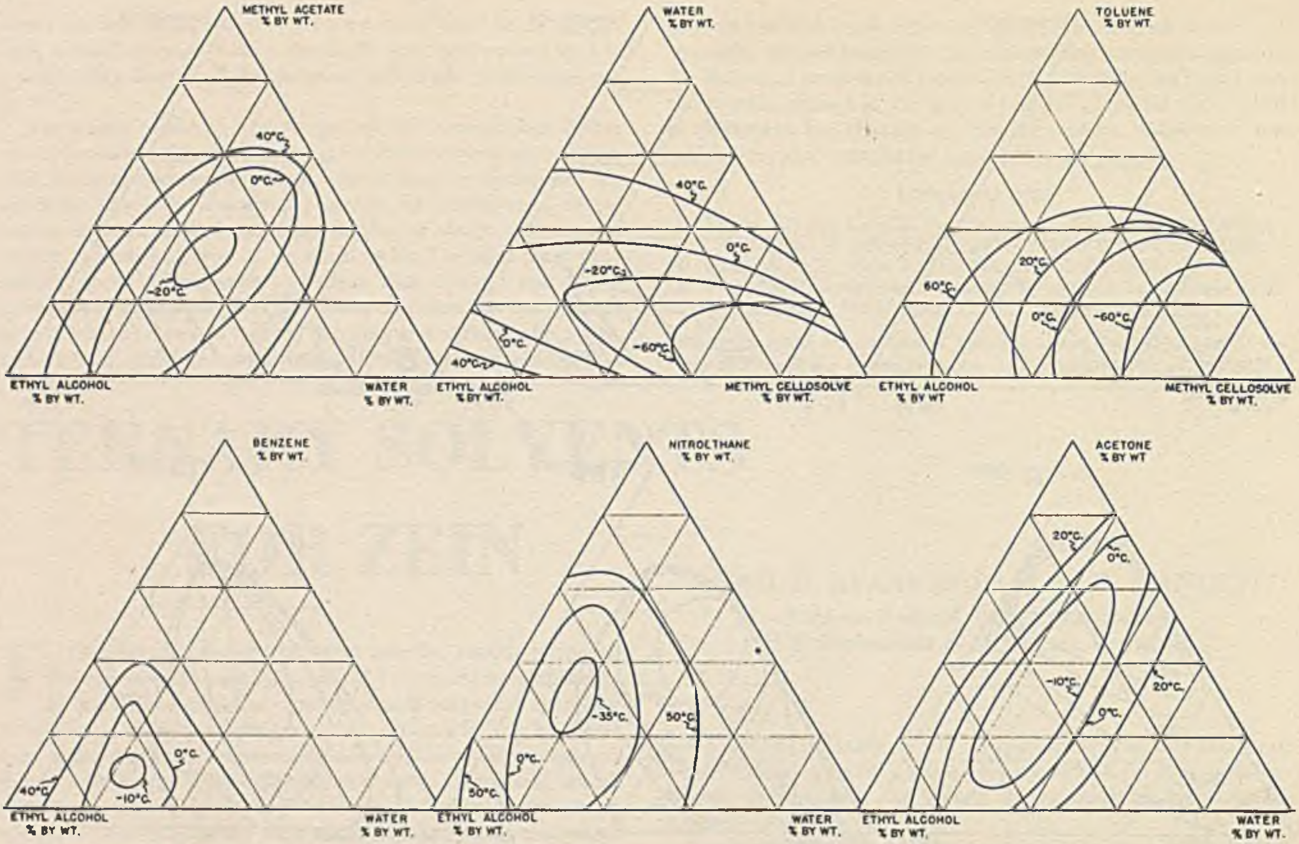

Figure 2. Trilinear Diagrams for Critical Peptization Temperatures

In recent years numerous patents have been issued on the subject of complex zein solvents. Hansen (*5*) found that triethanolamine may be added to alcohol-water solvent systems for zein to improve the transparency of films formed from such mixtures. He also described the use of leveling solvents such as *tert*-butyl alcohol and ethylene glycol monomethyl ether for use with aqueous alcohol solutions of zein to keep the protein from precipitating during the unequal evaporation of the water and lower alcohol from the films; he also proposed a large number of high-boiling alcohols, amides, and amines as components of zein solvents because of their plasticizing value. Sturken (*9*) was granted a patent covering the use of acetic acid as a stabilizing agent in zein-glue dispersions in aqueous alcohol and formaldehyde. Veatch (*11*) patented the use of benzene and of benzene-toluene mixtures as components of solvent systems for zein to improve their compatibility with waxes. Coleman (*1*) was granted numerous patents covering binary and ternary solvent systems for zein.

The authors (*3*) previously reported the use of aldehydes as gelation inhibitors in aqueous alcoholic zein dispersions. The first seven trilinear diagrams of Figure 1 indicate the wide range of alcohol-water-acetaldehyde and alcohol-water-butyraldehyde mixtures and the somewhat smaller range of alcohol-water-formaldehyde mixture, which can be used to produce good zein solvents. The dotted lines in the three alcohol-water-formaldehyde diagrams show that the addition of formaldehyde is limited because the aqueous solution used (commercial formalin) contains only 37% of the gas.

Ternary solvent systems for zein composed of acetone, water, and formaldehyde are similar in solvent characteristics to the ethyl alcohol-water-formaldehyde mixtures, but are distinctly superior in their resistance to gelation. Acetone-water systems containing as little as 5% formaldehyde are markedly resistant to gelation, whereas zein dispersions in ethyl alcohol and water containing low concentrations of formaldehyde gel readily, unless the water content is kept below 5–10%. The addition of rosin or shellac to binary solvents, such as alcohol and water, substantially lowers the critical peptization temperatures of zein in these mixtures. The presence of rosin in such systems greatly reduces the tendency of the protein dispersion to set to an irreversible gel.

The trilinear critical peptization temperature diagrams (Figures 1 and 2), prepared in the manner previously described (*2*), illustrate the foregoing generalizations relative to ternary solvent systems for zein and suggest the wide range of compositions available for commercial purposes.

Each system was thoroughly investigated throughout the range of zein solubility, and the critical peptization temperatures were determined for a series of particular solvent compositions covering this entire area. After the individual peptization temperatures were determined, lines were drawn connecting like temperatures to give the contour isotherm lines shown in the linear graphs.

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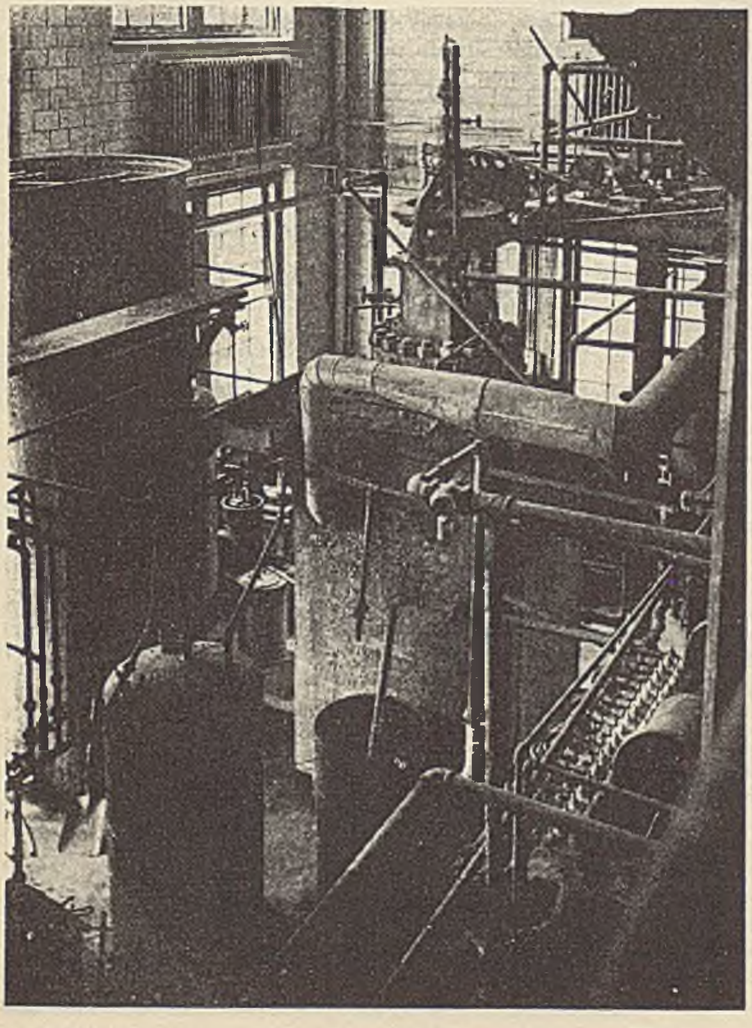
The Eighth Symposium on Unit Processes (pages 412 to 451) was presented before the Division of Industrial and Engineering Chemistry at the 106th meeting of the American Chemical Society in Pittsburgh, Pa., with R. Norris Shreve presiding. ~ ~ ~ The photograph (reproduced through the courtesy of the U. S. Bureau of Mines) shows the pilot-plant autoclave used for extracting potassium carbonate from wyomingite (see article on page 412).

Inorganic Aspects • • • • • •

There is no fundamental reason why the unit process concept cannot be applied as usefully and as extensively to the manufacture of inorganic chemicals as it has been to the fabrication of organic products. The grouping under unit processes started first with organic chemicals but is now being applied to the inorganic group. Therefore, it is with anticipation of a considerable extension in the future that we welcome the appearance, at this Eighth Symposium on Unit Processes, of various papers by C. E. McCarthy and associates regarding a new process for making potassium carbonate and the paper by H. F. Johnstone and W. E. Winsche on reactions in fused salt media.

Into the inorganic fold it will be possible to transfer some of the experience already found in the organic field and vice versa. Equipment is one of the most important phases of unit processes. Here are problems of corrosion and heat transfer that will be analogous, or at least closely related, in both inorganic and organic spheres. As an example, the control of heat in the reaction involving the oxidation of naphthalene to phthalic anhydride is similar to the control of heat in the oxidation of sulfur dioxide to trioxide. In both cases a large amount of heat must be carried through the interface; if this is not done, unwanted products arise.

Already in many of our organic reactions presented under the concept of unit processes such as hydrogenations and oxidations, the actual reactants themselves are inorganic on one side and organic on the other. In industrial procedures the important thing is to take raw materials, subject them to chemical reactions, and obtain good yields of salable products. The principles involved in the physical chemistry of the basic reactions, or the construction and control of the equipment, or the economics involved, are the same whether organic or inorganic products are obtained.



EXTRACTION of POTASSIUM CARBONATE from WYOMINGITE

Kinetics of Base-Exchange Reaction with Sodium Carbonate

Stanley J. Green and Charles E. McCarthy

U. S. BUREAU OF MINES, COLLEGE PARK, MD.

▶ ▶ ▶ In conjunction with the study of a process for the production of pearl ash and soda ash from wyomingite and trona, the kinetics of the base-exchange reaction between wyomingite and sodium carbonate have been investigated both in 1- and in 100-gallon autoclaves. The effect of concentration of reactants, time, and temperature on the rate of extraction of potassium from wyomingite is determined, and an equation relating these variables is derived. The range of temperature, ratio of sodium carbonate to wyomingite, and time are, respectively, 185° to 210° C., 0.303 to 0.550, 0 to 5 hours. Microscopic examination of the wyomingite before and after reaction shows that the only potassium-bearing mineral attacked is leucite, an indication that the Lemberg reaction is the only one occurring. At constant temperature the relation between extraction of potassium oxide, time, and initial ratio of sodium carbonate to wyomingite can be expressed by the equation:

$$\log \frac{1}{1 - (Z/C_e)} = aCt$$

THE wyomingite deposits of the Leucite Hills of Wyoming are an immense potential source of potash. Estimates by Schultz and Cross (*4*) indicate a deposit of at least a billion tons. A number of attempts have been made to extract the potash from this mineral, but to date none has proved feasible (*6*). In 1933 Pike described experiments in which a base exchange was effected by means of Green River brine and a sodium chloride solution (*3*).

Recently, however, a large deposit of practically pure trona was discovered about 18 miles west of Green River, Wyo. (*5*). The fortuitous proximity of the two deposits suggested a process whereby the trona could be calcined (to crude soda ash), dissolved in water, and reacted with the wyomingite to produce a solution of potassium and sodium carbonates. By suitable treatment (*1*) this solution would yield refined potassium and sodium carbonates.

In 1876 Lemberg first showed that the mineral leucite was converted to analcite by autoclaving with sodium chloride solution at 180° to 195° C. for 18 hours (*2*). He also found that potassium carbonate solution reacted with the analcite quantitatively and restored the leucite, an indication of the reversibility of the reaction. The equation for this base-exchange reaction is:

$$\underset{\text{(Leucite, 436.4)}}{K_2O.Al_2O_3.4SiO_2} + 2\,Na^+ + 2H_2O \rightarrow \underset{\text{(Analcite, 440.2)}}{Na_2O.Al_2O_3.4SiO_2.2H_2O} + 2K^+ \qquad (1)$$

EXTRACTIONS

RAW MATERIALS. Commercial soda ash was used with the following impurity content in weight per cent: chlorine, 0.25; SO_3, 0.013; CaO, 0.059. The wyomingite was part of a carload lot from Green River, Wyo. It was ground to −10 mesh. Chemical and screen analyses are given in Table I.

The mineral composition of wyomingite is 50% leucite, 15% phlogopite, 12% diopside, 15% kataphorite, and 8% glass and apatite, the potash-bearing minerals being leucite and phlogopite (*3*). Microscopic examination of the wyomingite before and after reaction showed that only leucite was altered, an indication that the potash is extracted only from the leucite.

METHODS. The experimental extractions were carried out both in a 1-gallon laboratory autoclave and a 100-gallon pilot-plant autoclave. The operating conditions are presented in Table II.

For each condition of initial sodium carbonate:wyomingite ratio and temperature, the reaction time at the selected temperature was varied from 0 to 5 hours. The filtered solutions were analyzed for sodium carbonate potassium carbonate, sulfate (SO_3), and silica, and occasionally for other impurities. The extractions per 100 pounds of wyomingite were then determined by the following calculations:

1. The ratios of sodium carbonate, sulfate, and silica to potassium carbonate.
2. The potassium oxide extraction per 100 pounds of wyomingite by use of the equation:

$$Z = \frac{88.7\,C}{1.302\,w + 1} \qquad (2)$$

where C = initial weight ratio of Na_2CO_3 to wyomingite
w = final weight ratio of Na_2CO_3 to K_2CO_3 in soln.
Z = extn. of K_2O, lb./100 lb. wyomingite

The derivation of this equation is based on the assumption that there is a stoichiometric base exchange between potassium carbonate and sodium carbonate, the sodium oxide replacing the potassium oxide in wyomingite, mole for mole. The use of this equation eliminated the need for closely controlling the water losses, particularly in the pilot-plant filtering step, in order to make yield calculations, since concentrations do not enter into the equation. The validity of this method was periodically con-

Table I. Analyses of Wyomingite

Composition		Screen Analysis	
Constituent	Wt., %	Fraction	Wt., %
SiO_2	49.0	− 10 + 14	7.56
Fe_2O_3	4.57	− 14 + 28	27.03
TiO_2	2.40	− 28 + 35	12.15
$Al_2O_3 + P_2O_5$	12.2	− 35 + 48	8.72
CaO	6.07	− 48 + 65	7.75
MgO	8.35	− 65 +100	5.39
Na_2O	1.40	−100 +150	5.57
K_2O	11.40	−150 +200	5.15
CO_2	0.24	−200	20.60
SO_3	0.31		
Ignition loss	2.79		

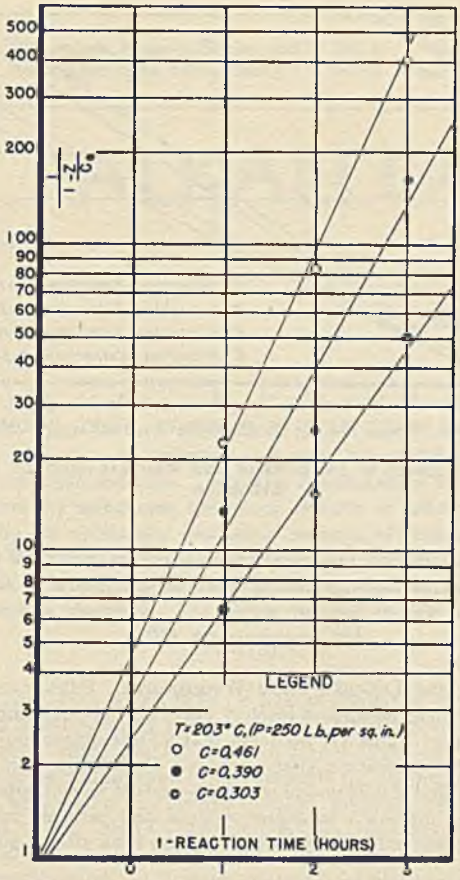


Figure 1. Typical Calculation of *K*

Table III. Effect of Reaction Time on Extraction in Laboratory and Pilot-Plant Autoclaving Experiment

C, Initial Wt. Ratio, Na_2CO_3: Wyomingite	*t*, Hr. at Temp. *T*	Extn., Lb./100 Lb. Wyomingite: K_2O	SO_3	SiO_2	Measurements for Precision of K_2O: No. duplicate runs	Av. deviation	% Av. deviation
LABORATORY, *T* = 191° C., PRESSURE = 200 LB./SQ. IN.							
0.303	0	3.30	0.132	1.08	2	0.01	0.3
0.303	1	6.35	0.210	1.54	2	0.09	1.4
0.303	2	6.98	0.193	1.55	1	..	...
0.303	3	7.35	0.210	1.62	1	..	...
0.303	4	7.93	0.214	1.60	3	0.02	0.3
0.390	1	7.22	0.226	1.41	1	..	...
0.390	2	7.83	0.212	1.36	2	0.05	0.6
0.390	3	7.95	0.216	1.57	1	..	...
0.461	1	7.66	0.210	1.43	1	..	...
0.461	2	7.97	0.214	1.47	1	..	...
0.461	3	8.14	0.219	1.52	2	0.01	0.1
LABORATORY, *T* = 203° C., PRESSURE = 250 LB./SQ. IN.							
0.303	1	6.43	0.198	1.34	2	0.19	3.0
0.303	2	7.13	0.220	1.59	2	0.10	1.4
0.303	3	7.46	0.240	1.73	1	..	...
0.390	1	7.63	0.217	1.54	1	..	...
0.390	2	7.91	0.231	1.57	2	0.01	0.1
0.390	3	8.18	0.214	1.72	2	0.02	0.2
0.461	1	7.87	0.214	1.62	2	0.06	0.8
0.461	2	8.15	0.220	1.83	2	0.02	0.3
0.461	3	8.28	0.223	1.87	1	..	...
PILOT PLANT, *T* = 185° C., PRESSURE = 150 LB./SQ. IN.							
0.314	0	3.78	...	1.56	1	..	...
0.314	1	6.05	...	1.81	1	..	...
0.314	2	6.61	...	2.30	1	..	...
0.314	3	7.22	...	2.13	2	0.32	4.4
0.314	4	7.51	...	2.10	2	0.09	1.2
0.314	5	7.67	...	2.52	2	0.07	0.9
0.314	6	7.84	...	2.33	2	0.15	1.9
PILOT PLANT, *T* = 198° C., PRESSURE = 200 LB./SQ. IN.							
0.314	0	4.58	0.192	1.76	7	0.17	3.7
0.314	1	6.40	0.206	2.11	9	0.25	3.9
0.314	2	7.36	0.219	2.12	25	0.21	2.9
0.314	3	7.56	0.218	2.09	9	0.21	2.8
0.314	4	7.75	0.229	2.14	8	0.12	1.6
0.414	1	7.20	0.222	2.11	1	..	...
0.414	2	7.67	0.208	2.33	2	0.03	0.4
0.414	3	7.82	0.240	2.47	2	0.07	0.9
0.550	1	7.75	0.206	2.34	2	0.21	2.6
0.550	2	8.29	0.218	2.58	2	0.03	3.6
0.550	3	8.37	0.246	2.62	3	0.18	1.9
0.550	5	8.31	0.233	2.90	2	0.19	2.3
PILOT PLANT, *T* = 209° C., PRESSURE = 250 LB./SQ. IN.							
0.314	0	5.64	0.236	2.03	4	0.28	5.0
0.314	1	6.85	0.214	1.91	2	0.11	1.6
0.314	2	7.43	0.219	2.01	2	0.18	2.4
0.314	3	7.91	0.231	2.47	4	0.16	2.0
0.314	4	8.02	0.210	2.59	7	0.23	2.9
0.414	0	5.78	0.204	1.89	2	0.10	1.7
0.414	1	7.80	0.213	2.17	1	..	...
0.414	$2^1/_2$	7.98	0.209	2.42	3	0.15	1.9
0.414	4	8.06	0.208	2.69	2	0.06	0.7
0.550	0	5.35	0.216	1.71	2	0.07	1.3
0.550	1	7.97	0.236	2.30	2	0.06	0.8
0.550	$2^1/_2$	8.67	0.258	2.57	2	0.06	0.7
0.550	4	8.75	0.217	2.65	2	0.05	0.6

firmed in the laboratory by simultaneously determining the potassium oxide yield by a direct measurement of potassium oxide extracted.

3. The sulfate and silica extractions by multiplying the final SO_3:K_2CO_3 and SiO_2:K_2CO_3 ratio by the K_2CO_3 extraction.

AUTOCLAVING RESULTS

The effect of reaction time on extraction for the several conditions of initial ratio of reactants and temperature is presented in Table III. As a measure of the over-all accuracy and precision of the experiments where duplicate runs were made, the average and percentage deviations of the potassium oxide extractions were calculated. The percentage deviations are less than 5% and in the majority of cases are less than 3%. A suitable equation expressing a relation between the time of reaction and yield of potassium oxide at constant initial ratios of sodium carbonate to wyomingite was then investigated. It was also desired to evaluate the effect of the heating period and to express this effect in terms of reaction time at the holding temperature. The equation of a first-order reaction was found to fit the experimental points closely:

$$\log \frac{1}{1 - (Z/C_e)} = Kt \tag{3}$$

where C_e = equilibrium yield of K_2O, lb./100 lb. wyomingite
t = reaction time, hr.
K = constant, reciprocal hr.

A plot of $\log \frac{1}{1 - (Z/C_e)}$ against t gave a straight line in all cases. Typical curves are shown in Figure 1. C_e was first approximated by plotting Z against t on rectangular coordinates. The asymptotic value of Z was estimated and taken as C_e. Then by trial and error the value of C_e was computed that gave the best straight line on the semilog plot. The approximate value was always within 1% of the computed. The slope of the semilog plot is K.

Table II. Autoclaving Conditions

Condition	1-Gal. Autoclave	100-Gal. Autoclave
Charge of wyomingite	650 grams	200 lb.
Charge of water	1000 grams	536 lb.
Water:wyomingite ratio	1.54	2.68
Method of heating	Gas burner	Gas burner
Heating period, min.	90	135–175
Type of agitation	Propeller	Paddle stirrer
Speed, r.p.m.	200	12.5
Temp. measurement	Thermometer	Thermocouple
Pressure measurement	Bourdon gage	Bourdon gage
Premixing of charge	None	100-gal. mix tank
Filtering of tails	Büchner funnel	No. 5 Sweetland filter

To evaluate the equivalent time at the reaction temperature of the heating period, the straight line on the semilog plot was extrapolated to the t-axis, where $\frac{1}{1 - (Z/C_e)} = 1$ and, consequently, where $Z = 0$. The negative value of t is the equivalent reaction time at the temperature. The values of constants C_e and K so determined are given in Table IV.

Table IV. Effect of Ratio of Reactants and Temperature on Reaction Rate and Equilibrium Yield in Autoclaving Experiments

T, ° C.	C	C_e	K	t, Hr.
		Laboratory Experiments		
191	0.303	7.55	0.384	0.90
191	0.390	8.01	0.540	0.97
191	0.461	8.18	0.628	0.80
203	0.303	7.61	0.423	0.91
203	0.390	8.24	0.565	0.88
203	0.461	8.25	0.661	1.00
		Pilot-Plant Experiments		
185	0.314	7.90	0.273	1.0
198	0.314	7.95	0.310	1.2
198	0.414	7.94	0.440	1.3
198	0.550	8.44	0.501	1.4
209	0.314	8.16	0.338	1.0
209	0.414	8.10	0.463	1.3
209	0.550	8.80	0.583	0.75

Employing these constants in Equation 3, a plot was made of Z against t on rectangular coordinates. The experimental data were then compared to these theoretical curves by plotting observed Z against net running time. The net running time was obtained by adding to the observed running time the calculated t equivalent term. Typical curves appear as Figure 2.

The effect of C on K is shown in Figure 3. K varies linearly with C; the rate of extraction at $C = 0$ is equal to zero, as would be expected. The equation for this relation is, therefore,

$$K = aC \tag{4}$$

The values for a follow; it is seen that the reaction rate increases only slightly with temperature, and that the rate is somewhat higher for the laboratory extractions:

T, ° C.	Speed, R.P.M.	Initial Ratio, H_2O:Wyomingite	a
191	200	1.54	1.32
203	200	1.54	1.43
198	12.5	2.68	1.03
209	12.5	2.68	1.11

Thus for any condition of temperature and initial ratio of water to wyomingite, the extraction of potassium oxide may be expressed in terms of the initial ratio of sodium carbonate to wyomingite and time; substituting Equation 3 in Equation 4,

$$\log \frac{1}{1 - (Z/C_e)} = aCt \tag{5}$$

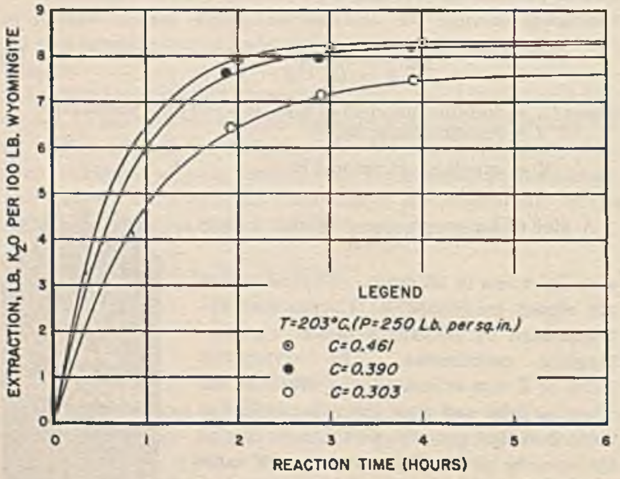


Figure 2. Effect of Sodium Carbonate:Wyomingite Ratio and Time on Extraction

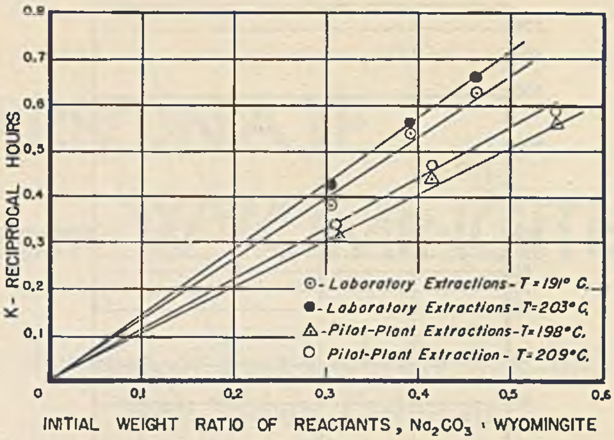


Figure 3. Effect of Temperature and Reactant Ratio on Rate of Extraction

Impurities Leached from Wyomingite. Sulfate and silica were the main impurities leached out with the potassium. Examination of Table III discloses that sulfate extraction did not vary with temperature, time, and ratio of reactants and had an average value of 0.22 pound per 100 pounds of wyomingite. Silica extraction increased with temperature and ratio of reactants, but increased only slightly with reaction time after 3 hours.

CONCLUSIONS

The equilibrium extraction, C_e, ranges from 7.75 to 8.80 pounds of potassium oxide per 100 pounds of wyomingite; it increases with temperature from 185° to 209° C. and with initial sodium carbonate:wyomingite ratio, C, from 0.303 to 0.550. With the higher temperatures and reactant ratios, negligible extraction was observed after 3 hours. Good agreement was obtained between laboratory and pilot-plant results, although as a result of the higher agitation rate and salt concentration in the laboratory tests, the value of a was 30% higher than for the pilot-plant runs.

The main impurities leached out with the potassium were sulfate and silica, in average quantities of 0.22 and 2.0 pounds per 100 pounds of wyomingite, respectively. The exact values varied with leaching conditions.

ACKNOWLEDGMENT

The authors wish to express their appreciation to John Ruppert, Theodore Ohlson, and Leo Gowen for valuable assistance in conducting laboratory and pilot-plant experiments. Acknowledgment is also made to Robert D. Pike, consulting chemical engineer of Pittsburgh who initiated the work, and to John E. Conley, chief of the Chemical Engineering Unit of this station, for valuable suggestions and criticisms throughout the investigation.

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Separation of Sulfate and Chloride from ALKALI CARBONATE BRINES

Guy Ervin, Jr., and Charles E. McCarthy
U. S. BUREAU OF MINES, COLLEGE PARK, MD.

▶ ▶ ▶ The problem of removing sulfate and chloride from alkali-carbonate brines has been encountered in connection with a process for the production of potassium carbonate and sodium carbonate from wyomingite and trona. The main constituents of the brine obtained are the carbonates, but minor amounts of sulfate are introduced by the wyomingite and minor amounts of chloride by the trona. These must be removed to prevent the contamination of the products. The problem has been solved by applying the methods of phase-rule chemistry. The sulfate removal process involves a combination of evaporation and carbonation, and essentially all of the sulfate is obtained in the form of potassium sulfate of commercial purity. The greater part of the sodium carbonate is produced as the monohydrate, and the remainder is produced as the bicarbonate. Chloride is separated by the fractional crystallization of $K_2CO_3.\frac{3}{2}H_2O$, followed by the recrystallization of the impure fraction with the production of pure potassium chloride. The procedures are applicable to brines of widely varying composition but are restricted to those whose chief components are the alkali carbonates.

NEAR Green River, Wyo., is a large deposit of wyomingite, a leucite-bearing rock, as well as a large deposit of almost pure trona, $Na_2CO_3.NaHCO_3.2H_2O$. Pike (*6*) proposed to recover potassium from the wyomingite by effecting a base exchange with sodium carbonate solution, prepared by dissolving calcined trona. $Na_2CO_3.H_2O$ and $K_2CO_3.\frac{3}{2}H_2O$ would then be produced from the resulting solution by a process of evaporation and crystallization. A laboratory- and pilot-plant investigation of the process was recently completed (*2*).

The problem of removing sulfate and chloride arises from the fact that the wyomingite contains small amounts of sulfate, and the trona, small amounts of chloride. Both impurities are dissolved almost quantitatively in the base-exchange process and must be removed in some way if high-purity products are to be made.

The wyomingite contains 0.3–0.5% sulfate, and the trona, about 0.04% chloride. Solubility data in the literature and later experiments have shown that, in the evaporation and crystallization process for separating sodium and potassium carbonate, essentially all of the sulfate comes out with the sodium carbonate and all of the chloride with the potassium carbonate. Upon this basis the soda ash produced would contain 0.4–1.0% sulfate and the pearl ash, 0.15–0.40% chloride, depending on the amount of excess sodium carbonate used in the base-exchange step.

A brief description of the process for separating the carbonates will facilitate an understanding of the problem. After effecting the base-exchange reaction and filtering, a solution is obtained containing sodium carbonate, potassium carbonate, and impurities. Its composition is approximately that of point *A* on Figure 1. The carbonates are separated in a continuous and cyclic manner by two successive evaporations at 100° C., followed by crystallization at 25° C. There are thus three major steps in the process. In the first, called the "monohydrate steps", the solution is concentrated from *A* to *S* and evaporated further with crystallization of $Na_2CO_3.H_2O$ to *F*. The evaporation is operated continuously; solution of composition *A* is continuously fed in, and solution of composition *F*, as well as solid monohydrate, is continuously withdrawn. The second, or "double-salt step", consists of evaporation from *F* to *G;* the double salt, $K_2CO_3.Na_2CO_3$, thus produced is recycled to the monohydrate step. The final step is "crystallization", in which solution of composition *G* is cooled from 100° to 25° C.; the result is crystallization of $K_2CO_3.\frac{3}{2}H_2O$ and production of a solution of composition *H*. This solution is recycled to the double-salt step. When a steady state is reached, the impurities will come out with the products in the same ratio in which they occur in the initial solution.

Attempts were made to remove the sulfate from the wyomingite by some simple treatment before the base-exchange step. In these tests the quantity of sulfate that could be dissolved was negligible, except under conditions approximating those of the base-exchange reaction. No chemical precipitating agent for sulfate was known to the authors which would be operative in this solution. The most obvious one, barium ion, fails because the high carbonate content of the solution renders barium carbonate less soluble than barium sulfate. However, a satisfactory procedure has been devised for separating the sulfate, based on the methods of phase-rule chemistry.

SULFATE REMOVAL PROCESS

The 75° C. isotherm for the system potassium-sodium-carbonate-sulfate is shown in Figure 2, using the Jänecke method of representation. The data in Table I are those of de Ropp (*7*). The relative proportions of the dissolved salts are shown in Figure 2, with no indication of the amount of water present. The mole fraction of sulfate is plotted on the horizontal axis and the mole fraction of potassium on the vertical axis. Thus the four corners of the diagram represent the compositions of the four salts as indicated or, more properly, the composition of the saturated solutions of the individual salts. The four sides of the square represent the four three-component systems, K_2CO_3–K_2SO_4–H_2O, K_2SO_4–Na_2SO_4–H_2O, Na_2SO_4–Na_2CO_3–H_2O, and Na_2CO_3–K_2CO_3–H_2O. The areas within the square represent four-component systems saturated with respect to the single salt indicated for each area. Points on the lines inside the diagram are saturated with the two salts whose regions they divide, and points of intersection of three lines are saturated with respect to three solid phases. The great advantage of this type of diagram is that the crystallization paths are straight lines. The change in composition of a solution on isothermal evaporation may be determined by producing the line connecting the original composition

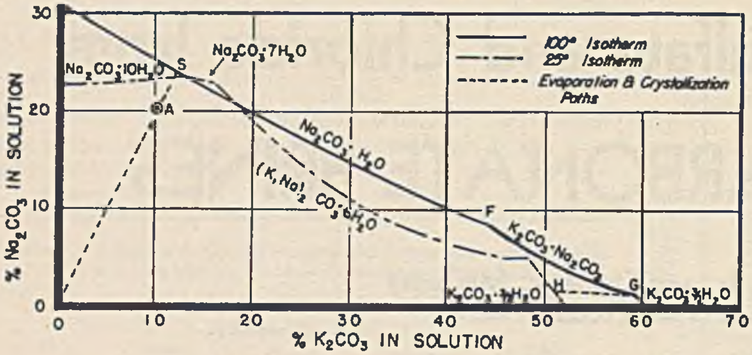

Figure 1. Solubility Curves for the System Potassium Carbonate–Sodium Carbonate–Water at 100° (2) and at 25° C. (4)

with the composition of the phase which is precipitating—that is, the phase in whose area the composition of the solution lies. When such a crystallization path intersects a boundary line of the phase area, the path may follow the boundary line or proceed into the adjoining area with a change in direction, depending on the particular situation. For a more complete discussion the reader is referred to a text on the phase rule (3).

Table I. Data on the System Potassium-Sodium-Carbonate Sulfate at 75° C.

Point	Mole Fraction (K_2)	Mole Fraction (SO_4)	Moles Salt per 1000 Moles H_2O	Point	Mole Fraction (K_2)	Mole Fraction (SO_4)	Moles Salt per 1000 Moles H_2O
A	1	0	177.7	*F*	0.807	Trace	150.2
B	1	1	21.3	*G*	0.955	Trace	182.0
C	0	1	55.6	*Q*	0.162	0.810	73.4
D	0	0	77.0	*E*	0.530	0.021	105.6
N	0.176	1	68.3	*L*	0.233	0.116	89.1
M	0.687	1	32.9	*S*	0.285	0.010	68.3
T	0.800	0	153.2	*S'*	0.560	0.020	115.5
U	0.953	0	182.5	*W*	0.188	0.096	93.5
V	1	Trace	176.9	*W'*	0.636	0.327	31.9
R	0	0.085	79.6	*K*	0.846	0.126	48.6
P	0	0.787	62.8	*K'*	0.826	Trace	155.0

The composition of the solution obtained in the base-exchange step of the wyomingite process is indicated by point *S*, Figure 2. Evaporation at 75° C. causes the separation of $Na_2CO_3.H_2O$ and alteration of the composition of the solution along line *DS* produced. This continues until the crystallization path intersects the boundary between the $Na_2CO_3.H_2O$ and K_2SO_4 fields at *S'*. At this point the solution is saturated with respect to both $Na_2CO_3.H_2O$ and K_2SO_4. Further evaporation causes $Na_2CO_3.H_2O$ and K_2SO_4 to crystallize simultaneously, and the composition of the solution follows the two-solid crystallization path, *EF*, in the direction of *F*, at which point the solution becomes saturated with a third solid—the double salt $K_2CO_3.Na_2CO_3$. When composition *F* is reached, the solid phase is separated from the solution before evaporation is continued. This marks the end of the first major step in the separation of the carbonates.

Table I shows that only a trace of sulfate is present at *F*. The actual amount was found to be 0.05% SO_3. This means that 95% of the original sulfate present has separated as K_2SO_4 along with $Na_2CO_3.H_2O$ during evaporation from *S'* to *F*. Thus the problem is solved if a means is found to separate K_2SO_4 from $NaCO_3.H_2O$.

In actual operation the $Na_2CO_3.H_2O$ also contains some K_2CO derived from the retained mother liquor. Washing with saturated Na_2CO_3 solution at 35° C. or higher removes both K_2SO_4 and the K_2CO_3. By countercurrent-decantation washing, the wash solution may be saturated with sulfate, and at the same time the monohydrate may be washed almost completely free of both sulfate and potassium. This is done by using the proper ratio of wash solution to monohydrate crystals and a sufficient number of stages in the countercurrent-decantation apparatus. The effluent wash solution then has the composition indicated by point *W*, Figure 2. It will be noted that the ratio of sulfate to carbonate has been increased considerably over that of the original solution at point *S*.

Removal of the bulk of the sodium carbonate present in the wash solution will increase still further the ratio of sulfate to carbonate and make possible the crystallization of potassium sulfate from the solution. This may be done by carbonating the solution and thereby precipitating sodium bicarbonate. Since only sodium and carbonate ions are removed, the composition of the solution alters in a direction away from the sodium carbonate composition along line *DW* produced, until composition *W'* is reached at complete carbonation. The location of point *W'* is fixed by the solubility of $NaHCO_3$ in the solution at the temperature of carbonation. The seeming inconsistency of passing through the glaserite field without precipitating any glaserite is explained by the fact that we are no longer dealing with the same system. At complete carbonation, the system to which the solution belongs is that of the bicarbonates and sulfates of sodium and potassium in water. During the carbonation we have a five-component system—namely, the carbonates, sulfates, and bicarbonates of sodium and potassium in water. The existing information on these systems is limited, but such information is unnecessary for the present purpose. It should be understood, however, that line *WW'* does not actually pass through the glaserite field and that point *W'* is actually the point obtained on converting the composition of the carbonated solution from bicarbonates to normal carbonates. This serves the purpose because, on evaporation at the boiling point, only the normal carbonates precipitate. The bicarbonates are decomposed into normal carbonates as evaporation proceeds; hence the solution never becomes saturated with bicarbonate.

Assuming that bicarbonates have been converted to carbonates, the composition of the carbonated solution after filtration of the precipitated bicarbonate is given by point *W'* in Figure 2,

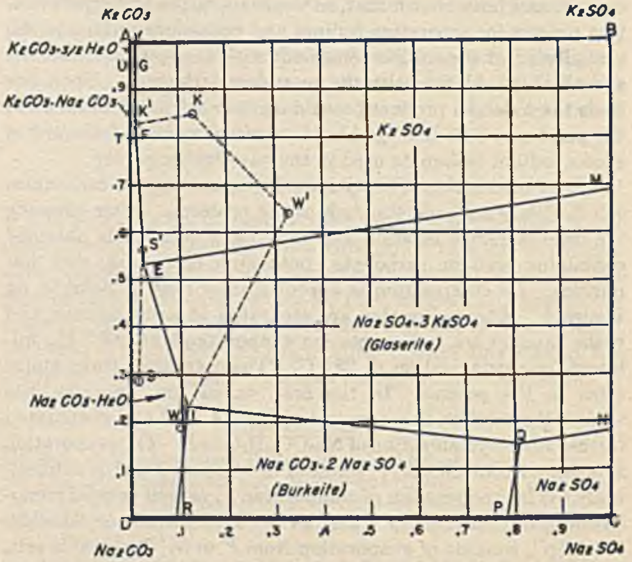

Figure 2. The System Potassium-Sodium-Carbonate-Sulfate-Wate at 75° C.

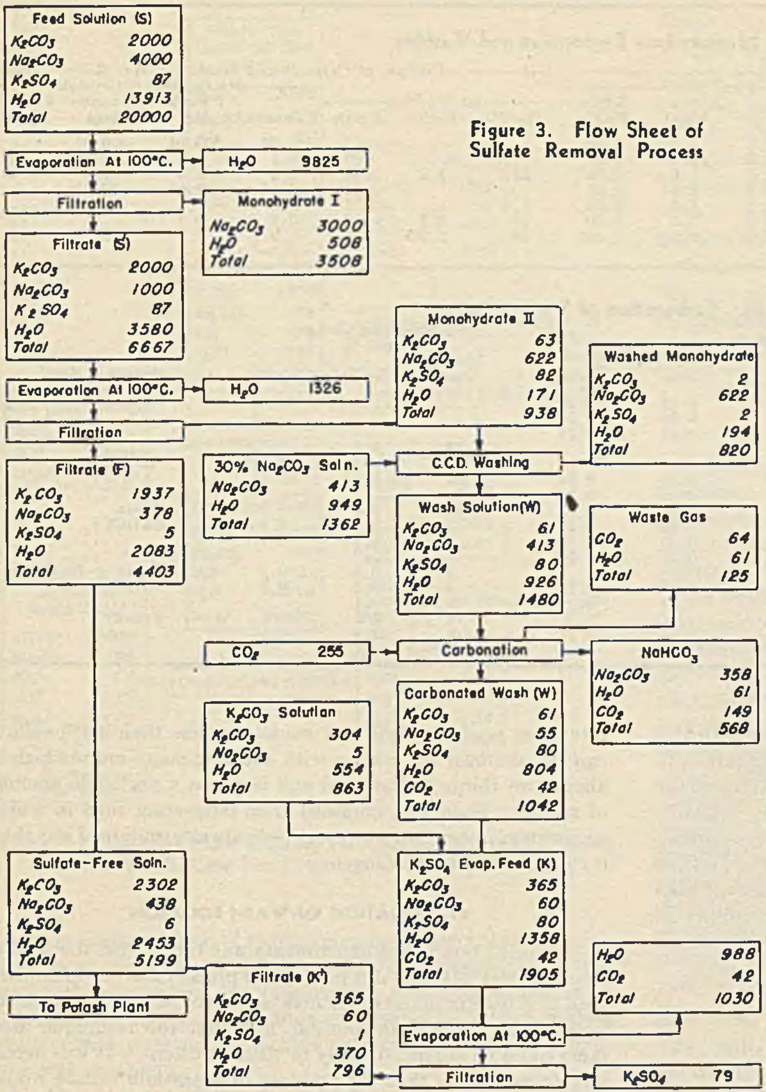

Figure 3. Flow Sheet of Sulfate Removal Process

which lies within the potassium sulfate field. However, evaporation of this solution will yield only a small quantity of pure potassium sulfate, following which glaserite will be deposited. This is evident from the fact that line *BW'* produced intersects line *EM*. A simple adjustment in the composition of the solution makes it possible to crystallize almost all the potassium sulfate by evaporation. Potassium carbonate is added to the solution until the composition shifts to the left of line *BE*. The more potassium carbonate added, the more complete is the removal of sulfate on subsequent evaporation. It is convenient to add enough potassium carbonate to shift the composition of the solution to point *K*. The potassium carbonate added need not be a pure finished product but may be any available material which is mostly K_2CO_3. A convenient source in this case is the $K_2CO_3.\frac{3}{2}H_2O$ washings, which would otherwise be recycled to the double-salt step. These washings may be used for the above purpose without incurring any losses or additional evaporation. The quantity of potassium carbonate required to change the composition to point *K* is about 15% of the total produced in the wyomingite process.

Evaporation of a solution of composition *K* results in crystallization of potassium sulfate and alteration of the solution composition along line *KK'*. At *K'* the evaporation is stopped, and potassium sulfate is separated by filtration. Since the solution at *K'* has almost the same composition as the solution at *F*, the filtrate from the monohydrate evaporation step, the two solutions are mixed and used as feed to the double-salt evaporation step.

The net result of the process is the production of essentially all sulfate in the form of commercially pure potassium sulfate. Sodium carbonate of low sulfate content is obtained, chiefly as the monohydrate and partially as the bicarbonate. The steps are simple and economical and require only standard chemical engineering equipment. Only the carbonation and potassium sulfate evaporation steps are additional to those of the main process, and in both cases relatively small quantities of materials are handled. No potash or soda salts are discarded.

The balanced flow diagram for the complete sulfate removal process is shown in Figure 3. The basis of the material balance is the production of 1 ton of potassium carbonate in the potash plant. One feature not previously discussed is included in this diagram. The monohydrate evaporation is carried out in two stages, separating pure $Na_2CO_3.H_2O$ in the first stage and $Na_2CO_3.H_2O$ plus K_2SO_4 in the second stage. The first stage consists of evaporation along line *SS'* (Figure 2) which lies within the monohydrate field, and in the second stage the evaporation proceeds along line *S'F* with simultaneous crystallization of Na_2CO_3.-H_2O and K_2SO_4.

EVAPORATION AND WASHING OF MONOHYDRATE CRYSTALS

Evaporations were carried out on synthetic solutions at 100° C. in a vacuum distillation apparatus. The apparatus consisted of a three-neck flask equipped with a stirrer, a thermometer, and a condenser whose exit led to a graduated cylinder which served as a receiver for the condensate. The cylinder was connected to a water aspirator and an open-end manometer. The pressure in the system was regulated by the needle valve of a Bunsen burner. The flask was heated in an oil bath. By controlling the pressure, the temperature of evaporation was kept at 100.0° ± 0.5° C. In some experiments an iron pot was used in place of the three-neck flask. If the composition of the initial solution and the solubility curve for the system were known, the quantity of water to be evaporated to give any desired solution composition could be calculated. Thus the evaporation could be stopped at the desired point, as indicated by the quantity of condensate in the graduated cylinder. The mixtures were filtered while still hot in a small laboratory centrifuge preheated to 100° C. The crystals were washed by repulping with 30% sodium carbonate solution at 60–75° C.

Compositions of initial and final solutions, as well as of the crystals and the first washing, are shown in Table II. Experiments 4 and 5 were run in two stages. The data show that no sulfate precipitates on evaporation until the solution reaches about 45% solids, which corresponds to point *S'*, Figure 2. This is demonstrated by the constancy of the K_2SO_4:K_2CO_3 ratio in initial and final solutions for experiments 1, 2, 4-I, and 5-I, and the decrease in the ratio for experiments 3, 4-II, and 5-II. The sul-

Table II. Monohydrate Evaporation and Washing

Expt. No.	Compn. of Solutions, Wt. %: Initial Soln. Na_2CO_3	K_2CO_3	K_2SO_4	K_2SO_4: K_2CO_3	Final Soln. Na_2CO_3	K_2CO_3	K_2SO_4	K_2SO_4: K_2CO_3	Compn. of Crystals and Washings, Wt. %: 1st Washing Na_2CO_3	K_2CO_3	K_2SO_4	SO_3 Content of Crystals: Unwashed	1 washing	2 washings	4 washings
1	20.0	10.0	0.5	0.05	20.5	20.6	1.4	0.07	..	...	...	0.04	<0.01	<0.01	...
2	20.0	9.5	1.0	0.11	21.7	23.9	2.2	0.09	..	...	0.5	0.7	0.1	0.07	...
3	21.1	9.5	3.4	0.36	14.9	26.1	1.0	0.04	28.7	4.3	4.4	6.6	1.0	0.8	0.6
4-I	20.0	10.0	0.5	0.05	16.6	26.4	1.3	0.05	..	...	...	0.05	<0.01	<0.01	...
4-II	16.6	26.4	1.3	0.05	12.0	36.7	1.2	0.03	..	...	...	0.3	....	....	...
5-I	20.0	10.0	2.0	0.20	22.0	16.0	3.2	0.20	29.6	0.7	0.5	0.8	0.1	....	...
5-II	22.0	16.0	3.2	0.20	7.9	43.4	0.2	0.005	28.6	2.3	6.4	7.0	0.7	0.4	0.3

Table III. Carbonation of Wash Solution

Expt. No.	Temp., ° C.	Solution Compn.: Weight %: Na_2CO_3	K_2CO_3	K_2SO_4	Mole Fraction: K_2O	SO_3	Solid-Phase Compn., Weight %: Mother liquor	K_2CO_3	K_2SO_4	Nature of Solid
1A	25	26.4	3.4	5.3	0.18	0.10	..	...	...	....
1B		5.3	4.6	7.1	0.59	0.33	..	...	...	....
2A	25	25.7	3.4	5.5	0.19	0.11	..	...	...	....
2B		..	...	...	..	..	37	0.9	2.5	....
2C		..	...	...	..	..	70	2.5	4.4	....
2D		5.2	4.3	7.3	0.60	0.34	27	1.1	2.6	....
3A	55	27.9	4.2	5.4	0.19	0.10	...	...	...	....
3B		17.2	4.9	7.0	0.32	0.17	16	0.8	1.2	Trona
3C		7.3	5.6	7.6	0.55	0.29	3	0.2	0.2	$NaHCO_3$
3D		5.3	5.7	7.9	0.63	0.33	1	0.1	0.1	....
4A	55	26.3	5.0	5.1	0.21	0.09	..	...	...	....
4B		..	...	...	..	..	8	0.3	0.5	Trona + $NaHCO_3$
4C		14.9	6.2	6.6	0.37	0.17	4	0.2	0.2	$NaHCO_3$
5A	55	26.3	5.1	5.0	0.21	0.09	..	...	...	....
5B		..	...	...	..	..	14	0.8	0.8	Trona
5C		16.7	5.3	5.8	0.31	0.14	9	0.5	0.5	....

fate contents of the crystals (Table II) are in accord with this conclusion. In experiments 1, 2, 4-I, and 5-I, the sulfate contents can be accounted for by the mother-liquor retentions of the crystals; in experiments 3, 4-II, and 5-II, the sulfate contents are much too high to be explained by mother-liquor retention. Thus the experiments verify the statement made earlier, on the basis of equilibrium data, that no sulfate precipitates on evaporating from *S* to *S'* but that K_2SO_4 and $Na_2CO_3.H_2O$ precipitate on evaporating from *S'* to *F* until the sulfate in solution is reduced to a low value at *F*. This conclusion was verified further by a series of evaporator runs on a pilot-plant scale.

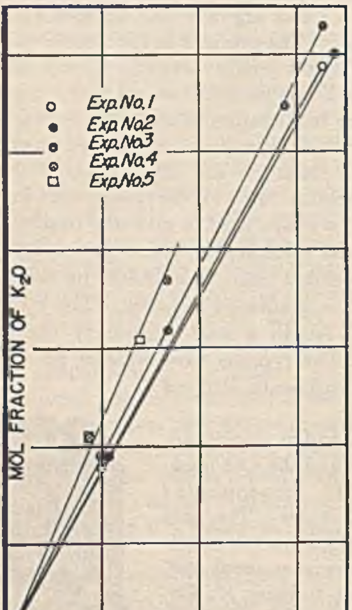

Figure 4. Change in Composition of Wash Solution on Carbonation

The data also show that the greater part of the K_2SO_4 may be removed from the $Na_2CO_3.H_2O$ crystals by washing with 30% Na_2CO_3 solution, and that the wash solution then has a composition in the neighborhood of point *W*, Figure 2. The wash solution is thus suitable for the carbonation and K_2SO_4 evaporation steps. The purity of monohydrate obtainable with a reasonable number of stages in a countercurrent decantation apparatus has not been determined. However, even if the crop from the second stage has as much as 0.5% sulfate after washing, soda ash containing less than 0.2% sulfate can be obtained by mixing with the first-stage crop, which is about two thirds of the total and contains a negligible amount of sulfate. Soda ash, obtained from large-scale runs in which single-stage operation was practiced, always contained less than 0.1% sulfate after washing.

CARBONATION OF WASH SOLUTION

A limited number of experiments was run to test the second step. It was felt that this part of the process is almost identical with that used in industry for making refined sodium bicarbonate from sodium carbonate solution, and that the technique used there could be applied directly to these solutions. It was necessary to show only that the presence of potassium sulfate would

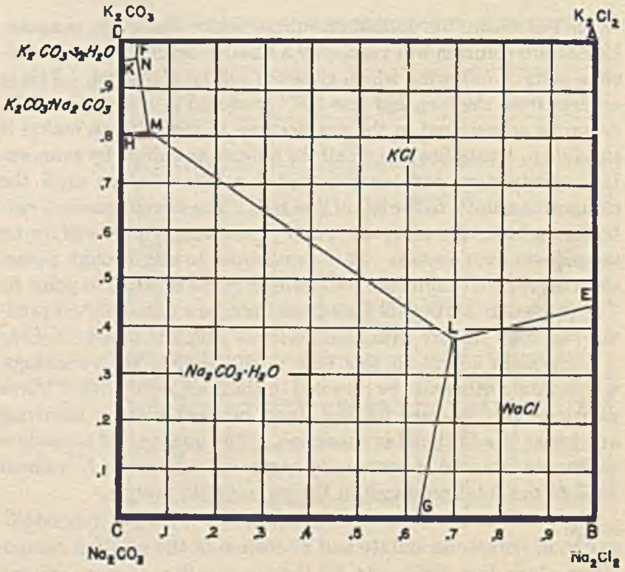

Figure 5. The System Potassium-Sodium-Carbonate-Chloride at 75° C.

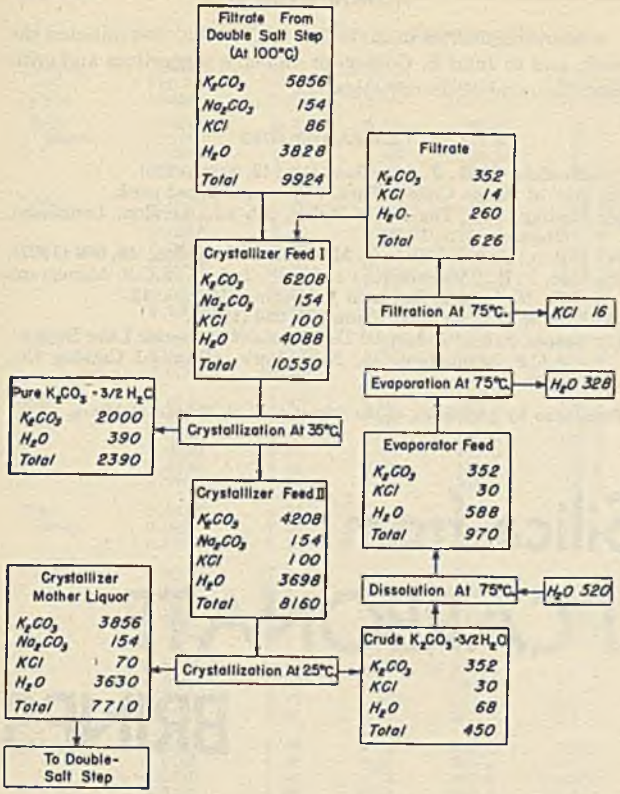

Figure 6. Balanced Flow Diagram for Chloride Removal Process (Basis, One Ton Potassium Carbonate)

cause no contamination of sodium bicarbonate and that the composition of the solution after evaporation corresponded to the predicted composition *W′* (Figure 2). Synthetic solutions of approximate composition *W* were carbonated in a 12-inch glass cylinder with pure carbon dioxide until conversion to bicarbonates was complete.

To prevent the slurry from becoming too dense, several crops of crystals were filtered off in each case in a small laboratory centrifuge. One experiment was run with a 30% carbon dioxide–air mixture. The first crop in each case was trona, $Na_2CO_3.NaHCO_3.2H_2O$, instead of $NaHCO_3$. This causes no change in the direction of line *WW′* and is just as satisfactory as producing $NaHCO_3$, since the product is to be calcined to soda ash in any case. It is assumed, however, that, if the operation were carried out in a Solvay tower, the trona which would form at the top of the tower would be converted to $NaHCO_3$ by the time it reached the bottom of the tower.

It may be concluded from data of Table III that at 50–55° C. pure $NaHCO_3$ (or a mixture of $NaHCO_3$ and $Na_2CO_3.NaHCO_3.2H_2O$) with good filtering characteristics is obtained. At room temperature the product is very fine and has a high mother-liquor retention, with consequent low purity. This corresponds with the experience of the ammonia-soda industry (*5*). Substitution of commercially available carbon dioxide-air mixtures apparently causes no change in the course of the reaction.

Table IV. Data on the System Potassium-Sodium-Carbonate-Chloride at 75° C.

Point	Mole Fraction (K_2)	Mole Fraction (Cl_2)	Moles Salt per 1000 Moles H_2O	Point	Mole Fraction (K_2)	Mole Fraction (Cl_2)	Moles Salt per 1000 Moles H_2O
A	1	1	60.0	*G*	0	0.630	75.3
B	0	1	58.2	*H*	0.800	0	153.2
C	0	0	77.0	*K*	0.952	0	182.5
D	1	0	177.7	*L*	0.376	0.701	91.8
E	0.449	1	77.7	*M*	0.806	0.059	152.8
F	1	0.035	182.0	*N*	0.964	0.031	187.3

The composition of initial and carbonated solutions is plotted in Figure 4. In experiments 4 and 5 carbonation was incomplete. The significant feature of the plot is the fact that the compositions of initial and carbonated solutions for any one experiment fall on a straight line passing through the composition of sodium carbonate. This demonstrates that only sodium and carbonate ions are precipitated during the carbonation. After complete carbonation and filtration at 25° C. (experiments 1, 2, and 3), the solution has a composition in the neighborhood of point *W′* Figure 2.

POTASSIUM SULFATE EVAPORATION

A few experiments on synthetic mixtures were run to test this third step. Evaporation at 75–100° C. of mixtures of sodium and potassium carbonates, bicarbonates, and sulfates, of the proper composition, caused the separation of pure crystalline potassium sulfate. The resulting solutions contained 0.5% sulfate or less. These results are sufficient to show that the evaporation follows its predicted course.

REMOVAL OF SULFATE WITH BARIUM CARBONATE. An alternative procedure is effective in removing sulfate from the carbonated solution. When barium carbonate is added and agitated in a stream of carbon dioxide, barium sulfate is formed, and the sulfate concentration in the solution is reduced to a negligible value. The barium sulfate probably could be recovered in a commercially valuable form. The choice of this method over the method of evaporation to produce potassium sulfate will be governed by the marketability of potassium sulfate and barium sulfate and the cost of barium carbonate. It should be made clear that barium is effective in removing sulfate only in the case of the carbonated solution after sodium bicarbonate has been precipitated (point *W′*, Figure 2). It was previously pointed out that barium could not be used in the original solution because of the high concentration of carbonate.

CHLORIDE REMOVAL PROCESS

As stated in the introduction, all of the chloride comes out with the potassium carbonate. The difference in behavior between sulfate and chloride is caused by the greater solubility of chloride in carbonate solutions of high potassium content. This is shown by the Jänecke diagram for the system potassium-sodium-carbonate-chloride at 75° C. (Figure 5). The data in Table IV are again those of de Ropp (*7*). Because of its greater solubility potassium chloride is not precipitated either with the $Na_2CO_3.H_2O$ or with the $K_2CO_3.Na_2CO_3$ on evaporation at 100° C. In the continuous process the cooled mother liquor from the crystallization step is recycled to the double-salt step, and the chloride thus builds up in the crystallizer until the solubility at 25° C. is exceeded. Potassium chloride then crystallizes with the $K_2CO_3.\frac{3}{2}H_2O$ in the same ratio as it occurs in the initial solution from the base-exchange step.

Separation of potassium chloride from $K_2CO_3.\frac{3}{2}H_2O$ is based on fractional crystallization. At the end of the double-salt evaporation step, the solution is saturated with $K_2CO_3.\frac{3}{2}H_2O$. It is not saturated with potassium chloride, however, until the solution is cooled to about 35° C. This means that the crystals coming out between 100° and 35° C. are pure $K_2CO_3.\frac{3}{2}H_2O$. All of the potassium chloride that comes out is concentrated in the fraction be-

tween 35° and 25° C. If the second fraction is dissolved in water and the solution evaporated to the point of saturation with $K_2CO_3.\frac{3}{2}H_2O$, some potassium chloride will precipitate. The remaining solution may then be recycled to the crystallization step. Thus the process is continuous and cyclic; pure $K_2CO_3.\frac{3}{2}H_2O$ comes out at one point and pure potassium chloride at another.

The balanced flow diagram for the process is shown in Figure 6. This is based on a brine whose chloride content is 0.4% of the potassium carbonate content. Smaller or larger chloride contents would simply lower or raise the temperature at which the two fractions are separated. The flow diagram was based on the solubility data of de Ropp (7) and of Blasdale (*1*). The procedure was checked on a laboratory scale and found to be satisfactory. Potassium carbonate was produced containing only 0.06% chloride.

ACKNOWLEDGMENT

Acknowledgment is made to Robert D. Pike, who initiated the work, and to John E. Conley for valuable suggestions and criticisms throughout the investigation.

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Removal of Dissolved Silica from ALKALI CARBONATE BRINES

▶ ▶ ▶ **The removal of silica from alkaline brines by a two-step process involving the use of a basic magnesium carbonate, hydromagnesite, has been studied. Either compound formation or adsorption or a combination of both was considered possible as the desilication mechanism. Compound formation is ruled out because of the inconstancy of the mole ratio of magnesia to silica. Adsorption is indicated as the correct mechanism by calculating the data in the form of Freundlich adsorption equations. A logarithmic plot of the Freundlich adsorption isotherms gives straight lines whose slopes are constant. The intercepts of these lines are proportional to the Na_2CO_3-K_2CO_3 molar concentration of the solutions from which silica is adsorbed. Thus there is a relation between the Freundlich coefficient and carbonate concentration of the solutions. The basis for this relation is explained. A final equation is established for the desilicating efficiency of basic magnesium carbonate as a function of the concentrations of silica and alkali carbonates in solution.**

E. Gerald Meyer and Charles E. McCarthy
U. S. BUREAU OF MINES, COLLEGE PARK, MD.

IN A PROCESS for extracting $K_2CO_3.\frac{3}{2}H_2O$ from wyomingite, a leucite-bearing rock (*1*), extraction is effected by a base-exchange reaction with sodium carbonate. During the reaction a considerable amount of silica is leached into solution, along with potassium carbonate. This silica must be removed to make the wyomingite process practical.

The silica is removed by a combination of thermal and chemical means. For thermal desilication, the variation of silica solubility with temperature is pronounced enough to permit crystallization of 80% of the silica present when the solution is cooled from 100° to 25° C. However, the resulting brine still contains enough silica to contaminate the products badly unless an additional desilication process is employed. For this additional process the following technique was devised. Its operation was originated in the laboratory and confirmed on a pilot-plant scale.

Obviously some chemical desilicating agent must be employed. This desilicating agent must be relatively cheap, completely effective, and easy to handle, and must not introduce any additional impurities into the solution. A slurry of basic magnesium carbonate was found to approach the requirements most nearly. This basic magnesium carbonate was prepared by mixing solutions of Epsom salts with solutions of soda ash. The compound

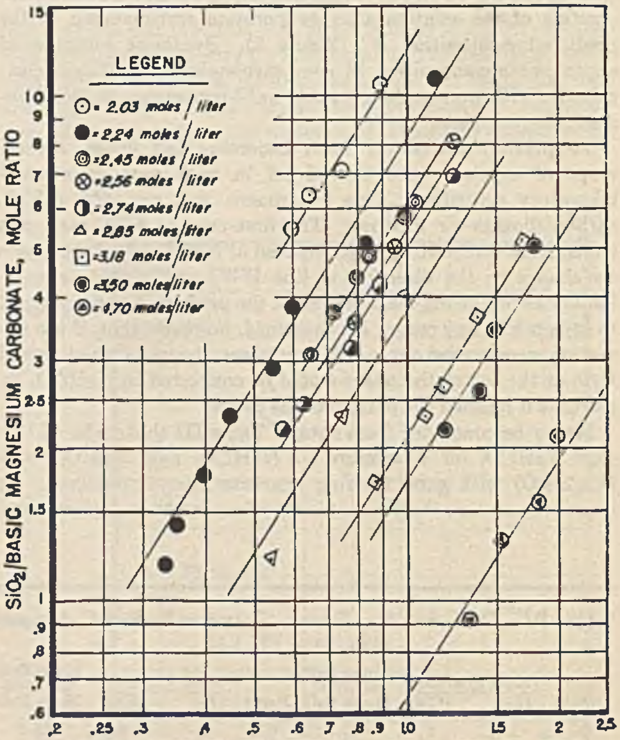

Figure 1. Adsorption Isotherms for Various Carbonate Concentrations

Table I. Data on Desilication Experiments

Source of Data	Basic $MgCO_3$, Mole/L.	SiO_2, Grams/L. Before desil.	SiO_2, Grams/L. After desil.	Na_2CO_3, Grams/L.	K_2CO_3, Grams/L.
Pilot plant	0.0128	9.0	0.90	168.8	61.2
	0.0193	9.0	0.75	168.8	61.2
	0.0225	9.0	0.65	168.8	61.2
	0.0257	9.0	0.60	168.8	61.2
Lab.	0.0106	7.90	1.15	145.5	119.6
	0.0224	7.90	0.85	145.5	119.6
	0.0316	7.90	0.60	145.5	119.6
	0.0425	7.90	0.55	145.5	119.6
	0.0532	7.90	0.45	145.5	119.6
	0.0708	7.90	0.40	145.5	119.6
	0.0887	7.90	0.35	145.5	119.6
	0.1064	7.90	0.33	145.5	119.6
Lab.	0.0105	6.40	1.25	200.4	92.6
	0.0183	6.40	0.95	200.4	92.6
	0.0262	6.40	0.80	200.4	92.6
Pilot plant	0.0191	7.00	1.05	153.0	139.0
	0.0191	7.62	1.00	153.0	139.0
	0.0284	9.00	0.85	153.0	139.0
	0.0286	8.20	0.80	153.0	139.0
	0.0382	9.33	0.72	153.0	139.0
	0.0478	9.32	0.65	153.0	139.0
Pilot plant	0.0251	7.00	1.00	208.0	122.5
	0.0453	7.00	0.75	208.0	122.5
	0.0932	6.80	0.55	208.0	122.5
Lab.	0.0306	11.4	1.70	325.0	15.0
	0.0461	11.4	1.40	325.0	15.0
	0.0615	11.4	1.20	325.0	15.0
	0.0790	11.4	1.10	325.0	15.0
	0.1024	11.4	0.88	325.0	15.0
Lab.	0.0123	5.50	1.75	257.0	141.0
	0.0193	5.50	1.50	257.0	141.0
	0.0257	5.50	1.40	257.0	141.0
	0.0322	5.50	1.20	257.0	141.0
Lab.	0.0082	4.96	1.23	200.0	118.6
	0.0163	4.96	0.88	200.0	118.6
	0.0220	4.96	0.78	200.0	118.6
	0.0295	4.96	0.63	200.0	118.6
	0.0333	4.96	0.57	200.0	118.6
Lab.	0.0154	4.00	2.00	285.0	276.0
	0.0233	4.00	1.85	285.0	276.0
	0.0311	4.00	1.55	285.0	276.0
	0.0493	4.00	1.30	285.0	276.0

thus precipitated was filtered and washed free of sulfate, and then repulped to facilitate handling. Experiments designed to detect any variation in the basic magnesium carbonate precipitate, due to varying the mole ratio of magnesium sulfate to sodium carbonate, indicated that only one compound was formed. Chemical analysis of this compound showed it to have the empirical formula $4MgO.3CO_2.4H_2O$. An x-ray diffraction study of the dried substance indicated that its crystallographic structure corresponds to that of hydromagnesite, $4MgO.3CO_2.4H_2O$. Thus it is concluded that the compound involved in this study is a hydrated double salt of magnesium carbonate and hydroxide, which may be written $3MgCO_3.Mg(OH)_2.3H_2O$. The solutions desilicated with the basic magnesium carbonate varied in composition from 14% Na_2CO_3–5% K_2CO_3 to 20% Na_2CO_3–20% K_2CO_3 to 6% Na_2CO_3–48% K_2CO_3. In all cases the starting concentration of silica was not varied appreciably, but the final concentration was recorded as a function of amount of desilicating agent used. The reaction temperature was held at 27° C., and the time allowed for equilibrium to be attained was one hour.

Table I summarizes the experiments conducted under the conditions described. Some of the data were obtained in the laboratory, where the batch consisted of 100 ml. of solution; other data were collected in the pilot plant, where the batch consisted of 90–100 gallons. The fact that data from these two sources can be correlated verifies the adaptability of the process to large-scale operation.

Table II. Ratios of Hypothetical Compounds

Basic $MgCO_3$ as MgO, Mole/L.	SiO_2 Removed, Mole/L.	Mole Ratio, MgO: SiO_2	Change in Mole Ratio
0.0420	0.0858	0.4895	0.4895
0.0732	0.0908	0.806	0.4165
1.048	0.0924	1.134	0.338
0.1224	0.1615	0.7578	0.758
0.1844	0.1665	1.107	0.349
0.2460	0.1698	1.448	0.341
0.3160	0.1715	1.842	0.394
0.4096	0.1755	2.333	0.491
0.0512	0.0633	0.809	0.809
0.0772	0.0660	1.158	0.349
0.1028	0.0683	1.506	0.348
0.1288	0.0699	1.844	0.338
0.0512	0.1348	0.380	0.380
0.0772	0.1373	0.5625	0.1825
0.0900	0.1390	0.6475	0.085
0.1028	0.1398	0.7355	0.088
0.424	0.1135	0.3735	0.3735
0.0896	0.1168	0.767	0.3935
0.1264	0.1210	1.045	0.278
0.1700	0.1222	1.392	0.347
0.2128	0.1235	1.722	0.330
0.2832	0.1244	2.278	0.556
0.3548	0.1252	2.832	0.554
0.4256	0.1256	3.386	0.554
0.0764	0.116	0.659	0.659
0.0764	0.110	0.6945	0.355
0.1136	0.135	0.842	0.1475
0.1144	0.123	0.931	0.089
0.1528	0.143	1.069	0.138
0.1912	0.144	1.327	0.258
0.1004	0.0999	1.005	1.005
0.1812	0.1041	1.740	0.735
0.3728	0.1037	3.594	1.854
0.0330	0.0603	0.5475	0.5475
0.0652	0.0678	0.962	0.4145
0.0880	0.0693	1.265	0.303
0.1180	0.0719	1.641	0.376
0.1332	0.0730	1.826	0.185
0.0616	0.0333	1.849	1.849
0.0932	0.0358	2.603	0.754
0.1244	0.0408	3.048	0.445
0.1972	0.0450	4.385	1.337

MECHANISM OF DESILICATION REACTION

An investigation indicated that the reaction can take three possible courses: (*a*) A definite compound can form between the basic magnesium carbonate and the silica; (*b*) the silica can be adsorbed on the surface of the reagent; or (*c*) a combination of compound formation and adsorption can occur. Possibility (*a*) can be ruled out by the following evidence. If a compound is formed, it should show a constant mole ratio of magnesia to silica. This mole ratio can be calculated from the values of the silica concentration before and after desilication and the values of basic magnesium carbonate used and Mg^{++} concentration in the desilicated solution. An attempt to ascertain the latter by standard chemical analysis resulted in figures which bordered on the limit of quantitative detection. Spectrographic determination of the solids obtained on evaporating the solution to dryness further indicated the low concentration of Mg^{++}. Consequently, since the concentration of magnesium in the solution was of the order of 0.1 millimole per liter, no error is introduced in assuming that all of the magnesia added as basic magnesium carbonate is withdrawn from the solution with the silica after desilication is complete. Thus the ratio of magnesia to silica can be calculated for the solid obtained by desilication (Table II). The inconstancy of these calculations rules out the possibility of compound formation.

In addition, x-ray data substantiate the contention that no compound is formed. Examination of the basic magnesium carbonate after it had been used for desilicating revealed a pattern similar to that of amorphous silica. That is, only a few broad diffraction bands were discernible. This pattern was compared with that of a prepared magnesium silicate and found to differ, despite the fact that the prepared silicate was nearly amorphous itself. The inference is that a coating of amorphous silica is adsorbed on and surrounds each particle of basic magnesium carbonate.

Since the reaction does not yield a compound, the possibilities of an adsorption phenomenon or of compound formation plus adsorption must be examined. The standard procedure for testing possible adsorption is to calculate the data in the form of the Freundlich adsorption isotherm equation,

$$x/m = kc^{1/n}$$

where x = SiO_2 removed, moles
m = MgO required, moles
c = residual SiO_2 concn., gram/liter
k, n = constants

Results for all experiments are listed in Table III in order of increasing concentration of sodium carbonate plus potassium carbonate. A plot of these data on logarithmic paper produces a series of straight lines. This plot (Figure 1) indicates that the removal of silica from the alkaline solution proceeds along the lines of an adsorption. Furthermore, since there is no tendency of the lines toward curvature, compound formation followed by adsorption is improbable (*3*)

Table III. Calculated Silica Adsorption Data

Basic $MgCO_3$, Mole/L.	SiO_2 Removed, Mole/L.	Moles SiO_2 Removed/Mole Basic $MgCO_3$	SiO_2 Concn. after Desilication, Grams/L.	Dissolved Alkali Carbonates, Moles/L.
0.0128	0.1348	10.53	0.90	2.03
0.0193	0.1373	7.12	0.75	2.03
0.0225	0.1390	6.18	0.65	2.03
0.0257	0.1398	5.44	0.60	2.03
0.0106	0.1135	10.71	1.15	2.24
0.0224	0.1168	5.21	0.85	2.24
0.0316	0.1210	3.83	0.60	2.24
0.0425	0.1222	2.88	0.55	2.24
0.0532	0.1235	2.32	0.45	2.24
0.0708	0.1244	1.76	0.40	2.24
0.0887	0.1252	1.41	0.35	2.24
0.1064	0.1256	1.18	0.33	2.24
0.0105	0.0858	8.17	1.25	2.56
0.0183	0.0908	4.96	0.95	2.56
0.0262	0.0924	3.53	0.80	2.56
0.0191	0.116	6.10	1.05	2.45
0.0191	0.110	5.76	1.00	2.45
0.0284	0.135	4.75	0.85	2.45
0.0286	0.123	4.30	0.80	2.45
0.0382	0.143	3.74	0.72	2.45
0.0478	0.144	3.01	0.65	2.45
0.0082	0.0603	7.35	1.23	2.74
0.0163	0.0678	4.16	0.88	2.74
0.0220	0.0693	3.15	0.78	2.74
0.0295	0.0719	2.43	0.63	2.74
0.0333	0.0730	2.16	0.57	2.74
0.0251	0.0999	3.98	1.00	2.85
0.0453	0.1041	2.30	0.75	2.85
0.0932	0.1037	1.11	0.55	2.85
0.0306	0.1615	5.28	1.70	3.18
0.0461	0.1665	3.62	1.40	3.18
0.0615	0.1698	2.76	1.20	3.18
0.0790	0.1715	2.17	1.10	3.18
0.1024	0.1755	1.71	0.88	3.18
0.0123	0.0633	5.15	1.75	3.50
0.0193	0.0660	3.42	1.50	3.50
0.0257	0.0683	2.66	1.40	3.50
0.0322	0.0699	2.17	1.20	3.50
0.0154	0.0333	2.16	2.00	4.70
0.0233	0.0358	1.53	1.85	4.70
0.0311	0.0408	1.31	1.65	4.70
0.0403	0.0450	0.091	1.30	4.70

The lines of Figure 1 are parallel as well as straight. This signifies that the exponent of the residual silica concentration is constant for the various experiments. The only factor varied in the experiments was the concentration of sodium carbonate and potassium carbonate in the solution; also the only factor varied in the plot is the value of the intercept. The intercepts are equal to *k;* therefore an attempt was made to correlate these values with the alkali carbonate concentrations of the solutions. The result is shown in Figure 2.

DERIVATION OF STRAIGHT-LINE RELATION

A straight-line relation can be derived between the Freundlich *k* and the concentration of alkali carbonates when these variables are plotted on a logarithmic scale. The following equation, obtained from Figure 2, holds for concentration between 2.0 and 4.7 moles per liter:

$$k = 131.3\, C^{-3.44}$$

where C = concn. of alkali carbonates, moles/liter

If an attempt is made to give *k* theoretical significance by comparing the Freundlich equation with the Langmuir adsorption isotherm (*2*), it becomes apparent that *k* is a measure of the fraction of silica molecules condensing on the basic magnesium carbonate surface as compared with the fraction evaporating into the solution phase. Because the attractive force between silica and solid and the attractive force between silica and solution governs this fraction, the concentration of the major constituents of the solution will be a controlling factor. That is, the attractive force between silica and solid is unchanged (the same adsorbent, basic magnesium carbonate, is used throughout); therefore it may be concluded that the attractive force between silica and solution is changing. This force would undoubtedly be some function of the concentration of the major solution constituents. However, the above picture is probably oversimplified, and the empirically derived relation between *k* and the concentration would be expected to hold for limited concentration ranges only.

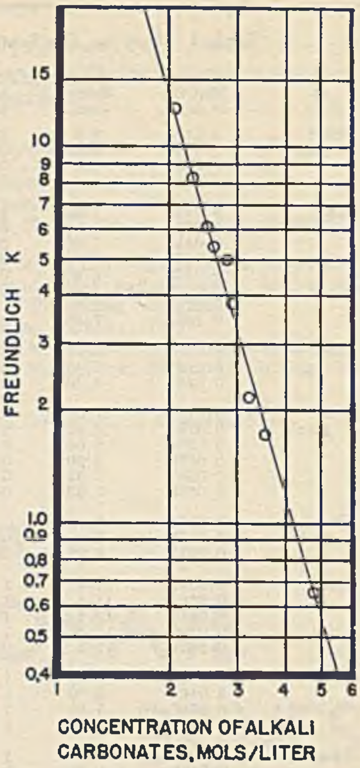

Figure 2. Correlation of Freundlich *K* Values with Solution Concentrations

No particular significance can be attached to the value obtained for *n*. Although $1/n$ usually varies between 0 and 1, these limits are by no means fixed, especially for solution adsorptions. That $1/n$ should remain constant seems in line with the fact that, throughout the experiments, the chief variable was the nature of the solution from which silica was adsorbed rather than the adsorbent or the adsorbate. Numerically the value for $1/n$ as obtained from Figure 1 is 1.55. Hence, for carbonate concentrations between 2.0 and 4.7 moles per liter we obtain the following complete expression for adsorption of silica with prepared hydromagnesite:

$$\frac{x}{m} = 131.3\, \frac{c^{1.55}}{C^{3.44}}$$

where C = Na_2CO_3 and K_2CO_3, moles/liter
x/m = SiO_2 removed per mole basic $MgCO_3$, moles

ACKNOWLEDGMENT

Acknowledgment is made to Robert D. Pike, who initiated the work, and to John E. Conley for valuable suggestions and criticisms throughout the investigation.

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PROCESS for AMINOGUANIDINE

R. Norris Shreve and R. P. Carter
PURDUE UNIVERSITY, LAFAYETTE, IND.

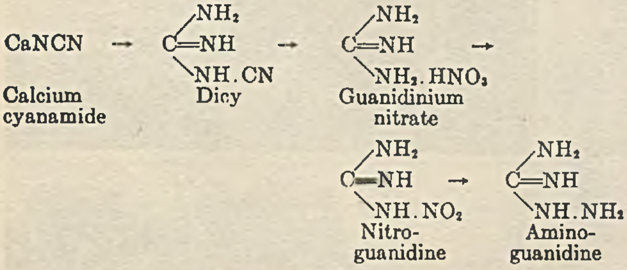
▶ ▶ ▶ In making dyes from aminoguanidine it was first necessary to elaborate a process for its preparation. This involved the electrolytic reduction of nitroguanidine. The nitroguanidine resulted from the dehydration with sulfuric acid of guanidinium nitrate which, in turn, was derived from dicyandiamide by heating with ammonium nitrate. Yields of 73% nitroguanidine were obtained, based on the dicyandiamide used. Yields on the reduction process for converting nitroguanidine to the sulfate and recovering the product as the bicarbonate were around 50%.

FOR the past fifty years the preparation of aminoguanidine and its derivatives has been a problem of only theoretical interest. The free amine is hygroscopic and unstable, hydrolyzing readily in the presence of dilute bases. However, it is quite basic in character and forms salts by addition to common acids. The bicarbonate is the only insoluble salt, and the compound is generally isolated in this form.

Aminoguanidine was made by Thiele in 1892 (*1*, *27*) by reduction of nitroguanidine with zinc dust and acetic acid, with a yield of 65% or less. A modification of this reaction was reported by Conard and Shriner (*3*) and Stefanowski with Janiszewski (*26*). Wyler (*29*) in 1935 was granted a patent using zinc acetate instead of acetic acid with zinc dust, with yields claimed to be 90%. We were unable to obtain better than 50%. Yields of 60–70% of aminoguanidine were obtained by the reduction of nitroguanidine with sodium and liquid ammonia in the presence of ammonium chloride (*14*). Lieber and Smith (*12–15*) studied thoroughly the production of aminoguanidine by hydrogen and a catalyst from nitroguanidine. McGill (*17*) obtained a patent in 1936 for a somewhat similar method.

Various methods have been published on the synthesis of aminoguanidine with hydrazine as reagent. They are divided into hydrazination, or the addition of hydrazine to a compound, and hydrazinolysis. Pelizarri and Gaiter reacted cyanamide with hydrazine sulfate (*19*, *20*). Similar reactions were carried out by Hofmann and Ehrhart (*9*) and Fantl and Silbermann (*6*). Thiele (*28*) in 1893 prepared aminoguanidine by reacting equimolecular amounts of nitrosoguanidine and hydrazine hydrate. In 1927 Heyn (*7*) prepared aminoguanidine by the reaction of 3-alkyl isothiourea sulfate and hydrazine. Schering-Kahlbaum (*21*), Smith and Anzelmi (*23*), and Kirsten and Smith (*11*) investigated the same reaction; the latter prepared substituted aminoguanidinium salts.

Boehringer (*2*) patented an electrolytic reduction of nitroguanidine, using a tin cathode and very little acid. This is the process studied here and improved. The nitroguanidine is easily made from dicyandiamide (Dicy). The latter material is obtained by the hydrolysis of calcium cyanamide at 60–65° C. The reaction sequences may be represented as:



$$CaNCN \rightarrow C(=NH)(NH_2)NH.CN \rightarrow C(=NH)(NH_2)NH_2.HNO_3 \rightarrow C(=NH)(NH_2)NH.NO_2 \rightarrow C(=NH)(NH_2)NH.NH_2$$

GUANIDINIUM NITRATE

One mole equivalent of Dicy was fused with slightly over 2-mole equivalents of commercial ammonium nitrate (*4*), resulting in a 90% yield of guanidinium nitrate. The crude material was converted immediately into the nitro compound by sulfuric acid dehydration (*5*). The nitrate is fairly soluble in water; the nitro compound is only slightly soluble cold but more so hot. Hence the nitroguanidine is easily purified by recrystallization from water.

The following was the procedure for a typical run. Four moles (420 grams) of Dicy and 11 moles (880 grams) of ammonium nitrate were mixed and ground well. This mixture was charged into a 2-liter round-bottom flask heated by an oil bath. The temperature at the start was 120° C. and at the end of half an hour was 160° C. This temperature was maintained for 4 hours without stirring. However, Smith, Sabetta, and Steinbach (*25*) reported that after 1 hour of fusion the yield of by-products, melamine and ammelide, is greatly increased, and that on heating over an hour, less product was recovered. The mixture at first melted and then set as the reaction proceeded. The final solid was guanidinium nitrate.

To purify the product, the flask was allowed to cool to 100° C., and the contents were extracted with 4 liters of hot water. Small quantities of melamine and ammelide were present, but since they are insoluble, they could be filtered out. The materials remaining in solution were guanidinium nitrate and ammonium nitrate; an excess of the latter was used because it greatly increases the yield. The solution was evaporated until the water content was very small, as indicated by rapid crystallization from the boiling solution and the tendency to set. This material could have been purified by recrystallization from a small volume of water, but the pure product was not necessary for the next reaction.

NITROGUANIDINE

The crude guanidinium nitrate was dehydrated by dissolving it in 1500 ml. of 96% sulfuric acid. The acid was cooled by an ice-salt mixture surrounding the 4-liter beaker in which the reaction took place. It was stirred vigorously while the temperature was kept below 20° C., the rate of addition of guanidinium nitrate being used to regulate the temperature. Later Ludlow (*16*) found in this laboratory that, even if the temperature rises to 26° C., no decrease in yield is apparent. This allows the use of tap water as a cooling medium. Ludlow also found that maximum conversion was reached at the end of an hour. The reaction mass is diluted at this stage, and the insoluble crystals of nitroguanidine are filtered off. Here Ludlow found that crystals with much better filtering characteristics could be obtained by pouring the mass into water held at a maximum of 40° C. than by pouring it over ice as directed in "Organic Syntheses" (*5*). The product was purified by recrystallization from water and gave long needle-shaped crystals. The yield was 760 grams, melting at 232° C. (reported, 231–232° C., *18*), or 73% based on the Dicy used.

Table I. Electrolytic Reduction of Nitroguanidine

Nitroguanidine, Grams	95% H_2SO_4, Grams	Amperage	Voltage		Temp., ° C.	Time, Hr.	Aminoguanidine Bicarbonate	Yield
			Begin	End			Grams	%
104	150	10	7.0	15	17	16	40	30
104	200	10	6.5	8.5	16	15.75	57	42
104	200	10	6.5	8.5	16	18	60	44.2
104	250	10	6.7	8.5	16	18	48	35.3
104	300	10	6.0	8.0	15.5	18	54	39.7
104	200	15	8.5	10.7	16.5	12	78.5	57.7
104	200	20	9.5	12.5	17	9	62	45.6
104	200	20	9.0	12.0	17	9.75	66	48.5
52	150	15	9.0	11.0	16	6.25	34	50
26	125	15	9.7	10.7	16.5	3	17	50
52	150	15	9.0	11.5	16	7.5	38.6	56.8
52	150	15	8.5	10.5	25	5.5	21	31
52	150	15	8.5	10.5	25	5.5	22.3	32.8
52	150	15	9.0	11.0	20	6	32.6	48
52	150	15	9.0	11.0	20	6	34	50.1
52	150	15	10.0	12.0	13	7	38.7	57
52	150	15	10.0	11.0	10	8.5	41.3	61
52	150	15	10.0	12.2	5	10.5	43.6	64.2
104	200	15	8.3	10.7	16.5	12	72	53
104	200	15	8.3	10.7	16.5	12	73	53.6

A cheaper method for the preparation of nitroguanidine uses calcium cyanamide and ammonium nitrate as raw materials rather than the more costly Dicy (*22*).

AMINOGUANIDINE

The basis for the electrolytic cell was suggested by the procedure for reducing nitrourea to semicarbazide (*10*). Smith and Sabetta (*24*) reported that the reduction of nitroguanidine to nitrosoguanidine in neutral or basic media is reversible. Lieber and Smith (*15*) determined that aminoguanidine is very resistant to hydrolysis in an acid medium; they reported earlier (*16*) that in acid media the nitroso derivative is not formed by catalytic reduction.

A cell was constructed from a hard rubber battery box (Figures 1 and 2). The partitions separating the cells had been removed as well as the risers from the bottom. A diaphragm was made from birch veneer, $^1/_8$ inch thick, and was cemented in place with a melted plastic. This plastic was made by heating equal molal quantities of ethylene glycol and phthalic anhydride to 200° C. for 24 hours (*8*). This material withstood the action of the dilute sulfuric acid very satisfactorily.

The cathode was a layer of mercury on the floor of the cathode chamber. This layer was thick enough to cover the bottom completely without breaking. Electrical contact to this mercury was made by heavy copper wire, sealed in the end of an 8-mm. glass tube with the plastic. The wire was bent at right angles to the tube at the point at which it projected from the tube. The tube was clamped in such a way that it dipped into the mercury, and the copper wire was completely covered. A small amount of mercury was placed inside the tube, and the negative lead from the generator dipped into the mercury (Figure 1).

A sheet of lead, $^1/_8$ inch thick, was employed as the anode. It was bent at 90° along each of two parallel lines, so that it would line the anode cell on the three outside walls. A small piece was left projecting upward, to which the positive lead from the generator was attached. The diaphragm was cemented in the cell so as to make the cathode side have twice the volume of the anode compartment. The cell was cooled by tap water running through 10 feet of 10-mm. Pyrex tubing in the cathode chamber and 6 feet of similar tubing in the anode side (Figure 1). Since nitroguanidine is not soluble in the catholyte, a rapid motor stirrer was used to agitate the suspension. For runs at cell temperatures lower than that of tap water, an alcohol-water solution was pumped intermittently through the cooling coils and copper tubing in an ice-salt mixture. An ammeter was connected in series with the cell and a voltmeter across the leads just outside of the cell (Figure 2). Direct current was supplied by a rotary converter (Figures 1 and 2). The over-all resistance of the cell when filled with 8% sulfuric acid was only 0.6 ohm, calculated from the voltage necessary to force the required current through the cell.

EXPERIMENTAL REDUCTIONS

Forty experimental reductions were made in the electrolytic cell. Twenty representative runs were used to furnish the data for Table I. The following procedure was found most satisfactory for this reduction:

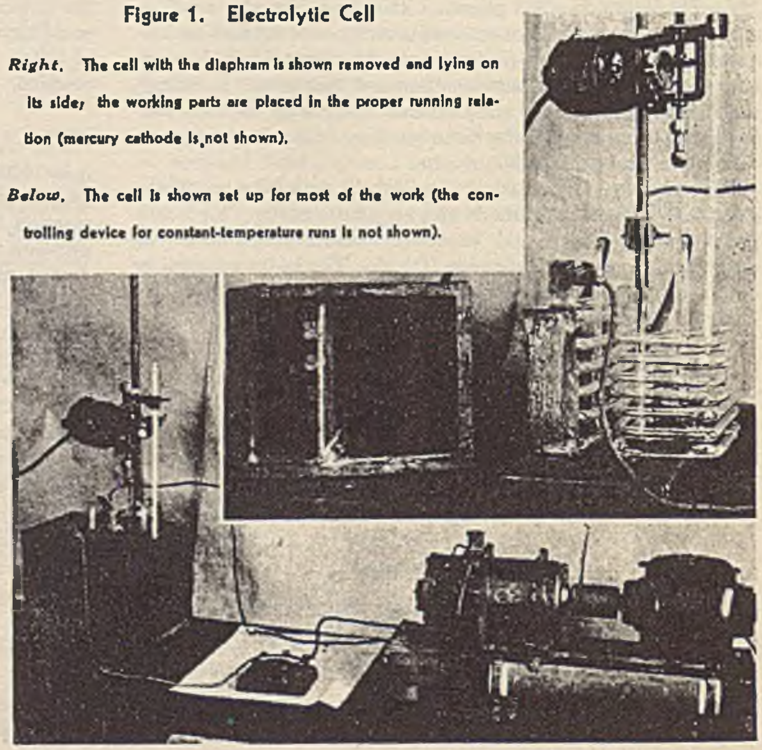
The cell was assembled, and the proper electrical connections were made to the anode and cathode. Two liters of water were poured into the cathode compartment and one liter into the anode side. Ninety grams of concentrated sulfuric acid (95%) were added to the anode compartment and 150 grams to the cathode cell. The stirrer was started and the cooling water turned on. When the temperature of the cathode chamber reached 16° C., 52 grams (0.5 mole) of nitroguanidine were added to this compartment. The direct-current generator was started and the resistance of the field adjusted to put 15 amperes of current through the cell. At the start the voltage was 9 volts and the temperature 15.5° C. The nitroguanidine was in suspension at first, but as it was reduced to the very soluble amino derivative, a clear solution finally resulted. After $7^1/_4$ hours the solution had become clear and excess hydrogen began to bubble off. No hydrogen came off during the initial stages of the reduction and very little during the final part. The reduction was continued an additional 15 minutes. By this time the temperature had reached 16° C. and the voltage was 11.5 volts, the current having been held constant at 15 amperes for the entire reaction.

The cathode solution was sucked into a calibrated flask, and 1 cc. was withdrawn and titrated with a standard base to phenolphthalein end point. After neutralization with the calculated amount of calcium carbonate, the solution was filtered to remove

Figure 1. Electrolytic Cell

Right. The cell with the diaphram is shown removed and lying on its side; the working parts are placed in the proper running relation (mercury cathode is not shown).

Below. The cell is shown set up for most of the work (the controlling device for constant-temperature runs is not shown).



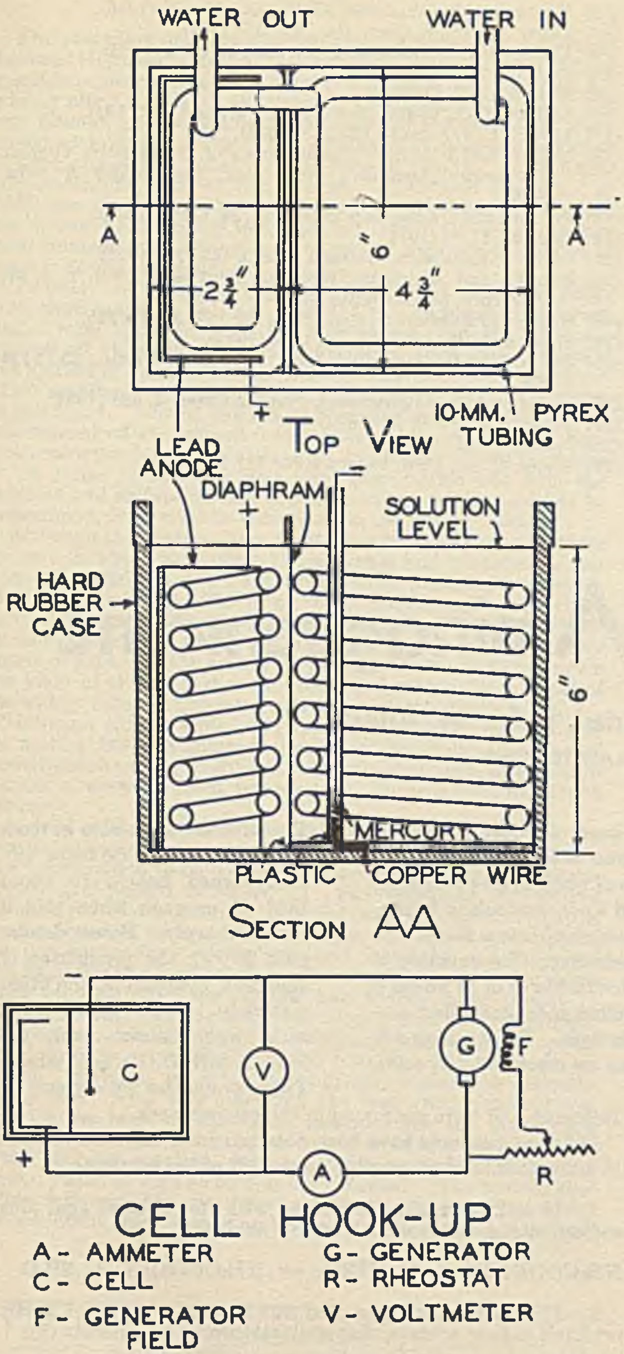


Figure 2. Diagram of Electrolytic Cell and Hook-up

the calcium sulfate, evaporated to 300 ml., and filtered again to remove the remaining hydrated calcium sulfate. The solution now contained the aminoguanidine in the form of the sulfate. Water was added to bring the final volume up to 600 ml., and 42 grams of sodium bicarbonate were dissolved in it with rapid stirring; the solution turned from clear to a brown-pink color. In about one minute all of the bicarbonate had dissolved, and in a few additional seconds the fine white precipitate of aminoguanidine bicarbonate had begun to form. After standing overnight, the precipitate was filtered and the cake washed with water and methyl alcohol. After air drying the yield was 38.6 grams, or 56.8% based on the nitroguanidine used.

Aminoguanidine bicarbonate was analyzed for nitrogen content by the Dumas procedure, and showed 41.20 and 41.23%. By calculation $NH_2C(NH)NHNH_2.H_2CO_3$ has 41.18% N_2. A sample melted at 177.6° C. (reported, 177–178° C., *14*).

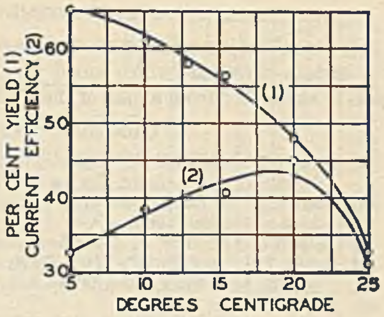


Figure 3. Electrolytic Reduction of Nitroguanidine to Aminoguanidine Bicarbonate (½ Mole, 6% Sulfuric Acid, 15 Amperes)

The values for sulfuric acid given in Table I were the amounts used in the cathode solution, and that in the anode was enough to produce a similar concentration of acid. An excess of acid is needed during the reduction because acid concentration decreases in the cathode compartment as the amine salt is formed. If too little acid is used, the resistance of the cell is greater and more heat is produced; consequently the cooling of the cell is more difficult. Too concentrated an acid medium results in a lower cell resistance; but more sulfuric acid has to be subsequently removed by calcium sulfate precipitation, and the aminoguanidine is decomposed as it forms. Enough acid to produce an 8% solution at the beginning of a 1-mole reduction, or a 4% solution at the end, was the optimum proportion.

The amperage is also an important factor. Too small a current gives a reduced yield; too great a current causes a similar decrease in amount of product recoverable, probably because of the excess heat produced. The voltage is governed by the amperage desired and the resistance of the cell itself. From Table I an optimum current of 15 amperes seems to be indicated for this particular cell.

Lower temperatures give better yields of desired product (Table I). However, then it was necessary to continue the reaction for a longer time in order to produce a clear solution, an indication that all of the nitroguanidine previously in suspension had reacted. At this lower temperature the resistance is greater and the current efficiency is decreased (Figure 3). The latter effect is partially caused by the decreased solubility of nitroguanidine in water. Hydrogen escaped during the entire reduction when the temperature was 10° C. and especially at 5° C. Curves in Figure 3 were plotted from the data in Table I.

CALCULATION OF CURRENT EFFICIENCY

To evaluate the current efficiency, a calculation made from that of the typical run described under "Experimental Reductions" is as follows: A yield of 38.6 grams of aminoguanidine bicarbonate was recovered. Dividing this value by the molecular weight (136), the moles of product are obtained. Since six hydrogens are necessary to balance the reduction of 1 mole

$$H_2NC(NH)NH(NO_2) + 6H = H_2NC(NH)NHNH_2 + 2H_2O$$

the number of moles multiplied by six times Faraday's number (96,500) gives the coulombs of electricity actually used:

$$(38.3 \times 6 \times 96{,}500)/136 = 164{,}300 \text{ coulombs}$$

Since the cell was operated at 15 amperes for 7½ hours,

$$15 \times 7.5 \times 3600 = 405{,}000 \text{ coulombs}$$

were put into the cell. The output divided by the input times 100 gives the current efficiency:

$$(164.300 \times 100)/405{,}000 = 40.5\%$$

This type of calculation was used to give curve 2 of Figure 3.

ACKNOWLEDGMENT

Appreciation is expressed to American Cyanamid Corporation for certain chemicals which aided this investigation. This report is abstracted from a part of the Ph.D. thesis of R. P. Carter.

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Azo Dyes from Aminoguanidine

R. Norris Shreve, R. P. Carter[1], and J. M. Willis[2]

PURDUE UNIVERSITY, LAFAYETTE, IND.

▶ ▶ ▶ Aminoguanidine has been diazotized and hot-coupled with various intermediates to furnish a whole new series of azo dyes which possess of good dyeing properties on animal fibers such as silk and wool, particularly in conjunction with a mordant. The dyes are of various shades with the browns and oranges predominating. The coupling of the aminoguanidine diazonium hydroxide or of its isomer is carried out in a hot aqueous solution under controlled conditions of pH to give the various dyes. The latter are soluble in alkaline solution, but they are precipitated by acids.

PREVIOUS attempts to diazotize and couple aliphatic amines generally have been unsuccessful. Ordinary reagents and procedures for aromatic diazotization have given no similar diazonium compounds in the aliphatic series (*6*). Indirect methods have been tried on ordinary aliphatic amines (*7*) but with no success. However, aminoguanidine can be subjected to the action of sodium nitrite in the absence of free acid and a diazonium compound be obtained; this work was done by Hofmann and Roth (*4*, *5*) in Germany in 1910, but prior to the present research little or no use was made of the compound produced. Hofmann, Hock, and Kirmreuther (*3*) repeated the work and gave a more detailed report. Their method was to treat aminoguanidine nitrate with an excess of neutral sodium nitrite in an aqueous medium at room temperature. After the solution had stood for 40 hours, the reaction was complete and aminoguanidine diazonium hydroxide precipitated in almost quantitative yields. The same investigators reported color reactions produced by the diazonium material, but their method required a week for the color to develop. No dye formation or precipitation was reported.

The diazonium material was analyzed by several methods (*3*). Hofmann's theory that it is in equilibrium with the nitrosoamine, as shown below, was based upon its insolubility in water and other common solvents:

$$\underset{\text{Diazonium hydroxide}}{H_2NC(NH)NHNHN{=}NC(NH)NHN{=}NOH} \rightleftharpoons \underset{\text{Nitrosoamine}}{H_2NC(NH)NHNHN{=}NC(NH)NHNHNO}$$

The substance is stable at room temperature, but explodes violently when heated to about 130° C. or even when cold if struck sharply. Bases decompose it with the production of ammonia, cyanamide, and other materials. Acids form salts; with hydrochloric acid the formula $C_2N_{10}H_7Cl$ was obtained. These properties were given by Hofmann and were confirmed in the present work.

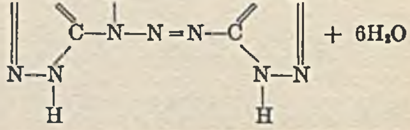
Different products have been obtained from the diazotization of aminoguanidine, depending on the pH of the solution:

1. If aminoguanidine is treated with free mineral acid plus sodium nitrite, the product is guanyl azide (*13*, *14*):

$$NH_2C(NH)NHNH_2 + HNO_2 \rightarrow NH_2C(NH)N_3 + 2H_2O$$

2. If diazotization is carried out in the presence of acetic acid and sodium acetate, diazoaminotetrazolic acid results (*9*):

$$2NH_2C(NH)NHNH_2 + 3HNO_2 \rightarrow$$



3. In neutral aqueous solutions, guanylnitrosoaminoguanyl tetrazene is formed (*9*):

$$2NH_2C(NH)NHNH_2(HNO_3) + 2NaNO_2 \rightarrow NH_2C(NH)NHNHN{:}NC(NH)NHNHN{:}O + 2NaNO_3$$

The product from the latter reaction or its isomeric diazonium hydroxide serves as the reagent in the coupling reactions to give the dyes dealt with in this paper.

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[1] Present address, Hercules Powder Company, Wilmington, Del.

[2] Present address, E. I. du Pont de Nemours & Company, Inc., Gibbstown, N. J.

DIAZOTIZATION

The procedure employed for making the diazonium hydroxide followed Hofmann's method (*3*): One mole (136 grams) of aminoguanidine bicarbonate was dissolved in 1500 ml. of water by adding nitric acid until the solution was neutral to litmus. It was filtered, and 80 grams (1.15 moles) of sodium nitrite were added with rapid stirring. The solution was clear and colorless at first, but after 2 hours it began to turn cloudy. In 48 hours the diazonium material was filtered. A yield of 78 grams or 83% was obtained. This substance was dried by exposure to the air and used directly in the preparation of the dyes. If it is used immediately, drying is unnecessary and the substance is far less dangerous to handle.

To study the progress of the diazotization reaction more fully, runs were made at 25°, 35°, and 45° C. Samples in different flasks were removed from the thermostat, and the products filtered off at frequent intervals to obtain yield data. Results are plotted in Figure 1. Higher temperatures increase the speed of the reaction but give lower yields since the product decomposes in hot water. During one run at room temperature the product was filtered off at frequent intervals to obtain the yield *vs.* time characteristics for the reaction; the results are shown in Figure 2. A series of diazotizations were also carried out with the chloride and sulfate instead of the nitrate. As far as could be determined, there were no differences in the rate or yield.

Although the diazotization reaction is relatively simple, there are two factors which affect yields—rapid and continued agitation and control of pH. Apparently after precipitation begins, the suspension of the solids in the solution gives surfaces on which further precipitation will occur more easily. When the aminoguanidine nitrate is prepared, care must be taken to avoid any excess of acid. Slight acidity of the solution tends to cut down the yield of the desired diazo compound materially because of the widely different products obtained with variations in pH.

Hofmann (*3*) attempted to couple diazotized aminoguanidine by adding the precipitated chloride to alcoholic solutions of naphthylamines and naphthols. He reported that, after standing for a week at room temperature, the solutions developed colors.

Instead of the chloride, the diazonium hydroxide was used in this investigation. The method as employed initially follows: The intermediate to be coupled was ground in water to a paste, diluted, and heated to 80-85° C. The suspension was stirred vigorously. The diazonium material was also ground with a small amount of water to make a paste and added gradually to the hot suspension. Color appeared instantly and deepened rapidly. Heating and stirring were continued for a few additional minutes after the solution had become clear (about 15 minutes in all). The solution was filtered and the dye precipitated by acidification. Very little free acid is needed, and apparently all acids act similarly in this respect. The crude dye is filtered. Standing for a few hours greatly lessens the difficulty of filtering. With this procedure the best yield obtained was 50% on the basis of diazonium intermediate, the usual yield being below 40%. Later, in an endeavor to increase the yields of the coupling reaction, sodium acetate was added with good results, yields as high as 86% being obtained. The revised procedure follows: The dye intermediate, 4 grams (0.0266 mole) of β-naphthol, for example, and 2 grams (0.0244 mole) of sodium acetate were added to 300 ml. of water in a beaker, and the temperature was raised to 80° C. with efficient stirring. Five grams (0.0266 mole) of the diazo compound in the powdered form were added gradually over a period of 10 minutes. A color developed with first addition in every case. The coupling reaction was continued at 80° C. for 25 minutes to obtain the complete coupling. The reaction mixture was cooled by placing the beaker in an ice bath. In most cases cooling tended to bring any unreacted intermediate out of solution, and this was removed by filtration. To precipitate the dye, 10 ml. of concentrated hydrochloric acid were added, the solution was allowed to stand a few hours and filtered. The filter cake was washed thoroughly and allowed to dry by exposure to the air.

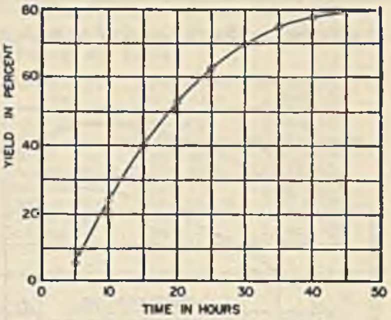


Figure 2. Yield from Diazotization Reaction *vs.* Time

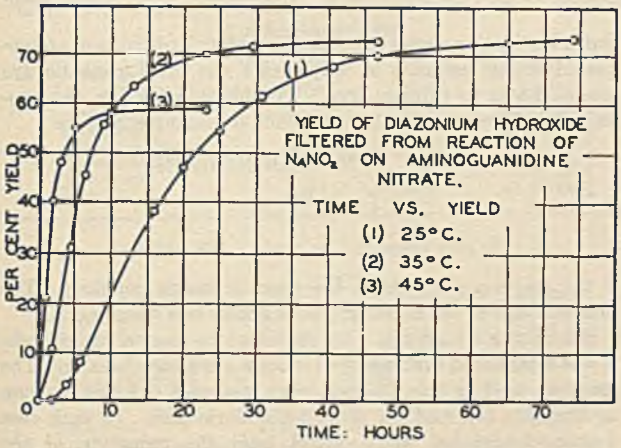


Figure 1. Diazotization of Aminoguanidine

RESULTS OF COUPLING

The effect of using sodium acetate in the coupling bath is apparent in Figure 3 and Table I. The yield of 2-methyl-6-naphthol dye is increased from 25.6 to 64.3% by the addition of 0.4 gram of sodium acetate per gram of diazo used. In like manner, the yield of *m*-aminophenol dye was increased from 54.9 to 84.5%.

Results of other coupling runs are shown in Tables II to V. The maximum yield obtained was 86.4% for the coupling with β-naphthol (Table II). A series of couplings was made with Tobias acid (2-naphthylamine-1-sulfonic), and with α- and β-naphthol as intermediates, to determine the optimum temperature. The runs for the first two intermediates were made according to the earlier procedure (without sodium acetate); although the yields in general were low, best results were obtained at 80° C. The second method (in the presence of sodium acetate) was used for the β-naphthol coupling. Table III-*A* shows the results, 80° C. being the temperature for maximum yield. Below this temperature the reaction rate is too slow; above it, decomposition reduces the yield.

A number of runs were carried out with the temperature at 80° C. and time as the variable. For the couplings of Tobias acid and α-naphthol in the absence of sodium acetate, the best yields were obtained after heating 15 minutes. In the case of the β-naphthol in the presence of sodium acetate, the maximum yield of dyestuff was obtained when the reaction was allowed to proceed for 25 minutes (Table III-*B*).. It is to be assumed that the rate of decomposition exceeds the rate of formation beyond this time.

The effect of ratio of reactants on coupling was another variable studied. The results of β-naphthol couplings in the presence of sodium acetate are listed in Table IV. Optimum results were obtained with 0.8 mole of diazo compound per mole of aromatic intermediate. An increase in the excess of intermediate gave no better results, but below this value a decided drop was observed.

The optimum conditions for the coupling reaction are: Ratio of reactants, 1.25 moles intermediate per mole diazo compound; amount of sodium acetate, 0.4 gram per gram diazo compound (0.92 mole per mole diazo); time and temperature of reaction, 25 minutes and 80° C.

α-Naphthol and β-naphthylamine were coupled in solutions of different acidity to determine the effect on yield of dye. In this series 1 gram of intermediate, 2 grams of diazonium hydroxide, and 200 ml. of water were used. Sulfuric acid (3.48 *N*) was added to each coupling in varying amounts. The temperature was 75° C. and the time of heating 30 minutes. A small amount of ammonia solution was then added to dissolve the dye. After filtering out any insoluble material, the dye was precipitated with 5 ml. of the same acid (Table V).

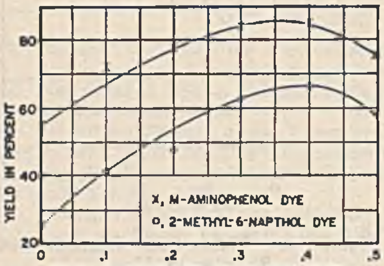


Figure 3. Effect on Yield of Amount of Sodium Acetate Used in Coupling Reaction

PURIFICATION OF DYES

The dyes produced by this reaction are, without exception, very soluble in basic solutions; up to 25 per cent by weight of the dye dissolves. Since most of the dyes are insoluble in acid solutions, this gives a good method of purification. The crude dye is suspended in water and just enough aqueous ammonia added to dissolve it. Precipitation with any acid (hydrochloric and acetic were used most) gives the dye again. This method of purification results in an improved dye color; the shade is brightened in almost every case. However, little change in nitrogen content was found after purification.

The use of organic solvents for the purification of these dyes is not very practical because of the large amount of solvent required. For example, 1 liter of boiling toluene is needed to dissolve about 2 grams of β-naphthol dye; upon cooling in ice almost a gram of purified dye can be filtered out.

Comparison of the relative merits of acid precipitation and of toluene recrystallization methods for purifying the β-naphthol dye may be of interest. A sample of crude precipitated dye melted at 147–148° C.; when purified by acid precipitation, a sample melted at 151–152° C. When some of the same crude dye was crystallized from toluene, it melted at 167° C. A second toluene crystallization gave a melting point of 169° C.; two more successive crystallizations gave products melting at the same point.

Table I. Course of Diazotization Reactions (48 Hours at Room Temperature)

Aminoguanidine Bicarbonate, Grams	$NaNO_2$, Grams	Mole Ratio, $NaNO_2$:Amino Compound	Yield	
			Grams	%
136	69	1:1	62	66
136	69	1:1	61	65
136	76	1.1:1	70	74.6
136	76	1.1:1	73	78
136	80	1.15:1	76	81
136	80	1.15:1	77	82
136	80	1.15:1	75	80
136	80	1.15:1	76.4	81.4
136	83	1.2:1	88	82
136	90	1.3:1	76	81

Table II. Effect of Intermediate on Yields from Coupling Reaction

(5 grams diazo compound, 2 grams sodium acetate, 80° C., 25 minutes)

Intermediate Used		Yield, Grams	% Yield Based on:	
Name	Grams		Intermediate	Diazo compound
β-Naphthylamine	4	3.8	59	62
p-Nitroaniline	4	3.6	56	60.7
5-Nitro-2-aminotoluene	4	4.8	76.5	75
p-Phenylenediamine	3	2.4	45	46.7
o-Nitroaniline	4	3.3	50.5	55
2-Methyl-6-naphthol	4	4.0	65	62
m-Aminophenol	3	4.5	83.5	85
α-Naphthol	4	4.8	75	82
Tobias acid	5.5	5.3	70	64.5
H-acid	9	10.3	81	86
β-Naphthol	4	5.3	82.8	86.4
α-Naphthylamine	4	4.5	71	74

Table III. Effect of Reaction Temperature and Time on Coupling Yields

(5 grams diazo compound, 4 grams β-naphthol, 2 grams sodium acetate)

A. Time of Runs, 25 Minutes				B. Temperature of Runs, 80° C.			
		% Yield Based on:				% Yield Based on:	
Temp., ° C.	Yield, grams	β-Naphthol	Diazo compd.	Time, min.	Yield, grams	β-Naphthol	Diazo compd.
25	0.15	2.96	3.1	5	4.0	63.0	65.5
60	1.0	19.7	20.5	10	4.2	65.5	68.0
70	2.4	47.2	49.1	15	4.4	69.2	72.1
75	4.1	64.5	67.1	20	4.5	70.0	73.0
80	5.3	82.6	86.1	25	5.3	82.6	86.4
85	4.9	76.4	79.5	30	4.7	74.0	77.0

Table IV. Effect of Ratio of Reactants on Coupling Yields

(2 grams sodium acetate 80° C., 25 minutes)

Mole Ratio, Diazo Compd.: Intermediate	Diazo Compd., Grams	β-Naphthol, Grams	Yield, Grams	% Yield Based on:	
				β-Naphthol	Diazo compd.
0.5	5.0	7.65	5.20	32.6	85.3
0.6	5.0	6.32	5.25	51.7	86.0
0.7	5.0	5.45	5.15	59.2	84.5
0.8	5.0	4.80	5.25	68.5	86.0
0.9	5.0	4.25	4.40	64.8	72.1
1.0	5.0	3.83	4.50	73.5	73.8
1.1	5.0	3.48	4.30	77.5	70.5

Table V. Effect of pH on Coupling Yields

(1 gram intermediate, 2 grams diazo compound, 200 ml. water, 75° C. 30 minutes)

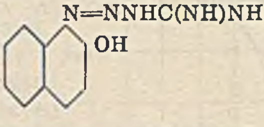
H_2SO_4 (3.48 *N*), Ml.	α-Naphthol Dye, Grams		β-Naphthylamine Dye, Grams	
	Insol. matter	Wt. of dye	Insol. matter	Wt. of dye
None	0.26	1.51	0.00	0.90
0.1	0.25	1.47	0.02	1.00
0.2	....	....	0.05	1.07
0.4	....	....	0.07	1.23
0.5	0.38	1.43	....	....
0.6	....	....	1.02	1.10
1.5	0.82	1.25	....	....

ANALYSIS OF DYES

Hofmann's formulation for the diazotization of aminoguanidine is as follows, although the isomer (nitrosoamine) is probably present:

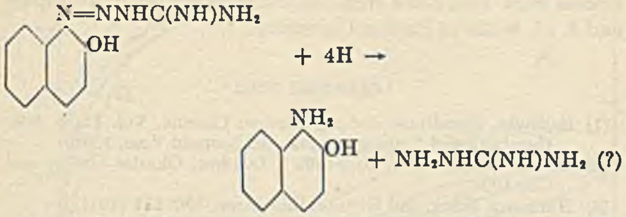
$$2NH_2C(NH)NHNH_2(HNO_3) + 2NaNO_2 \rightarrow NH_2C(NH)NHNHN{=}NC(NH)NHN{=}NOH + 2NaNO_3 + 3H_2O$$

Our investigation shows that this diazonium hydroxide of aminoguanidine can be made to couple with the usual aromatic dye intermediates to furnish dyes. The formula for the dye produced by the reaction with β-naphthol, for example, may be



if the reaction proceeds as the usual aromatic coupling. The present stage of the investigation indicates this formulation.

Reductive Splitting. By reduction to known compounds, it was established that the dyes contain a true azo linkage. The reagents used in this reaction were stannous chloride, sodium hydrosulfite (*2*), and tin plus hydrochloric acid. In each case 1-amino-2-naphthol was isolated from the reduction of the 2-naphthol dyestuff. The isolation and identification (*1*) of this compound serves to indicate that these dyes are true azo compounds, the splitting of the β-naphthol dye to give the 1-amino-2-naphthol probably proceeding according to the following equation:



In this equation aminoguanidine has been written as the other product. If this is true, it should remain in the filtrate from the reduction reaction. However, present attempts to recover this substance from the liquor have been unsuccessful. This would seem to indicate that the other part of the molecule may have decomposed at some point during the reaction. However, no ammonia evolution was detected, and this should have been one of the decomposition products. The details of the coupling reaction and the decomposition products of the reductive splitting are being further investigated.

Nitrogen Analyses. Percentage nitrogen in the dyes was determined by the Dumas method (*10, 11, 12*). All the dyes, with the exception of the β-naphthol, were purified by reprecipitation. The molecular weights shown were calculated with the assumption that the —N=NNHC(NH)NH₂ group takes the place of one hydrogen atom in the original aromatic intermediate used in the coupling reaction. The nitrogen contents of a number of different dyes are given in Table VI. Mixtures of disazo and azo molecules were apparently the chief difficulty encountered in purifying dyes to a constant nitrogen content. The Tobias acid dye was made with a large excess of diazonium intermediate, and the values for it are figured assuming that a disazo dye was produced. More recently evidence has been found to show that the sulfonic acid group may have been displaced by the diazo group. This is being studied further. Aromatic compounds which couple readily and offer two equally active points for attachment give disazo structures very easily, especially if an excess of the coupling intermediate is used. This would probably be true for the dyes made from phenols and 1-naphthol (Table VI).

PROPERTIES OF DYES

All of the dyes produced by coupling the diazotized derivative of aminoguanidine with various substances are extremely soluble in basic solutions. When such a solution is rendered slightly acid, the dye will largely precipitate and leave only a small amount in solution. The solubility in a weak acid solution is approximately the same as that in distilled water, as determined by colorimetric measurements, or about 0.03 gram per 100 grams of water.

Table VI. Nitrogen Analysis of Dyes Made from Diazotized Aminoguanidine

Coupled Intermediate	Calcd. Mol. Wt. of Dye	% Nitrogen Calcd.	% Nitrogen Found
α-Naphthol	229	30.6	31.7, 31.6
β-Naphthol	229	30.6	30.55, 30.6
α-Naphthylamine	228	36.8	36.4, 36.0
β-Naphthylamine	228	36.8	36.5, 36.6
Tobias acid	393	39.2	38.7, 38.8
Phenol	179	39.1	40.6, 40.4

Table VII. Dye Color Changes with pH

Intermediate	Color in: Acid	Color in: Base	pH Range[a]
α-Naphthol	Yellow	Red	5.6–6.9
β-Naphthol	Yellow	Orange	5.7–6.8
α-Naphthylamine	No change		....
β-Naphthylamine	No change		....
Tobias acid	No change		....
Resorcinol	Light yellow	Gold	3.5–5.8

[a] Determined by a glass electrode apparatus.

Table VIII. Color of Coordination Compounds of Several Metals with Four of the Dyes

	α-Naphthol Dye	β-Naphthol Dye	α-Naphthylamine Dye	β-Naphthylamine Dye
$Hg(Ac)_2$	Red-purple	Pink-red	Blue-pink	Blue-pink
$AlCl_3$	Orange	Yellow	Clear	Clear
$CrCl_3$	Orange-brown	Yellow	Light gold	Dull yellow
$AgNO_3$	Red-purple	Red-orange	Light pink	Light pink
$Pb(NO_3)_2$	Red-purple	Pink-red	Light pink	Light pink
$Fe(NO_3)_3$	Brown	Green-yellow	Dull yellow	Dull yellow
$CoSO_4$	Cherry red	Pink-orange	Pink	White-pink
$CuSO_4$	Deep purple	Dull red	Clear	Light yellow
$Ni(NO_3)_2$	Purple	Pink-brown	Clear	Clear

Table IX. Color of Dyes

Dye	Appearance of Dye	Color on Wool, 5% Dye in Tannin Mordant
β-Naphthylamine	Red-brown	Red-orange
p-Nitroaniline	Tan	Yellow
5-Nitro-2-aminotoluene	Brown	Brown (dark)
p-Phenylenediamine	Black	Gray-brown
o-Nitroaniline	Brown	Yellow-brown
2-Methyl-6-naphthol	Orange	Orange
m-Aminophenol	Brown	Orange-brown
α-Naphthol	Deep red	Red-brown
Tobias acid	Red	Tan
H-acid	Purple	Red
β-Naphthol	Orange	Orange-brown
α-Naphthylamine	Red	Orange

The solubility of these dyes in organic solvents is rather low for the most part. The usual solvents such as benzene, ethanol, acetone, and dioxane dissolved enough to give a colored solution but only a trace was actually in solution. The best solvents for these dyestuffs were aniline and pyridine, probably because of their basic properties. Methanol and toluene were found to be of some value as solvents in the purification of the dyes.

A number of the dyes exhibited striking color changes when their acid solutions were made basic. The colors so produced with the approximate pH value at which the change is clearly distinguishable are indicated in Table VII.

A number of heavy metals give precipitates quite specific in color for the particular metal and dye employed. Saturated solutions of four dyes made from the two naphthols and two naphthylamines were added to dilute solutions of a number of metallic salts. The heavy metals gave precipitates which were varied in color. Alkali or alkaline earth metals showed no such effects. A few of the more interesting results are listed in Table VIII. As a rule, the metal complex was less soluble than the dye itself and in most cases gave flocculent precipitates; those of silver and mercury were very insoluble, leaving the solutions clear.

DYEING PROPERTIES

The dyes made in this research so afr are acid dyes. However, the fabrics dyed without the use of mordants were not very fast. This led to investigations of possible mordants. Sodium dichromate was tried in various ways—pre-chrome, after-chrome, and meta-chrome. All the methods gave somewhat similar results. The dyes were fast but the colors had a brownish cast, regardless of the individual dye. Other mordants such as tannic acid and aluminum chloride proved interesting. The color of the dyed fabrics with the latter mordant was nearer the shade of the unmordanted dye than when chrome was used. The tannic acid mordant was employed because the dyes were very fast on the fabrics and

the colors closely approximated those of the dyestuffs themselves. The procedure followed for this mordant was that suggested by Whittaker and Wilcox (*15*). The dye bath in each case was fairly well exhausted, which proves the ready absorption of the dye by the fabric. The colors of the dyestuffs and the fabrics dyed with them are listed in Table IX.

Fastness of Dyed Fabrics. Standard tests (*8*) were applied to the samples of dyed wool. The results follow:

Acid. All dyes, both with and without mordants, were fast to boiling acetic and sulfuric acids.

Alkali. Hot neutral or alkaline soap solution caused the unmordanted dyes to run. The H-acid dye mordanted with chrome is fast to hot soap, and the other dyes tested were fairly fast.

Stoving. All samples showed no change when washed in dilute soap and suspended in sulfur dioxide medium for 6 hours.

Bleaching. Little change was observed when samples were soaked in dilute bleaching powder solution for an hour. The mordanted dyes were somewhat faster.

Rubbing. All dyes were fast to rubbing against a piece of white linen.

Fading. No fading was observed on exposure to the sun for a month.

Apparently all of these dyes are stable to both acid and alkali. One remarkable stability is noted in the case of oxidizing agents; fuming nitric acid seems to have little or no effect; e. g., the 2-naphthol dyes can be heated to boiling in fuming nitric acid and when the solution is diluted, the dye will precipitate apparently unchanged. As is the case with all azo dyes, reducing agents will destroy the color and oxidizing agents will not restore it.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance, particularly in supplying chemicals, received from Mallinckrodt Chemical Works and American Cyanamid Corporation. This paper represents work abstracted from the Ph.D. theses of R. P. Carter and J. M. Willis at Purdue University.

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TALL OIL . . . . Separation of Stearic and Abietic Acids by Selective Adsorption after Hydrogenation

George Papps and Donald F. Othmer
POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.

ABOUT the beginning of the twentieth century, tall oil (a waste product of the paper industry) had become a commercial product. It was soon realized that, if the fatty and resin components were separated, a much higher value would result. The following figures for tall oil are representative:

Saponification No.	150–160	159	174
Acid No.	160–170	168	178
Iodine No. (Hanus)	150–180	163	161
Unsaponifiable, %	6–10	7	8
Fatty acids, %	45–55	53.4	54.9
Resin acids, %	40–45	38.8	35.8
Citation	(*19*)	(*9*)	(*11*)

Resin acids in tall oil consist mainly of abietic acid (60-90%). The fatty acids consist almost entirely of oleic (15–23%), linoleic (71–79%), and linolenic (6%). Wallach (*19*) mentions that a small amount of palmitic acid may also be present.

Many methods have been proposed and patented for refining tall oil. Some of these are contacting with fuller's earth (*12*), vacuum distillation (*2, 11, 16*), selective esterification (*10, 15, 17*), selective splitting of fatty and resin soaps (*1, 7*), selective extraction by solvents of tall oil soaps and esters (*5, 6*), and the selective splitting of tall oil glyceride (*6*). In some methods of separation, the resin acids were destroyed. Thus, Blengsli (*3*) oxidized tall oil by air blowing and then separated the fatty acids by dissolving the oxidized tall oil in gasoline and filtering off the insoluble resin acid products.

Of the methods proposed for separating the fatty and resin acids, fractional distillation has been most used. Distillation, however, is expensive; the yields are poor because of decomposition, and separation is relatively inefficient. A literature search failed to disclose the use of selective adsorption in the separation of resin and fatty acids in either tall oil or hydrogenated tall oil. Some work has been done, however, on the selective adsorption of fats and fatty acids. The conclusions arrived at for specific systems have been somewhat contradictory. Many systems do not conform either to Freundlich or Langmuir equations for adsorption. One theory (*4*) to account for the apparent abnormali-

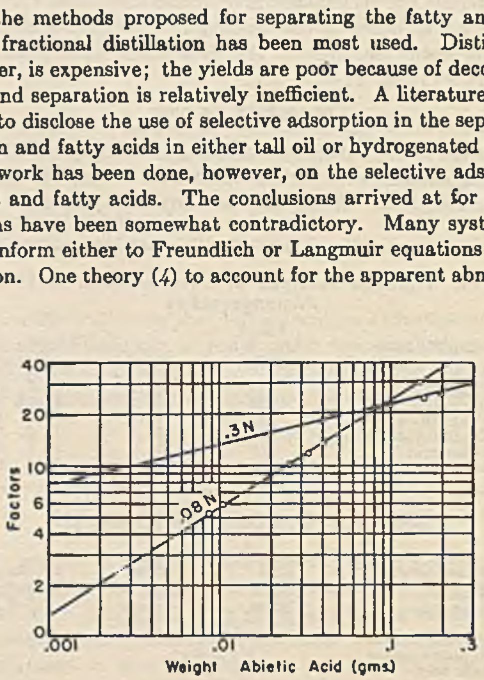

Figure 1. Determination of Abietic Acid with 0.08 *N* and with 0.3 *N* Potassium Hydroxide

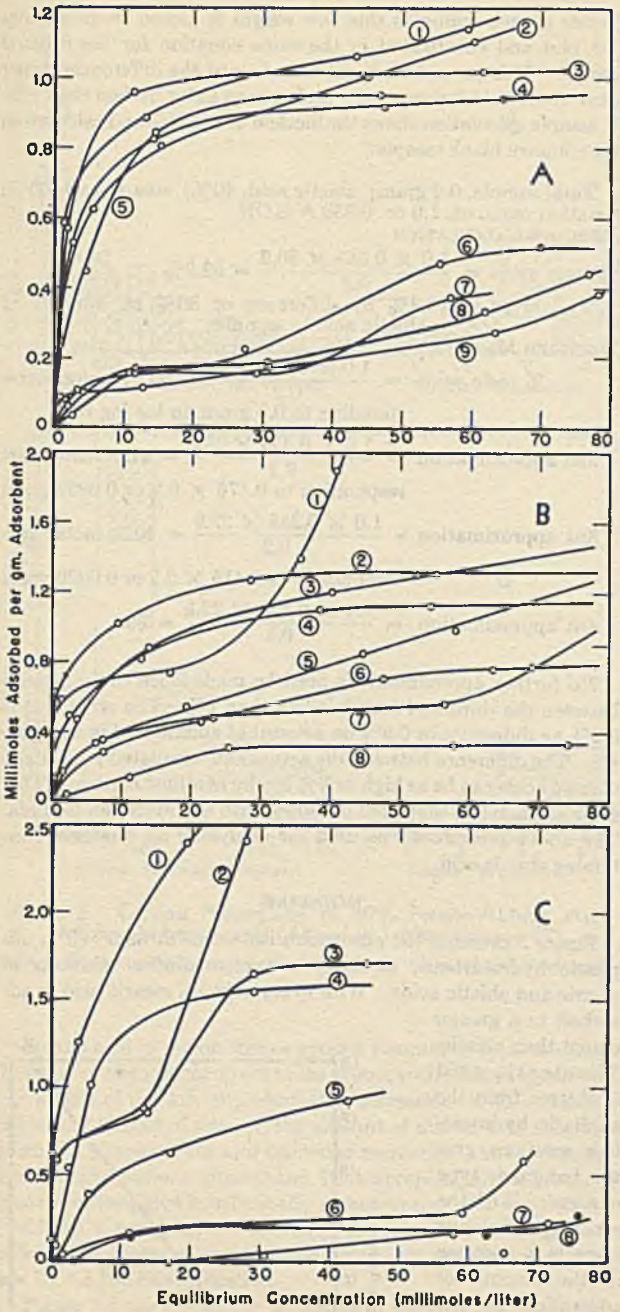

Figure 2. Adsorption Isotherms of Stearic and Abietic Acids at 35.5° C.

A. Aliphatic Hydrocarbons

(1) Stearic acid in hexane
(2) Stearic acid in heptane
(3) Stearic acid in petroleum ether 1
(4) Stearic acid in isooctane
(5) Stearic acid in petroleum ether 2
(6) Abietic acid in Solvesso 1
(7) Abietic acid in Solvesso 2
(8) Stearic acid in Solvesso 2
(9) Stearic acid in Solvesso 1

B. Alcohols

(1) Stearic acid in isopropanol
(2) Stearic acid in methanol
(3) Stearic acid in ethanol
(4) Abietic acid in methanol
(5) Abietic acid in ethanol
(6) Abietic acid in isopropanol
(7) Stearic acid in *n*-propanol
(8) Abietic acid in *n*-propanol

C. Nitroparaffins

(1) Stearic acid in nitromethane
(2) Stearic acid in nitroethane
(3) Stearic acid in 1-nitropropane
(4) Stearic acid in 2-nitropropane
(5) Abietic acid in nitromethane
(6) Abietic acid in nitroethane
(7) Abietic acid in 1-nitropropane
(8) Abietic acid in 2-nitropropane

▶ ▶ ▶ The two main components of hydrogenated tall oil, stearic and abietic acids, are separated by selective adsorption using activated carbon. Separation is accomplished by feeding an 8% solution of hydrogenated tall oil in a suitable solvent through a glass column containing activated carbon. After the hydrogenated tall oil is fixed on the adsorbent, the abietic acid is first washed through and out of the column by additional fresh solvent, followed by the stearic acid which is preferentially adsorbed. The efficiency or sharpness of separation and the rate of throughput depend mainly on the solvent. 1-Nitropropane is the best solvent among twenty-nine considered. The solvents are evaluated by adsorption isotherms for individual components (stearic and abietic acids) on activated carbon, and for mixtures containing 50% of each. A modified McNicoll method is developed for abietic acid content in mixtures.

ties holds that, at higher concentrations, the solute begins to enter the capillaries of the adsorbent (capillary condensation). Another theory assumes that multimolecular layers are formed.

In the present work the tall oil was hydrogenated in the conventional manner to reduce the components substantially to two (stearic and abietic acids). Then these components were separated by passing a solution down through a column containing the adsorbent (activated carbon). The method is essentially the so-called chromatographic adsorption (*18*), although separation does not depend on the formation of colored bands in this case.

PROCEDURE AND MATERIALS

Individual adsorption isotherms were determined for pure stearic and abietic acids adsorbed on activated carbon at 35.5° C. from a series of solvents. Adsorption isotherms of 50% mixtures of abietic and stearic acids were obtained for solutions in a few of the solvents previously used. Then 50% mixtures of abietic and stearic acids were percolated through glass columns containing the adsorbent, and the degree of separation by this selective adsorption was determined. Solutions of hydrogenated tall oil were passed through the column and actual separations accomplished.

For determining the individual isotherms, C.P. stearic acid was prepared from corn oil by the methods of Rollet (*14*) and Kass and Keyser (*8*). Pure abietic acid was also prepared from rosin, stored as the stable sodium tetra-abietate salt and converted to free abietic acid as required.

The solvents were a highly purified grade and were distilled twice before use; a middle fraction was taken in each case. They included benzene, toluene, xylene, methanol, ethanol, *n*-propanol, isopropanol, *n*-, *sec*-, and *tert*-butanol, petroleum ether, hexane, heptane, isooctane, Solvesso 1 and 2, methyl ethyl ketone, dioxane, ethylene dichloride, chloroform, carbon tetrachloride, methyl, ethyl, and butyl acetates, nitromethane, nitroethane, and 1- and 2-nitropropanes. In the present report only a few will be discussed. The adsorbent was Darco G-60, which adsorbed stearic acid to a greater extent than other carbons tried.

A standard procedure was used for determining the isotherms: A weighed amount of activated carbon and a known amount of solution of definite acid concentration were placed in a test tube, which was then shaken in a constant-temperature bath long enough for equilibrium to be reached. It was allowed to stand; a sample of supernatant liquor was pipetted off and analyzed for acid. From the determined concentration and the known amounts of three materials added, the distribution of the acid was calculated between the adsorbent and solvent phases.

For studies of selective adsorption, glass columns made of $^3/_4$-inch tubing were set up with the activated carbon held in place by wads of cotton. The height of the adsorbent in the column was 6.5 inches. Ten grams of Darco G-60 were used per gram of hydrogenated tall oil. The spent activated carbon was usable a number of times without revivification. In the preliminary col-

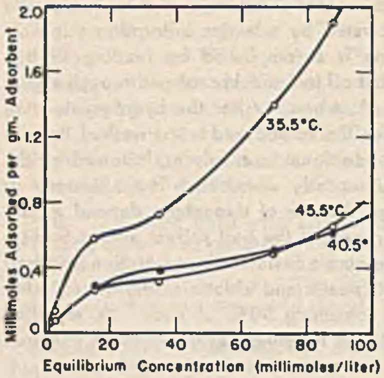

Figure 3. Adsorption Isotherms of Stearic Acid in Isopropanol

umn experiments, 4% solutions of the acids were used. Later the concentration was increased to 8%. After adsorption of the components on the carbon, fresh solvent was passed through the column until the separation was completed and then until the second component was removed. Each fraction of solution removed at the bottom of the column was evaporated to remove the solvent; the residue was weighed and analyzed for abietic acid. Stearic acid was determined by difference.

For some of the column runs the second component was recovered by removing the adsorbent containing it from the glass column. The cylinder of adsorbent was divided into four parts, and each was eluted with solvent to remove adsorbed material. This procedure was used to determine the distribution of solids remaining on the carbon in the column. The data are plotted on the column curves and designated "column segments".

The hydrogenated tall oil had an acid value of 165, an iodine value of 75.4, a melting point of 54° C., and contained 29.6% resin acids. This material was light brown in color. The abietic and stearic acids recovered from the selective adsorption were white. Their progress through the column could be followed by observing crystal formation in the various fractions removed from the column after the solvent had been evaporated. Abietic acid formed no crystals but gave a uniform transparent layer of solid. Stearic acid formed characteristic crystals. The intermediate mixtures gave residues varying from milky deposits to indistinct crystals. (It is possible that the two fractions separated, called "abietic acid" and "stearic acid", contain small amounts of some additional materials present in the original hydrogenated oil, since no further purification would be encountered in this separating operation. The abietic acid fraction, even if it was not entirely hydrogenated prior to separation, would be acceptable industrially.)

ABIETIC ACID DETERMINATION

The McNicoll method (*13*) for determining rosin in mixtures was the quickest and most reliable available. It is based on a selective esterification of fatty acids in the presence of β-naphthalene sulfonic acid. In determining the percentage of abietic acid in a series of mixtures containing known weights of stearic and abietic acids the percentages calculated differed considerably from known percentages. The known values were substituted in the McNicoll formula for calculating the percentage of resin acids, and new values for the factor corresponding to 30.2 were obtained (as shown by the sample calculation). A log-log plot of factors from analysis of blank samples against the actual weight of abietic acid in the sample gave straight lines (Figure 1). The slope of the lines varied with the normality of the potassium hydroxide solution used for titration. The following method of calculating was evolved, by which the McNicoll method could be used for determining as little as 0.001 gram of resin acids in mixtures. The titration value from the regular McNicoll determination was substituted in the equation:

$$\%\text{ resin acids} = \frac{(A\text{-}B)\ (\text{factor})(\text{normality of KOH soln.})}{\text{weight of sample}}$$

where A = alcoholic KOH required to saponify resin acids and catalyst (green end point), ml.
B = alcoholic KOH required to neutralize catalyst (yellow end point), ml.

Thymol Blue is used as indicator for the titration. The first resin acid percentage calculated is used to get the weight of resin acids by multiplication with the weight of sample. The factor corresponding to this new weight is picked from the log-log plot and substituted in the same equation for the original factor. This procedure is continued until the differences in per cent resin acid between two estimations differ by less than 1%. A sample calculation shows the method of analysis and calculation for a known blank sample:

Total sample, 0.2 gram; abietic acid, 40%; stearic acid, 60%; titration required, 1.0 cc. 0.353 *N* KOH.

REGULAR CALCULATION

$$\%\text{ resin acids} = \frac{1.0 \times 0.353 \times 30.2}{0.2} = 53.2\%$$

error = 13.2% by difference or 30% on amount of abietic acid in sample

MODIFIED METHOD

$$\%\text{ resin acids} = \frac{1.0 \times 0.353 \times 27}{0.2} = 47.6\text{, factor corresponding to 0.2 gram on log-log plot}$$

$$\text{2nd approximation} = \frac{1.0 \times 0.353 \times 23.5}{0.2} = 41.5\text{, factor corresponding to } 0.476 \times 0.2 \text{ or 0.0952 gram}$$

$$\text{3rd approximation} = \frac{1.0 \times 0.353 \times 22.8}{0.2} = 40.2\text{, factor corresponding to } 0.415 \times 0.2 \text{ or 0.0830 gram}$$

$$\text{4th approximation} = \frac{1.0 \times 0.353 \times 22.5}{0.2} = 39.8$$

No further approximations need be made since the difference between the third and fourth is less than 1%. The error here is 0.2% by difference or 0.5% on amount of abietic acid in the sample. The difference between the actual and calculated percentage of resin acids can be as high as 3% by the modified method. This error is much less than that obtained with the McNicoll formula. The above procedure was used for analyzing all mixtures containing abietic acid.

ISOTHERMS

Figure 2 presents the adsorption isotherms at 35.5° C. in aliphatic hydrocarbons, alcohols, and nitroparaffin solutions of stearic and abietic acids. With every solvent, stearic acid is adsorbed to a greater extent than abietic. The stearic acid isotherms from the aliphatic hydrocarbon solutions give the Langmuir type of curve. With the alcohol solutions there is a decrease in the amount of adsorption as the molecular weight of the alcohol increases. Both Freundlich and Langmuir types of curves are obtained in this series, as well as two curves which do not conform with either. The isotherms of isopropanol and *n*-propanol solutions of stearic acid, after leveling off, give a second region of increasing adsorption rate.

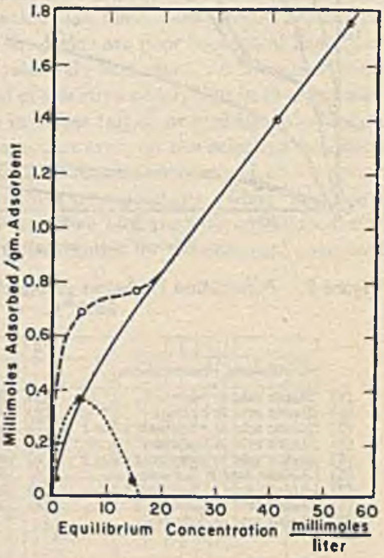

Figure 4. Adsorption Isotherms of a 50% Mixture of Abietic and Stearic Acids in Nitroethane

Dotted curve, adsorption of abietic acid
Dashed curve, adsorption of stearic acid
Solid curve, sum of adsorption of both acids (above about 17 millimoles per liter, stearic acid alone since no abietic acid is adsorbed)

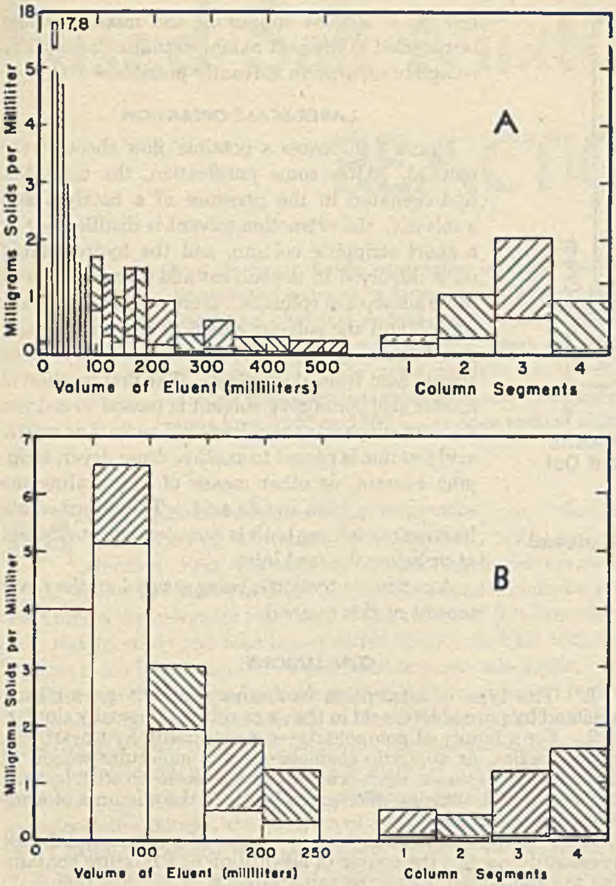

Figure 5. Column Adsorption of 50% Stearic-Abietic Acid Mixture in Isopropanol (*A*) and in 1-Nitropropane (*B*)

Height of open bars indicates amounts of abietic acid; of shaded bars, stearic acid.

Stearic acid in nitromethane gives a Freundlich type isotherm. For the subsequent members of the group, with increasing molecular weight of the solvent, adsorption decreases. With increasing molecular weight of solvent, the amount of abietic acid adsorbed from the nitroparaffins also decreases markedly. At low equilibrium concentrations nitroethane, 1-nitropropane, and 2-nitropropane solutions give substantially no adsorption of abietic acid.

Of the three groups of solvents, nitroparaffins show greatest adsorption of stearic and least adsorption of abietic acid. They are by far the most selective.

Figure 3 gives adsorption isotherms of stearic acid solutions in isopropanol at three temperatures. The curves for 40° and 45.5° C. follow each other rather closely. Adsorption decreases with temperature increase; but above 40.5° C. the decrease is negligible. The same trend was given by other solvents.

Figure 4 shows adsorption isotherms of a 50% mixture of stearic and abietic acids in nitroethane. The lower dotted curve rising abruptly to a maximum and then falling rapidly to zero adsorption of abietic acid indicates the phenomenon of selective adsorption. Here, as equilibrium concentration (total for both acids) increases from zero, the adsorption of abietic acid increases rapidly at first. As the total concentration increases, the preferential action of carbon for stearic acid is apparent; abietic acid, which had been adsorbed at the lower concentrations, is displaced by stearic. Finally, no abietic acid is present in the adsorbent, and the adsorbed phase is pure stearic acid. Stearic acid adsorption follows a smooth curve. Total adsorption is the sum of the other two; this curve coincides with that for stearic acid alone above the point where the curve for abietic acid has dropped to zero.

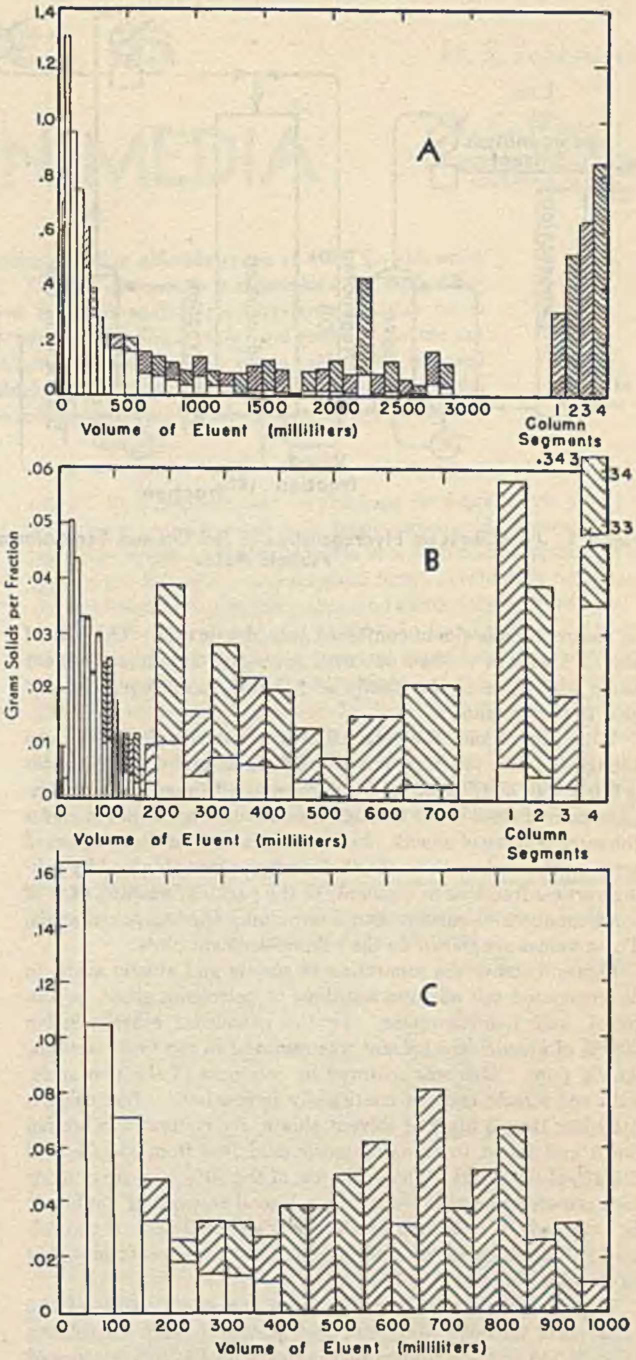

Figure 6. Column Adsorption of Hydrogenated Tall Oil in Petroleum Ether (*A*), Isopropanol (*B*), and 1-Nitropropane (*C*)

Height of open bars indicates amounts of abietic acid, of shaded bars, stearic acid.

Figure 5 gives the relative amounts of solids (stearic and abietic acids) carried through the $6^1/_2$-inch layer of carbon in the column for the indicated amounts of solvent; 50 cc. of an 8% solution of a 50% mixture of the two acids in isopropanol and in 1-nitropropane were first passed through. The column was washed with successive amounts of pure solvent, and in each case the first few washes contained high amounts of abietic acid. The first 50 ml.

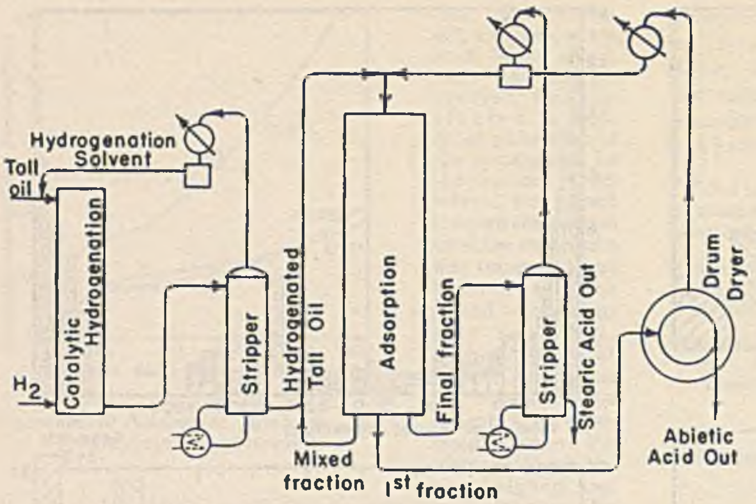

Figure 7. Flow Sheet for Hydrogenation of Tall Oil and Separation of Stearic and Abietic Acids

of 1-nitropropane eluent contained only abietic acid. The bulk of abietic acid was washed out with successive amounts of eluent along with some of the stearic acid, leaving almost pure stearic acid in the column.

With isopropanol the separation was not complete, for even though the first few fractions are high in abietic acid, the latter is fairly well distributed in the column at all times. 1-Nitropropane carried more solids through the column than isopropanol for the same volume of eluent. In Figures 5 and 6 the distribution of acids on the carbon throughout the column was obtained by taking vertical fractions or segments of the packing, washing each of these amounts of carbon, and determining the individual acids. These values are shown on the column-segment plots.

Figure 6 shows the separation of stearic and abietic acids, in hydrogenated tall oil from solutions of petroleum ether, isopropanol, and 1-nitropropane. In the petroleum ether solution 49.8% of abietic acid present was removed in the first fractions, 99.5% pure. This was followed by mixtures of the two acids, with the stearic content continually increasing. After using a little less than 3 liters of solvent eluate, the column was broken down and found to contain stearic acid free from abietic acid (35.3% of the total). The isotherms of the 50% mixture of acids (not presented here) indicated that a good separation would not be obtained. The results are better than predicted; if the column had been longer, a more efficient separation would probably have been obtained.

With isopropanol (Figure 6*B*) there is a confirmation of the behavior of the 50% mixture of acids passed through the column (Figure 5*A*) and the adsorption isotherms of the 50% mixture of acids which were determined but not graphed. These are in contrast to the individual isotherms (Figure 2*B*) which predicted a good separation. In the first 80 ml. of eluate solvent, 71.4% of abietic acid was pushed through at a purity of 99.3%. Subsequent washes were richer in stearic acid; however, at no time was any fraction obtained containing pure stearic acid. Much abietic acid was found to be retained by the column (column-segment analyses).

1-Nitropropane gave by far the best results (Figure 6*C*); 78.4% of abietic acid was removed in the first 150 ml. of wash solvent, 99.5% pure. The next 250 ml. washed out the remaining abietic acid with some stearic acid, to leave 87% of the total stearic acid retained by the column, 100% pure. The stearic acid was washed out completely by the use of 600 ml. of solvent. If the column length were increased here, it appears that a complete separation would be obtained; in any case, the intermediary 250 ml. of solvent containing the mixture would be recycled in the next batch, so that an essentially complete separation is readily possible.

LARGE-SCALE OPERATION

Figure 7 indicates a possible flow sheet of the method. After some purification, the tall oil is hydrogenated in the presence of a catalyst and a solvent; the extraction solvent is distilled out in a short stripping column, and the hydrogenated oil is dissolved in the solvent and passed to one or more adsorption columns. Here stearic acid is adsorbed and the solvent eluent is passed through, first to carry through abietic acid and then to wash stearic acid from the carbon. The first fraction of abietic acid containing solvent is passed to a drum dryer to evaporate the solvent. The final or stearic acid fraction is passed to another drum dryer, stripping column, or other means of evaporating the solvent away from stearic acid. The intermediate fraction containing both is recycled back to a point at or below the feed inlet.

A patent protection is being secured on the novel aspects of this method.

CONCLUSIONS

1. The type of adsorption isotherms given by pure stearic acid and by pure abietic acid in the same solvent is usually similar.
2. For a family of compounds—e.g., aromatic hydrocarbons, nitroparaffins, or aliphatic alcohols—as the molecular weight of the solvents increases, there is a shift of the isotherm with less adsorption and decreasing differences between the amounts of acids adsorbed individually.
3. The individual adsorption isotherms of a compound do not necessarily predict the course of adsorption of a mixture containing the compound, using the same solvent.
4. Stearic acid, which is adsorbed to a greater extent in the individual isotherms, is adsorbed to an even greater extent from the solutions of both stearic and abietic acid.
5. The stearic-abietic system, in different solvents, reverses the general rule in adsorption, that unsaturated compounds are preferably adsorbed to saturated ones.
6. Rough figures for a large-scale plant indicate that the separation of the components of hydrogenated tall oil may be economical. This process has an additional advantage that, in the future should the demand for hydrogenated rosin increase, the hydrogenation of tall oil can be carried further to hydrogenate the abietic acid too, after the unsaturated fatty acids have first been hydrogenated.

ACKNOWLEDGMENT

Appreciation is expressed to National Oil Products Company for the use of their laboratory facilities where the experimental work was done.

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Fused Salt Mixtures as REACTION MEDIA

H. F. Johnstone
and
W. E. Winsche
UNIVERSITY OF ILLINOIS,
URBANA, ILL.

▶ ▶ ▶ Ferric oxide suspended in fused sodium chloride–ferric chloride reacts at 400° C. with sulfur dioxide and oxygen to form insoluble ferric sulfate. The rate of reaction is determined by both diffusional and chemical resistances. Ilmenite suspended in fused sodium chloride–ferric chloride reacts above 550° C. with a preferential attack on the iron constituent. The beneficiated titanium dioxide can be recovered in the same particle size as the original ilmenite. Zinc oxide suspended in fused sodium chloride–zinc chloride reacts with sulfur dioxide and oxygen at a negligibly slow rate in the range from 420° to 530° C., as does sodium chloride in fused sodium chloride–sodium sulfate at 700° C.

MIXTURES of inorganic salts such as ferric chloride, zinc chloride, aluminum chloride, etc., with sodium chloride form low-melting conducting liquid systems. These liquids are stable at high temperatures and should be solvent media for inorganic reactions. The object of this investigation was to study the reaction of sulfur dioxide and air with inorganic materials suspended or dissolved in fused salt media.

Three equilibrium studies were made: the existence and region of stability of ferric oxychloride in fused sodium chloride–ferric chloride, the fused system sodium chloride–sodium sulfate–ferric chloride–ferric sulfate, and the phase diagram for the system sodium chloride–zinc chloride. In addition, four reactions were investigated—namely, the reaction of sulfur dioxide and air with ferric oxide suspended in fused sodium chloride–ferric chloride, with ilmenite suspended in fused sodium chloride–ferric chloride, with zinc oxide suspended in fused sodium chloride–zinc chloride, and with sodium chloride dissolved in fused sodium chloride–sodium sulfate.

EXISTENCE OF FERRIC OXYCHLORIDE IN FUSED SODIUM CHLORIDE–FERRIC CHLORIDE

The phase diagram of the system sodium chloride–ferric chloride was determined by Johnstone *et al.* (*2*). It forms a simple eutectic, having the composition of 46 mole % sodium chloride and melting at 158° C. The vapor pressure of ferric chloride is strongly depressed by the presence of sodium chloride. This lowering is due to the normal solute action of the sodium chloride and there is no evidence for the existence of a compound. In the system ferric oxide–ferric chloride, ferric oxychloride is the stable compound below 540° C. (*4*). Above this temperature it decomposes to ferric chloride and ferric oxide according to the equation,

$$3FeOCl \longrightarrow FeCl_3 + Fe_2O_3$$

The vapor pressure of ferric chloride above ferric oxychloride and for fused sodium chloride–ferric chloride mixture is shown in Figure 1. The area enclosed by the lines for liquid ferric chloride, solid ferric chloride, and solid ferric oxychloride represents the region in which ferric oxychloride is a stable solid phase. The area to the left of the line for solid ferric oxychloride represents the conditions in which this compound exists only in solution.

The formation of ferric oxychloride in fused sodium chloride–ferric chloride was proved by several experiments in which the time of contact between the ferric oxide and the melt was varied. The data obtained are given in Table I. The solubility of ferric oxychloride was found to be 4.15 millimoles per mole of 40.3 mole % sodium chloride at 300° C. In all runs at 300° C. the oxychloride was present in excess of solubility. In run 5 the experimental conditions were such that ferric oxychloride existed only in solution.

Table I. Formation of Ferric Oxychloride from Ferric Oxide in Fused Sodium Chloride–Ferric Chloride

Run No.	Starting Material, Millimoles			Temp., ° C.	Fe_2O_3 Converted to FeOCl, Millimoles	Time, Hours
	NaCl	$FeCl_3$	Fe_2O_3			
1	42.2	104	25.1[a]	300	2.21	6.0
2	56.4	138	12.5	300	3.67	3.0
3	55.5	137	12.5	300	5.79	12.0
4	54.8	134	12.5	300	6.95	15.5
5	135	138	16.3	350	3.75	15.0

[a] Hematite was used in run 1.

Table II. Experimental Results on Stability of Sodium Sulfate in Fused Sodium-Ferric Chloride

Run No.	Charge, Millimoles			Temp., ° C.	Time, Min.	Liquid Sample, Millimoles		
	$FeCl_3$	NaCl	Na_2SO_4			$FeCl_3$	NaCl	Total sulfate
E3	247	165	30.0	300	30	29.0	24.5	0.24
E4	261	174	30.6	350	30	46.1	47.4	0.91
E5	254	169	31.7	400	30	45.9	48.6	3.02
E6	242	161	30.0	350	30	57.0	58.8	2.27
E7	233	157	31.7	450	30	81.8	70.5	6.33

EQUILIBRIUM IN SYSTEM SODIUM CHLORIDE–SODIUM SULFATE–FERRIC CHLORIDE–FERRIC SULFATE

The addition of sodium sulfate to fused sodium chloride–ferric chloride produces a solid phase, which was found to consist mainly of iron and sulfate. The stability of sodium sulfate in the fused system was measured by determining the change in the ratio of iron to sodium in the melt after addition of the salt. The data obtained are shown in Table II. The expected change in mole % sodium chloride in the liquid phase for the complete reaction,

$$3Na_2SO_4 + 2FeCl_3 \longrightarrow Fe_2(SO_4)_3 + 6NaCl$$

was calculated and compared with the measured values as shown in Table III. The agreement is a good indication that ferric sulfate is the solid phase. A solubility product for the ionic melt,

$$k = (Fe^{+++})^2(SO_4^{--})^3$$

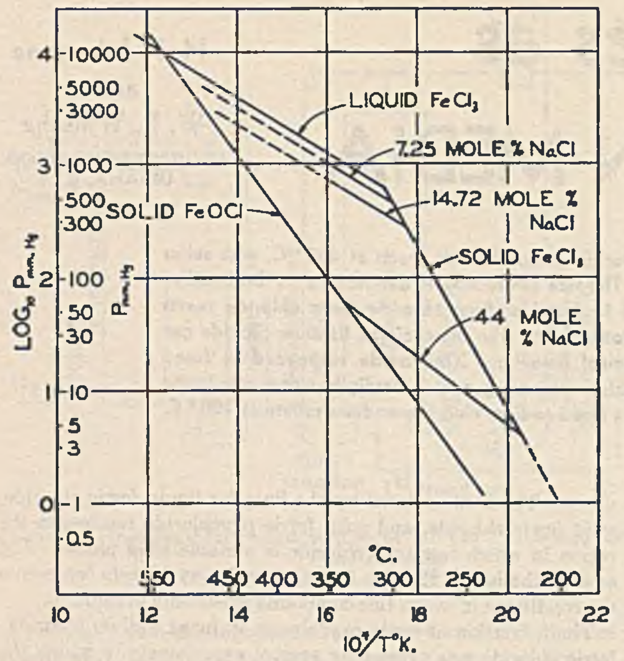

Figure 1. Vapor Pressure of Ferric Chloride in System Ferric Chloride–Sodium Chloride–Ferric Oxide–Ferric Oxychloride

was calculated from the data, and the results are shown in Table IV and Figure 2. The scatter of the data probably results from small errors in the sulfate determination which would be greatly magnified in calculating the solubility product. The slope of the line in Figure 2 gives $\Delta H = -37{,}000$ calories per gram mole for the reaction:

$$2Fe^{+++} + 3SO_4^{--} \xrightarrow[NaCl.FeCl_3]{\text{in fused}} Fe_2(SO_4)_3(S)$$

PHASE DIAGRAM FOR THE SYSTEM SODIUM CHLORIDE–ZINC CHLORIDE

The phase diagram was determined by the method of thermal arrests. The data in Figure 3 indicate a eutectic containing 34 mole % sodium chloride melting at 260° C. The eutectic temperatures found for mixtures containing 20.3, 47.2, and 53.3 mole % sodium chloride are slightly lower than those for compositions closer to the eutectic, probably because of the smaller amount of liquid phase present at these compositions and consequent greater thermal lag of the system.

The data also indicate the existence of a "peritectic", a compound that decomposes before melting, somewhere above 53.3 mole % sodium chloride. The peritectic temperature is 390° C. The composition is shown as 66.6 mole % sodium chloride although this was not proved. The mixture containing 71.9 mole % sodium chloride showed a solid phase present at 600° C. This indicates that a peritectic rather than a eutectic exists at 390° C.

RATE OF REACTIONS OF SULFUR DIOXIDE AND AIR

REACTION WITH FERRIC OXIDE SUSPENDED IN FUSED SODIUM-FERRIC CHLORIDE. In considering the kinetics of a heterogeneous reaction several possible rate-controlling steps exist. If there are two major resistances in the reaction of sulfur dioxide and air with ferric oxide suspended in fused sodium chloride–ferric chloride, the over-all resistance should be the sum of the mass transfer resistance for the transport of sulfur dioxide from the gas to the reaction zone and a chemical resistance of a reaction which is first order with respect to the sulfur dioxide concentration. For the mass transfer resistance, the appropriate equation is:

$$\frac{-d(SO_2)}{dt} = K_g a V(p_g - p_1) \tag{1}$$

For the chemical reaction resistance,

$$\frac{-dG}{dt} = k_r c(p_1 - p_e)G^n \tag{2}$$

Table III. Comparison of Experimental and Calculated Results for Formation of Insoluble Ferric Sulfate

Run No.	Mole % NaCl, Experimental, Original	Mole % NaCl, Experimental, Final	Mole % NaCl, Calcd. for complete reaction	Total Millimoles Sulfate Dissolved
E3	40.0	45.7	49.8	1.9
E4	40.0	50.7	49.5	5.2
E5	40.0	51.5	50.0	15.3
E6	40.0	50.7	49.9	8.6
E7	40.0	53.0	50.8	20.1

where n is the order of the reaction with respect to the amount of ferric oxide present. Combining these equations and assuming that the holdup in the liquid phase is negligible, the equation for instantaneous point conditions is

$$-\frac{dG}{dt} = \frac{p_g - p_e}{\dfrac{3}{K_g a V} + \dfrac{1}{k_r c G^n}} \tag{3}$$

In the range of temperatures covered in this work, the equilibrium pressure of sulfur dioxide over ferric sulfate is negligible. The equation is applicable to a bubbler-type reactor only under limited conditions. If it is assumed that the ferric oxide is uniformly distributed in the liquid and the concentration of dissolved sulfur dioxide does not vary throughout the depth of the liquid, then a logarithmic mean of the inlet and outlet partial pressures of sulfur dioxide in the gas can be used. The equation for instantaneous conditions in a bubbler becomes:

$$-\frac{dG}{dt} = \frac{(p_g)_{l.m.}}{\dfrac{3}{K_g a V} + \dfrac{1}{k_r c G^n}} \tag{4}$$

This implies that the outlet value of p_g is not too small for accurate determination. Further, the value of $(p_g)_{l.m.}$ may not vary too much with time; otherwise the assumption of a linear solubility function for sulfur dioxide will be in error.

Table IV. Solubility Product of Ferric Sulfate in Fused Sodium-Ferric Chloride

Temp., ° C.	Temp., ° K.	$\frac{1}{°K.} \times 10^4$	$k \times 10^8$	$8 + \text{Log}\ k$
300	573	17.50	2.58	0.412
350	623	16.05	21.3	1.328
350	623	16.05	86.4	1.937
400	673	14.85	668	2.825
450	723	13.83	1880	3.274

Equation 4 can be rewritten as:

$$\frac{1}{k_r c G^n} = \frac{(p_g)_{l.m.}}{-\dfrac{dG}{dt}} - \frac{3}{K_g a V} = F \tag{5}$$

This form will be used for the correlation of the experimental data. The values of $(p_g)_{l.m.}$ and $-(dG/dt)$ are experimental quantities, and the instantaneous value of G can be determined by a graphical integration of $-(dG/dt)$ against t. By trial-and-error methods, values of $3/K_gaV$ were assumed, and log G was plotted against log F until a straight-line relation was found. The slope of this line is $-n$, and the intercept is $-\log k_rc$.

Figure 4 shows a schematic arrangement of the apparatus. Reactor G consisted of a 30-mm. Pyrex tube, 36 cm. long with a standard-taper ground-glass joint. The temperature of the reactor was maintained by a radiant-coil furnace and was controlled by manual regulation. The temperature was measured by a thermocouple in a tube projecting into the fused salt and was recorded automatically. A sample of the exit gases, about one third of the total flow, was constantly drawn through sampler I and analyzed for the acidic constituents sulfur dioxide and sulfur trioxide, and for the ratio of these to nitrogen. The rate of reaction of ferric oxide is:

$$-\frac{dG}{dt} = \frac{(SO_2/N_2)_{in} - (\text{acidic}/N_2)_{out}}{(SO_2/N_2)_{in}} \times \frac{R}{3} \tag{6}$$

Since the gas was analyzed periodically, it was possible to plot $-(dG/dt)$ against t. A graphical integration gave the amount of ferric oxide reacted. Subtracting this value from the orignal ferric oxide gave G. The value of $(p_g)_{l.m.}$ was calculated from the flow of sulfur dioxide and air and the gas analysis. The experimental values necessary for the solution of Equation 5 were then available.

Material balances on the sulfur dioxide and oxygen showed that they reacted in the molecular ratio of 2 to 1 at all temperatures investigated. Analysis of the fused salt at the completion of the reaction showed only small amounts of the soluble iron present in the ferrous state. These two facts prove that the reduction is negligible in the presence of the large excess of oxygen in the reaction gas. Analyses of the gas at 400°, 425°, 448°, and 453° C. showed that most of the sulfur in the exit gas was sulfur dioxide whereas chlorine was present in small amounts. At 525° C. only traces of chlorine were found in the exit gas, and the sulfur was present mainly as sulfur trioxide.

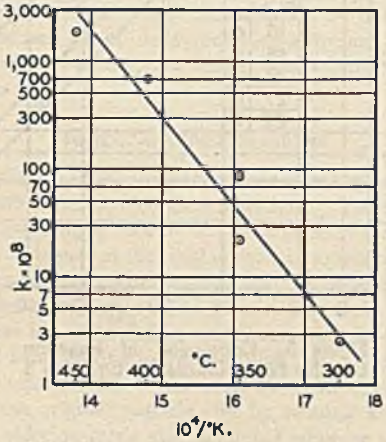

Figure 2. Solubility Product of Ferric Sulfate in Fused Sodium Chloride–Ferric Chloride

A plot of correlation factor F for the runs at 400°, 425°, 448°, and 453° C. is shown in Figure 5, and a summary of the results is given in Table V. Figure 6 shows the value of log F for $G = 30$ mg. moles plotted against the reciprocal absolute temperature. Values of k_rc itself were not plotted as this involved a large graphical or analytical extrapolation of the data to the value of $G = 1$ mg. mole of ferric oxide. Values of log F at any value of G could be used, but $G = 30$ was chosen because it represents the median value.

The theoretical Equation 5 correlates the data for 400°, 425°, 448°, and 453° C. The experimental conditions at 525° C. do not conform to the assumptions under which the equation was derived. The low partial pressure of the acid constituents in the exit gas at this temperature precludes the possibility of a uniform concentration of dissolved sulfur dioxide in the melt. This means that the particles of ferric oxide at different heights in the melt are reacting at different rates. Furthermore, the average driving force for the diffusion of the sulfur dioxide will be higher than a logarithmic mean average would give. The observed diffusion coefficients vary over a two and a half fold range, and no correlation with the experimental variables was possible. The reason for this is that the value of K_gaV depends somewhat on the position of the inlet gas tube in the fused medium. The order of magnitude of the diffusion coefficients is what would be expected for a gas film.

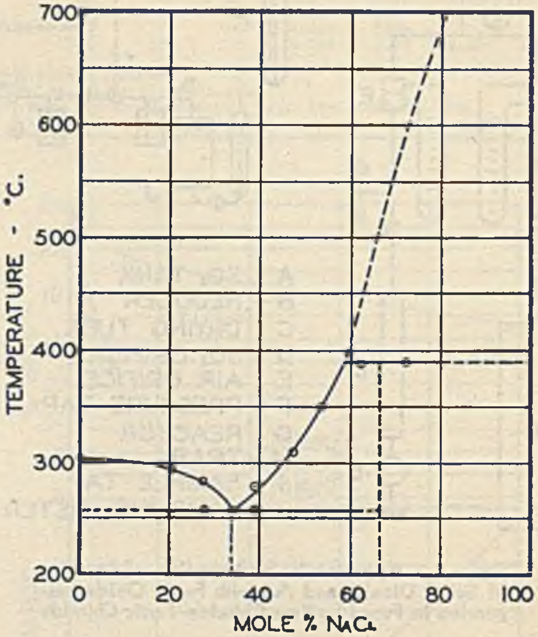

Figure 3. Phase Diagram for System Sodium Chloride–Zinc Chloride

The correlation proves the validity of Equation 5 for the experimental conditions for which it was derived and indicates the general application of Equation 3 to this reaction. Exact integration of Equation 3 for countercurrent or parallel flow of gas and suspension would give an equation applicable to these processes. The value of $1/F$, for $G = 30$ mg. moles of ferric oxide, increases rapidly with absolute temperature. The irregular temperature dependence of k_rc (apparent energy of activation is not constant) is caused by the simultaneous changes in k_r and c with temperature. The reaction of sulfur dioxide and air with ferric oxide suspended in fused sodium chloride-ferric chloride probably proceeds through ferric oxychloride as an intermediate. The rate of reaction in the fused system is comparable with the rate of reaction of sulfur dioxide and air or sulfur trioxide with ferric oxide. Keppeler (3) notes that this reaction begins at 230° and is quite rapid at 450° C.

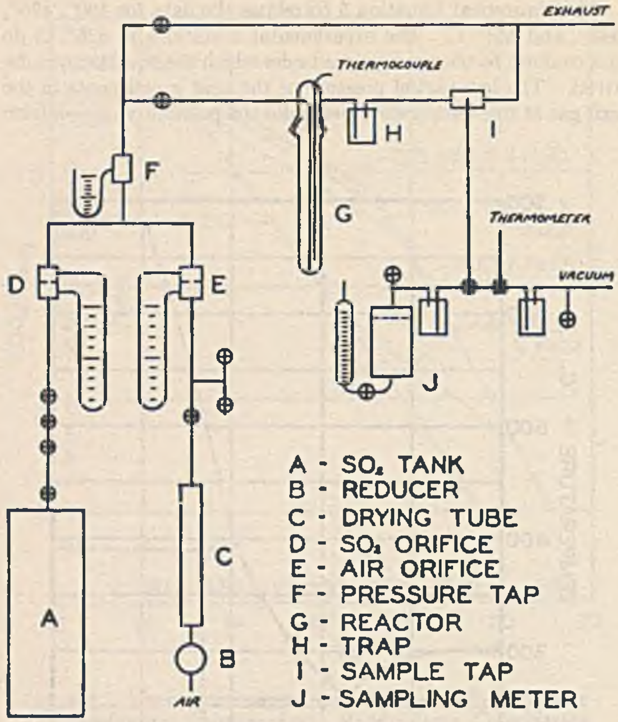

Figure 4. Apparatus for Studying Rate of Reaction of Sulfur Dioxide and Air with Ferric Oxide Suspended in Fused Sodium Chloride–Ferric Chloride

REACTION WITH ILMENITE SUSPENDED IN FUSED SODIUM-FERRIC CHLORIDE. The possibility of preferential attack of the iron constituent of the ore is of interest. Johnstone and Darbyshire (*1*) noted a preferential attack of the iron constituent in a somewhat similar system. Preliminary tests showed a slow rate of reaction for the ilmenite suspended in the fused melt, so the effect of reaction was determined by analysis of the residual melt. Ilmenite samples of different particle sizes were prepared by grinding Quilon ore in a ball mill and sieving. The ilmenite used in the C and E runs consisted of material passing a standard 200-mesh sieve. The ilmenite used in the D run passed the 100-mesh sieve and was collected on the 120-mesh sieve. Both samples were washed several times by decantation with water to remove the fine dust formed during grinding.

Table V. Summary of Results for the Reaction of Sulfur Dioxide and Air with Ferric Oxide Suspended in Fused Sodium-Ferric Chloride

Run No.	Temp., ° C.	Gas Flow (S.T.P.), Ft./Hr.		Charge, Grams			F at $G = 30$	n	K_GaV
		SO_2	Air	$FeCl_3$	NaCl	Fe_2O_3			
16	453	0.437	2.015	97.5	39.0	10.0	0.0186	2.07	27.8
18	448	0.437	2.015	86.0	35.0	12.0	0.0269	2.06	31.6
19	400	0.417	2.000	80.0	28.0	12.0	0.0933	2.04	13.5
21	400	0.350	1.625	81.9	35.0	12.0	0.0933	2.04	25.0
22	425	0.313	1.665	57.9	25.0	8.0	0.0630	1.93	34.8
23	525	0.323	1.690	97.0	39.0	12.0	....	..	..

Table VI. Reaction of Sulfur Dioxide and Air with Ilmenite Suspended in Fused Sodium-Ferric Chloride

Run No.	Time, Hr.	Charge, Grams		Temp., ° C.	Fines, Grams	Ore Recovered, Grams	Fe in Recovered Ore, %
		NaCl	$FeCl_3$				
C1	1.5	65	35	550	0.080	[a]	19.5
C2	3.0	65	35	550	0.330	8.14	18.0
C3	4.8	65	35	550	0.695	7.34	15.1
D1	2.0	65	35	550	0.130	8.80	19.1
E1	1.0	65	35	620	0.110	[a]	4.6
E2	0.5	55	45	620	0.070	7.35	11.9

[a] Some ilmenite was lost in charging.

The data are shown in Table VI and Figure 7. Considering the series of runs at 550° C., it is evident that the iron content of ilmenite can be reduced to approximately 21% without appreciable formation of fines. The iron content was reduced to 15% by 5 hours of treatment. Reduction of the iron content below 21% results in the formation of relatively large percentages of fines, the amount being a linear function of the iron content below 21%.

One run, D1, was made with a larger mesh size to determine the cause of disintegration. If it is the result of a weakening of the crystal structure at the surface, the amount of fines for the same reduction of iron content in a charge of larger original particle size should be greater. If it results from a general weakening of the entire crystal structure, the amount of fines for any given iron content will be independent of the original particle size. Run D1 shows that the latter is the case; it also shows that, for the range of particle size investigated, the reaction is controlled by a chemical resistance and not by the resistance to the diffusion of sulfur dioxide either to or into the particle structure. This conclusion is also borne out by examination of the products. If the materials are arranged in the order of decreasing iron content, a regular gradation of color from black to buff is observed. This eliminates any possibility of a surface attack.

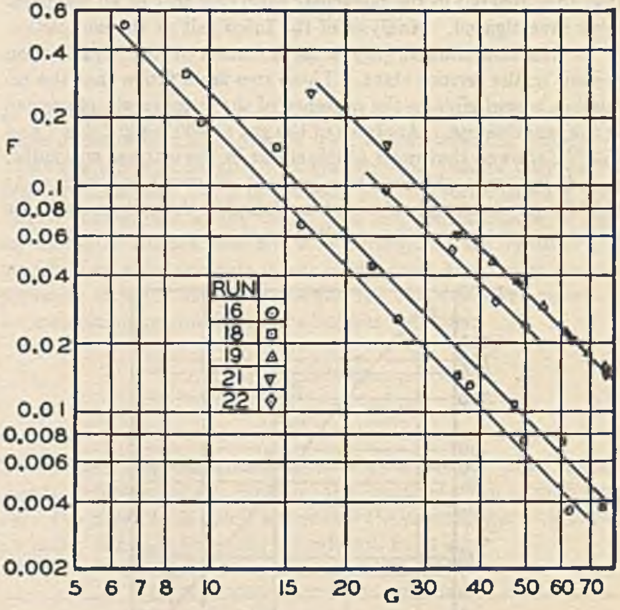

Figure 5. Correlation of Reaction Data for Ferric Oxide by Equation 5

At 620° C. the rate of reaction is greatly increased. This is further evidence that chemical resistance is the controlling step in the process. The amount of fines produced in the reduction of the iron content to 4% at 620° C. is comparable with that produced in reducing the iron to 20% at 550° C. The runs at 620° also show that the critical iron content is lower than that at 550° It is well known that the various modifications of titanium dioxide undergo phase modifications in the range 540° to 600° C. This may be reason for the difference in the critical iron content. The titanium dioxide lattice is sufficiently mobile at 620° C. to recover the strength lost by the removal of the iron constituent.

REACTION WITH ZINC OXIDE SUSPENDED IN FUSED SODIUM-ZINC CHLORIDE. This reaction is of interest because oxidation and reduction effects are absent in the reaction of zinc oxide.

The extent of reaction was determined by analysis of the melt for sulfate after gas treatment. Two runs were made to determine the rate of reaction of sulfur dioxide and air with zinc oxide suspended in fused sodium chloride–zinc chloride. The following data show that the reaction occurs at only a slow rate in the temperature range investigated:

Run No.	Charge, Grams			Temp., ° C.	SO_2 Reacting Mg. Mole/ Min.
	$ZnCl_2$	NaCl	ZnO		
1	106	24	7	420	0.075
2	100	20	7	530	0.143

CHLORINE-SALT CAKE REACTION IN A FUSED SYSTEM

The possibility of utilizing sulfur dioxide and sodium chloride for the nonelectrolytic production of chlorine exists in the reaction:

$$2NaCl + SO_2 + O_2 \longrightarrow Na_2SO_4 + Cl_2$$

The reaction was carried out in a fused system of sodium chloride and sodium sulfate at 700° C. The composition of the initial melt was selected to be near the saturation value of sodium sulfate. In runs A and B sulfur dioxide and air were bubbled through the fused melt. In runs C and D, the tube was filled with $^1/_4$-inch Berl saddles to increase the intimacy of liquid-gas contact. In runs B and D rutile was added to determine if it was a catalyst for the reaction as suggested by Johnstone and Darbyshire (*1*).

The data (Table VII) show that the rate of reaction of sulfur dioxide and air with sodium chloride suspended in fused sodium chloride–sodium sulfate is small. Since increased liquid-gas contact obtained by means of Berl saddles does not increase the rate of reaction, the slowness of the reaction is apparently caused by an unfavorable equilibrium. Rutile was not found to be a catalyst under the conditions of these experiments.

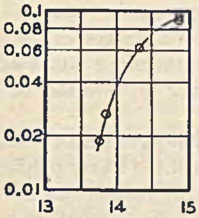

Figure 6. Temperature Dependence of Chemical Resistance in the Ferric Oxide Reaction

PRACTICAL CONSIDERATIONS

This investigation has shown that fused salts are reaction media for several heterogeneous inorganic reactions. The data indicate that for a bubbler-type reactor the mass transfer resistance may be an appreciable part of the total resistance to reaction.

In the reaction of sulfur dioxide and air with ilmenite suspended in fused sodium chloride–ferric chloride a preferential attack on the iron constituent was observed. This constitutes a method of beneficiating low-grade (high iron content) ilmenite ores. The major portion of the titanium-enriched ore can be recovered in the original particle size by settling after reaction. The sodium chloride–ferric chloride liquid adhering to the settled titanium-enriched ore can be removed in two ways. If the product, after settling, contains very little adhering liquid, the mass can be solidified, crushed, and water-washed. If there is an appreciable amount of the liquid, the product from settling can be washed with liquid ferric chloride, under pressure, to remove the sodium chloride. The ferric chloride then can be volatilized from the beneficiated ilmenite and the product water-washed.

NOMENCLATURE

c = Henry's law constant for SO_2 in fused NaCl–$FeCl_3$
F = correlation factor
G = Fe_2O_3 present at time t, mg. moles
k_r = specific reaction rate constant
K_gaV = over-all SO_2 diffusional coefficient, millimoles SO_2/(min.)(atm.)
n = a constant
p_g = partial pressure of SO_2, atm.
p_e = dissociation pressure of SO_2 over $Fe_2(SO_4)_3$, atm.
p_l = equilibrium partial pressure of dissolved SO_2, atm.
$(p_g)_{l.m.}$ = log mean value of inlet and outlet partial pressure of SO_2, atm.
R = rate of feed of SO_2, mg. moles/min.
t = time from start of reaction, min.
T = absolute temperature, ° *K*.

Table VII. Chlorine–Salt Cake Reaction in a Fused System[a] of Sodium Chloride and Sodium Sulfate

Run No.	Temp., ° C.	Rutile, % by Weight	SO_2, % in Gas	Gas Flow, Cu. Ft./ Min.	Space Velocity[b], L./Hr.	SO_2 Converted to Cl_2, %	
						By gas analysis	By residue analysis
A	700	0	22	0.050	2900	1.65	1.70
B	700	3	21	0.054	3200	0.95	0.65
C[c]	700	0	18	0.053	3050	....	1.00
D[c]	700	10	21	0.045	2600	2.40	0.50

[a] 40% sodium chloride.
[b] Based on volume of molten salt.
[c] Increased gas-liquid contact by $^1/_4$-in. Berl saddles in melt.

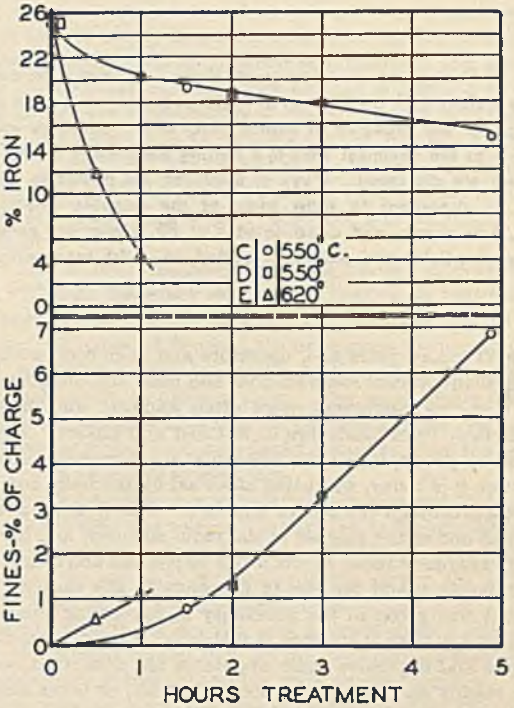

Figure 7. Reaction of Sulfur Dioxide and Air with Ilmenite Suspended in Fused Sodium Chloride–Ferric Chloride

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RADIO POWER
for
Processing Chemical Materials

John W. Robertson[1]
INTERNATIONAL TAILORING COMPANY, NEW YORK, N. Y.

▶ ▶ ▶ **During the past few years there has been a tremendous growth of interest in and experimental work on the uses of radio frequency power for dielectric heating and processing. This paper was prepared to answer many of the questions asked by chemical engineers, and to give to the chemical worker a starting knowledge of this new tool. Fundamentals of the process are discussed. Ways of applying the power to different loads are discussed, and data are presented to show some of the possible selective heating effects. Equipment costs, advantages, and disadvantages of RF power are covered briefly. A partial bibliography of articles and patents is added to assist readers in obtaining further information.**

NOT many years ago, operators and engineers working in high-powered radio stations and near high-frequency generating equipment were often annoyed and made uncomfortable from headaches or hot feet and ankles. The radio frequency power, which was not under the degree of control and direction it is today, was being absorbed by the body and thence grounded through the ankles and feet. This heating phenomenon was one of the plagues of the radio engineer, and his object was to eliminate those effects as far as possible and do away with the annoyance and the loss of efficiency to the station. Little thought was given to the possibility of harnessing this heating effect and putting it to work industrially; the prospect of using delicate and expensive radio apparatus for work that could be done readily and cheaply by steam, hot air, or other abundant power must have appeared ludicrous to radio and heating engineers alike. However, radio frequency is now rapidly coming to the fore as a leading method of industrial heating; not only is it doing some jobs more economically than other types of heating, but many jobs which could not be accomplished at all with conducted heat.

The possibilities of radio frequency power as a tool for processing chemicals have barely been touched, nor have the theoretical probabilities been widely explored; therefore a preliminary basic discussion of this tool is presented here in order to give those in the chemical field a working knowledge of its meaning and applicability.

The term "radio frequency power" (RF) will immediately be pictured by some as induction heating, because this was the first industrial application of medium high frequencies to the heating problem; and by others perhaps as heating by infrared radiations. These two methods of applying high-frequency electrical energy are today the most widely used means of employing radiant energy for heating; but they are not the main objective of the present article because induction heating is best applicable to good conductors, such as metals, by inducing eddy currents within them, and infrared heating is best suited for quickly heating and drying thin films uniformly.

The newest concept of the use of RF power in chemical work, particularly the heating of materials not considered good conductors, is to place the work or load in the electrostatic field set up between condenser plates located in a suitable part of the circuit. This means that the full voltage and power of the RF is sent directly through the material being processed rather than being induced in it by a magnetic field or irradiated by reflected rays.

BASIC PRINCIPLES

The currently accepted theory of the flow of electrical power is briefly that a direct current is one which flows in the same direction continuously and in which the positive and negative poles remain in the same positions. An alternating current reverses the direction of flow and polarity at regular intervals, and the number of times per second this reversal occurs is a measure of its frequency. Frequency is expressed as the number of complete cycles per second and is therefore numerically half the number of reversals or alternations.

Since these reversals of polarity are normally graduated changes in the flow of power, we may draw graphs of the waves produced during this flow which will aid in explaining further descriptive terms. Figure 1 shows only one cycle and indicates that the time required for these changes is $^1/_{60}$ second. This is called a 60-cycle current and is the frequency ordinarily used for industrial lighting and power. This wave also has a definite physical length, usually expressed in meters for the longer waves; this distance indicates how far the wave is projected in the course of its formation. This may be readily calculated, as these waves are propagated at the speed of light—i.e., about 300,000,000 meters per second. The distance traveled in $^1/_{60}$ second is therefore 5,000,000 meters, and this is the length of the wave form.

Frequency may be readily converted to wave length by dividing the speed of light by the desired frequency; conversely, wave length may be converted back to frequency by dividing it into the speed of light. Results of all such calculations are usually in terms of meters and cycles per second. As frequencies increase, they are expressed in terms of kilocycles (1 KC. = 1000 cycles) or in terms of megacycles (1 MC. = 1,000,000 cycles). In discussing wave length, the usual terminology of meters is often too large a unit; therefore centimeters, millimeters, and Ångstrom units are used for the shorter waves (1 Å. = 0.0000001 mm.).

Figure 2 shows the relative locations of various types of radiation in the spectrum. It is interesting to note the extreme variations in the wave length of the shortest and longest radiations. Without the logarithmic scale it would be impossible to show both on the same chart with any degree of meaning.

HIGHER FREQUENCIES

Waves which vibrate at a rate of 10,000 cycles per second are in the range used in induction furnaces. According to Figure 2, this wave length is 30,000 meters. Frequencies of 20,000 cycles or 20 KC. per second (15,000 meters) were used in radio transmission in the early days and are still utilized in much high-power transocean work; but all subsequent development has been toward higher frequencies (shorter wave lengths). Various semimechanical methods, such as the spark generator and alternator, were used up to this point in generating these frequencies, but the development of vacuum tube methods gave impetus to the generation of higher frequencies. With the advent of radio broad-

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[1] Present address, Ellis-Foster Company, Montclair, N. J.

casting for entertainment, the frequency range of 550 to 1500 KC. was assigned by the Federal Communications Commission for this purpose, and today many commercial programs are being broadcast at frequencies above 40,000 KC. (40 MC.). Most of them are based on frequency modulation or television. The range of 2 to 40 MC. is the most important in new applications to chemical work. The importance of higher frequencies will develop as higher power becomes available at those frequencies.

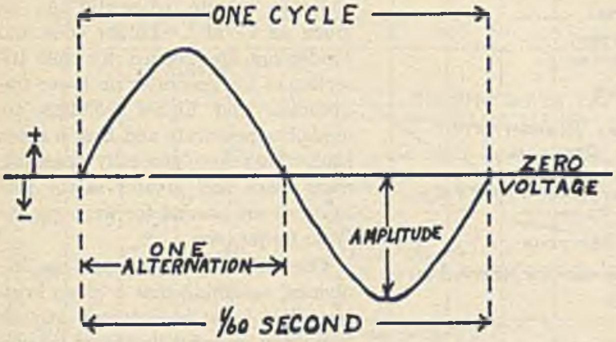


Figure 1. Wave Form Produced by Propagation of Pure Sine Wave

In discussing frequencies above 100 MC., where much work is being done in the fields of communication and detection, it becomes more practical to go back to the wave-length rather than the frequency concept because the physical limitations caused by the shortness of the wave are of prime consideration. At 100 MC. the wave form is only 3 meters long, and at 10,000 MC. it is 3 cm. long. Such wave lengths as these approach the mechanical and physical limitations of the vacuum tube generators, and very small amounts of power at best can be transformed and handled in this range. Perhaps methods other than vacuum tubes as we know them will be the medium for generating high power on these frequencies. However, in this little-known band of radiations, between wave lengths of 1 and 0.0001 cm., much interesting work is being done behind locked doors, and many ultra-short waves are now working in various capacities to help win the war.

The jump in wave length from 1 to 0.0001 cm. does not appear great when compared with the whole spectrum, but it holds secrets which will be well worth solving. The big problem now is the method of generating and handling these radiations with sufficient power behind them to permit practical studies.

This practically unknown region may hold the secrets of directed beam propagation of energy. We do know that the shortest waves described before war censorship were characterized by their ability to be directed toward any desired point with much more efficiency and in a more concentrated beam than any longer-wave radio transmission. In this region is the transition from radiations known as "radio" to those with more of the character of what we have termed "light" waves. It is interesting to speculate on what activity these little known radiations may bring forth. Will it be the "Buck Rogers" disintegrator rays or a real "death ray"? Will it be a means of stopping tank and aircraft motors, or will it be a method of transmitting large amounts of power between stations without transmission lines, as envisioned by the late Nikola Tesla, who was recently taken away almost on the threshold of seeing that vision come true?

To discuss still shorter waves it becomes more practical to employ the Ångstrom unit of measure. Since this unit is accepted as 0.0000001 mm., our 0.0001 cm. wave length becomes 10,000 Å. This is probably the upper limit of what we now call infrared radiation, with 7000 Å. the approximate lower limit. These radiations have achieved rather wide success as a heating and drying medium and are supposed to have high penetration as radiant energy, although actual tests show that this penetration is limited to a few thousandths of an inch. The drying of films such as paints and lacquers has been successful, and there are, no doubt, many valuable industrial uses.

Other radiations in the known spectrum which should be somewhat familiar to anyone working in the field of radiations include visible or light rays in the range 7000 to 4000 Å.; ultraviolet rays in the sun's spectrum, 4000 to 2920 Å.; x-rays, 150 to 10 Å.; gamma rays, 1.4 to 0.01 Å.; and cosmic rays, about 0.0005 Å.

UTILIZATION OF RAYS

We may pass briefly over the use of infrared heating, as it is considerably removed from those radiations (2–40 MC.) in which we are most interested at present. Commercially this type of radiant energy is generated in lamps similar to ordinary household lighting, but the filament is of relatively low intensity in the visible range and the light emitted is dull red in color. These lamps have self-reflectors or are mounted in individual reflectors, and numbers of these units are grouped side by side in "banks" or "tunnels" so arranged as to direct the energy on the product to be heated or dried. Infrared lamp tunnels were used extensively on automotive and refrigerator finishes and for other similar jobs.

The field of high-frequency induction heating is more closely allied with high-frequency electrostatic heating, in that the general types of vacuum tube methods of generation may be used. However, for induction heating, the frequencies are usually below 1 MC., and other means of generation, such as the alternator, may be used effectively to produce them. The much higher frequencies which are more desirable in electrostatic heating, for reasons to be given later, have not been found necessary when the heating effect is to be produced by induction.

In induction heating it is necessary to set up a rapidly alternating magnetic field and subject the material being treated to this field. In its simplest form the heating chamber, or crucible, is surrounded by a coil of conductor which carries the high-frequency power, and the rapid alternations of flow in this coil set up a strong field in the crucible and generate electric currents in the products being heated, in much the same manner that a transformer primary induces current in its secondary winding. These induced currents cause the rise in temperature of the charge. There are hundreds of industrial applications of this type of power, but the most important are in the heating of materials of good electrical and thermal conductivity, especially those with magnetic properties.

METHODS OF GENERATION

The phenomena described have been of great interest to electrical, radio, and metallurgical engineers, but very little of the work has been of value to chemical engineers. There is, however, a method of using high-frequency power to produce heat in chemical materials, which are normally considered relatively poor conductors of heat and electricity and even materials which are called "insulators". This phase is in its infancy, and many good applications are going to be sidetracked or called failures in the next few years because of a lack of understanding in applying the method as well as for economic reasons; but for the longer-term outlook there is a tremendous field of opportunity and there should be a rapidly changing picture of both technique and economics. As mentioned above, the first difference between electromagnetic and electrostatic applications is the frequency of the power used. For electrostatic heating, frequencies above 1 MC.

are used, and commercial units for this work range from 1.5 MC. in the highest power installations to almost 50 MC. in therapeutic work.

From a practical standpoint the highest power is most efficiently developed in the lower part of the range, and less difficulty is found there in handling and "piping" the power, although some 50-kw. radio stations operate efficiently on as much as 44 MC. Larger coils and condensers are needed for the RF section of the generator on lower frequencies, and higher voltages are needed to penetrate and heat a given load. Therefore, generally speaking, more space and greater safety precautions are needed for work on the lower frequencies.

The relation of voltage to frequency, assuming that a given heating effect is to be obtained at each frequency, may be illustrated by saying that the voltage required is inversely proportional to the square root of the frequency. In an application where 1,500,000 volts would be needed at ordinary 60-cycle frequencies, 12,000 volts would be sufficient at 1 MC. and approximately 2000 volts would be sufficient at 40 MC. Thus, among the great advantages of RF power for heating is the possibility of using lower voltages for any given job.

It follows, then, that in smaller operations, where portability and the safety necessary for more "intimate" handling by the operator are important, a trend to higher frequencies may be desirable; this trend is limited by efficiency of generation and transmission, and by increased difficulties in keeping the load "in tune" with the generator. The range of 15–20 MC. has been the chief range of work done by the writer, although some work has been done around 40–45 MC.

The greatest and the fundamental difference between electromagnetic and electrostatic heating lies in the placing of the work. In all high-frequency oscillating circuits a certain balance of inductance (coils) and capacity (condensers) is needed to make a "tuned circuit", which in turn is tuned to the frequency of the "load circuit". When the generating circuit and load circuit are in tune or in resonance, power will flow through the coil and condenser of the load circuit, and any load placed within the coil or between the plates of the condenser will absorb power and be heated. The load in the coil (Figure 3) is heated by induction which is electromagnetic in character, and the

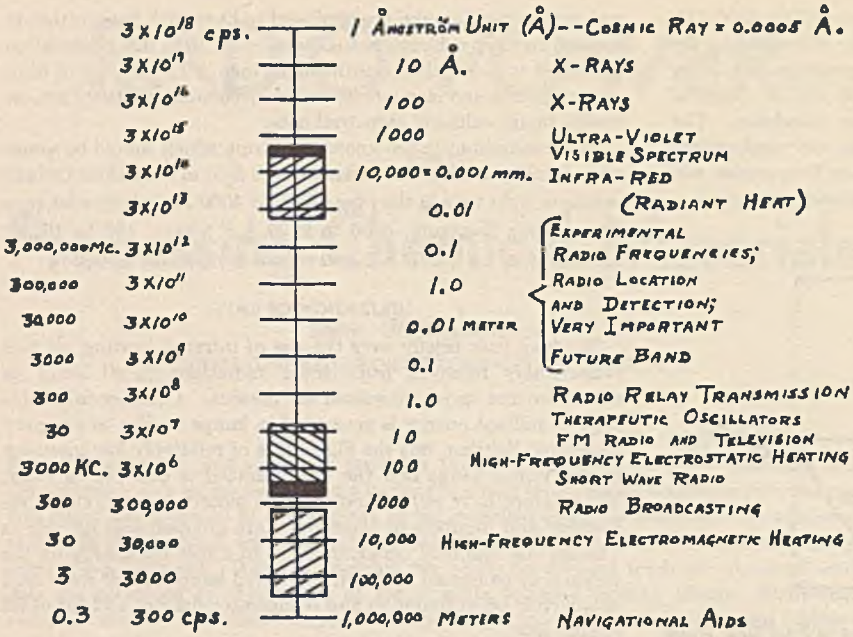
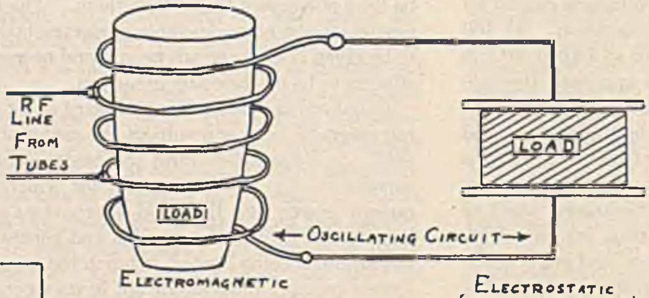


Figure 2. Spectrum Chart

Figure 3 (Right). Location of Electromagnetic and Electrostatic Loads



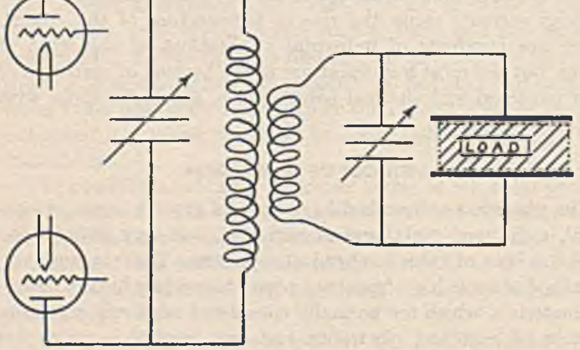


Figure 4 (Left). Simple Output Circuit for Electrostatic Heating

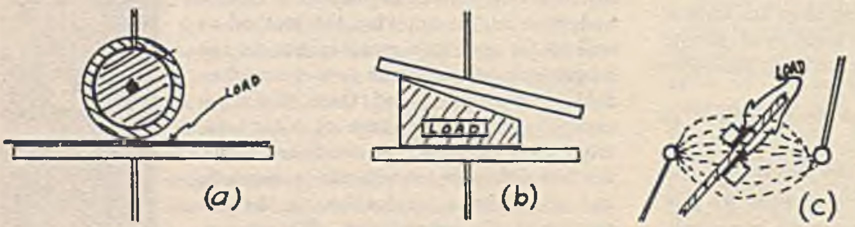


Figure 5. Ways of Applying Electrostatic Power to the Load

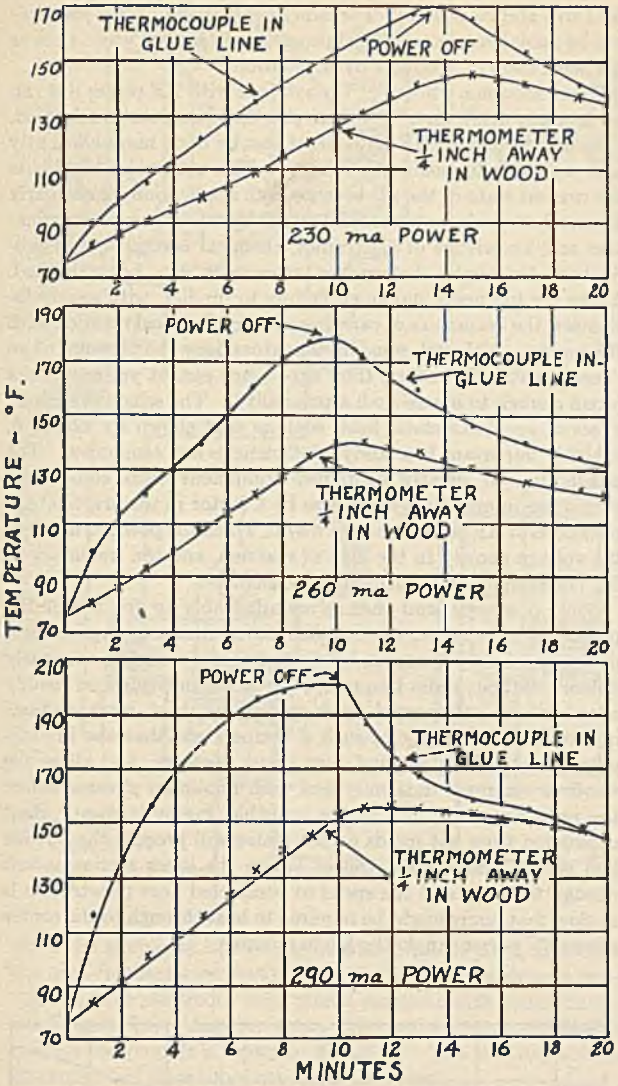


Figure 6. Low-, Medium-, and High-Powered Heating of a Glued Joint

load in the electrostatic field between the condenser plates is heated by dielectric loss. That is, the load forms all or part of the dielectric for the condenser; and since it is a better conductor than air, which forms an almost perfect condenser, some power tends to leak through it. This power "loss" or absorption by any load of semi-insulating material causes its temperature to rise at a rate dependent upon the power absorbed and to rise uniformly throughout the mass. This uniformity of mass heating is one of the chief characteristics of RF power which makes it of great potential value.

Figure 4 shows a simplified output circuit and the location of the load in relation to the other components. The complete circuit will be dealt with later. The electrodes form the plates of an auxiliary condenser and contain the load between them. When this circuit is in resonance with the output circuit of the tubes, the relatively poor dielectric of the load causes power leakage through it, and this flow of power causes heating in its path in somewhat the same manner as direct or low-frequency current causes heat in the iron or Nichrome wire forming the heating element of a hot plate, although the exact nature of this effect in a dielectric is still open to question.

As Figure 4 shows, in the ideal load the electrodes are the same in size and shape, are parallel, are close to or in contact with the load, and the load is uniform in thickness and dielectric constant. This should not be taken to limit all applications to this set of conditions, as valuable industrial work may be done under considerably different conditions, but it does give a basic set of conditions to aim for.

Some different methods of arranging electrodes which are not flat and parallel may be illustrated by Figure 5. (*a*) represents a rotating circular electrode in the form of a wheel, the bottom electrode being a flat surface below the wheel. This application is useful for such processes as the edge gluing of wood veneers and the so-called stitching of fabrics coated with resins or of sheet resins themselves. (*b*) represents the condition in which the load is a solid object but one face is at an angle to the bottom flat electrode; in this case the top electrode must be arranged so that air or some other insulator forms part of the electrostatic field on one side, the chief point being to have the same average dielectric constant. (*c*) represents point electrodes or small-diameter rod electrodes with the load being supplied to one side of a direct path between them. In this case the electric field fans out enough to bring the load within the path of the power and thus cause it to absorb sufficient power to be heated.

There are hundreds of ways of laying out electrodes and of feeding the RF power out of the generator and into the load; this final layout can be done accurately only on the job to be handled, because every variation in size and placement of electrodes and load and every different length of feed line can introduce a new set of conditions. However, much is known now of the capabilities of RF power in many applications, and a great deal can be calculated in advance, as a result of years of work by radio engineers in the communications industry. There is still room for improvement in the mutual understanding of problems between the chemical operator or manufacturer and the radio engineer; it is imperative that they work together to obtain best results in the use of RF power.

APPLICATIONS

The first potential use of RF power appeared when the Viennese doctor, Wagner Jauregg, proposed to cure diseases by creating a fever in the patient. His approach was drastic, in that he gave the patient mild forms of typhoid and malarial fevers to build up a body temperature to combat the disease. Later work in utilization of electric fields, both high-frequency electromagnetic and high-frequency electrostatic, showed that Jauregg was right in many of his deductions, and it is unfortunate that he did not live to see his artificial fever created by electrical means.

Only during the past ten or twelve years have commercial applications of high-frequency electrostatic power been seriously considered, and most of the valuable applications have been in the last five years. Apparently no uses in direct manufacture and processing of chemical materials have reached the stage of an issued patent or published data, although this would appear to be one of the greatest potential spheres of application.

One of the earliest patents, issued in 1933 to General Electric Company, concerns an apparatus for heating by means of an electrostatic field. Another about the same time deals with the rendering of fats, but the frequencies mentioned are rather low. Several applications made in 1935 and issued later are entitled "drying of felts", "drying of sponges", "making closures", and "cementing of shoe soles". Others appeared in the next few years covering special apparatus for drying leather, drying tobacco in hogsheads, etc. Apparently the field is wide open for specific applications as suitable techniques are worked out, for the principles of high frequency heating have been public property for some time.

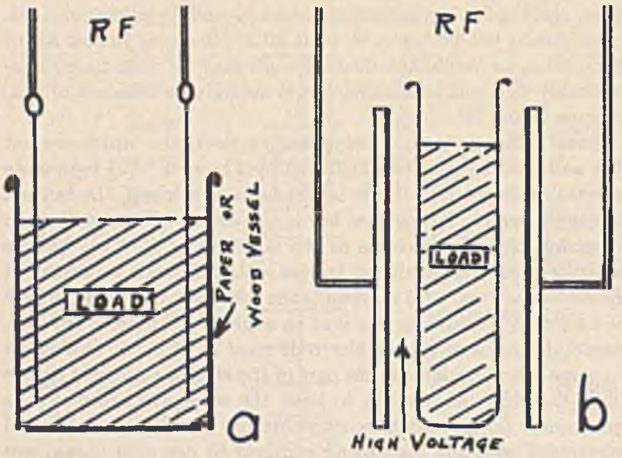


Figure 7. Arrangements for Cooking Resins

The bibliography at the end of this article lists reports on specific developments. Greatest industrial progress so far seems to have been made in the gluing of wood to make plywood and other wood structures. This activity has been considerably stepped up by the war program on wood planes and gliders. To illustrate the versatility of RF power, the following list shows uses mentioned in print for high-frequency electrostatic power:

Heating semi-insulators
Gluing plywood and gluing with resins, etc.
Deactivating enzymes (vegetables before freezing)
Preheat molding preforms
Peeling potatoes
Surgery
Distillation (destructive, etc.)
Plasticizing rubber before milling or thermoplastic resins before extruding or milling
Drying paper, ceramics, textiles, sensitive powdered materials, tobacco in hogsheads, etc.
Condensing or polymerizing resins
Curing rubber
Heavy Compreg wood propellers
Destroying grain infestation
Pasteurizing milk
Cooking (baking, toasting cereals, etc.)
Impregnating wood
Stitching
Seasoning lumber
Pasteurizing milk or beer
Chemical reactions

CHEMICAL REACTIONS

Some physicists and electronics experts state that molecules in the rapidly alternating electrostatic field try to reorient themselves with each alternation of RF current, and their great activity produces heat from molecular friction. Others contend that it is purely a resistance phenomenon, and that heating is due solely to resistance offered to the passage of current such as could happen in a d.c. circuit passing through a resistance wire. Since no one has satisfactorily explained the mechanics of the phenomenon, no definite statement regarding the mechanics of electrostatic heating can be made now. There is some evidence to support both theories, but more data should be gathered and carefully analyzed before a theory is evolved. The molecular structure of the material or combination of materials being heated, their dielectric constants, and the particular frequency and voltage density being applied will probably all have great bearing on the phenomena taking place.

Figure 6 shows selective absorption of electrostatic power in gluing together flat pieces of spruce. The upper line in each case represents the temperature registered by a thermocouple placed in the glue line proper; and the lower line, that by a thermometer placed about $^1/_4$ inch from the glue line. Different rates of power application are responsible for the increasing slopes of the curves. Figure 6 shows that certain materials within the electrostatic field will absorb power more readily than others. This principle can be made use of in chemical processing in several ways, such as the separation of products by distillation.

There are some who say, "Do not do it with RF power if it can be done any other way." A more practical viewpoint would read, "Do not do it with RF power if it can be done more efficiently and economically some other way." This statement highlights the present state of the art because each application, particularly in chemical work, needs careful study by workers with imagination and knowledge of electronics, chemical reactions, and production techniques before the economics can be estimated. There are too many unknown factors to predict, with exact efficiencies, the economics of carrying out any chemical reaction with RF power. Although some investigators deny the presence of an "energy catalytic" effect, their experience cannot yet have been broad enough to ignore such a possibility. The selective heating effect of an electrostatic field, such as that shown by Figure 6, is highly important in a study of efficiencies and economics. The possibilities of greatly simplified equipment with consequent economies in operation must also be a factor in the practical applications of RF power, and the way in which the power is applied, the voltage density in the field of reaction, and the frequency of RF power must have adequate attention.

Some processes lend themselves admirably to the use of RF power. For instance, the manufacture of Compreg airplane propellers and heavy Compreg blocks and sheets would be extremely difficult without radio frequency. It is the only method readily adaptable to commercial work which can heat large sections quickly and uniformly to such a temperature that the impregnated resin will soften and flow under pressure, and allow the wood to compress uniformly and with minimum stresses before the resin has cured to a rather infusible, insoluble state. Heat conducted from hot molds or hot plates will precure the outside and set up undesirable stresses before the inner section is soft enough to flow; and the speed of conducted heat penetration is so slow that hours might be required to heat through to the center where RF power can do the job in minutes.

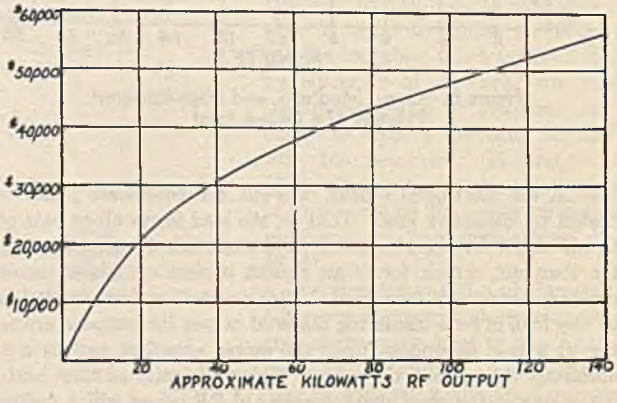


Figure 8. Equipment Cost–Power Output Chart

Another example recently showed how preheating with RF power could enable a molder to turn out articles efficiently from tougher molding compounds than have been in commercial production before because the entire preform could be heat-plasticized uniformly to flowing temperature without starting precure in spots before the mold closed. Such processes indicate more efficient heat application to the cooking of resins and other poor heat conductors, and the practical elimination of hot spots with consequent improvement in color and uniformity of product. Some work has been done by the writer in the cooking of alkyd resins and in making ester gums and polymerizing rosin. To

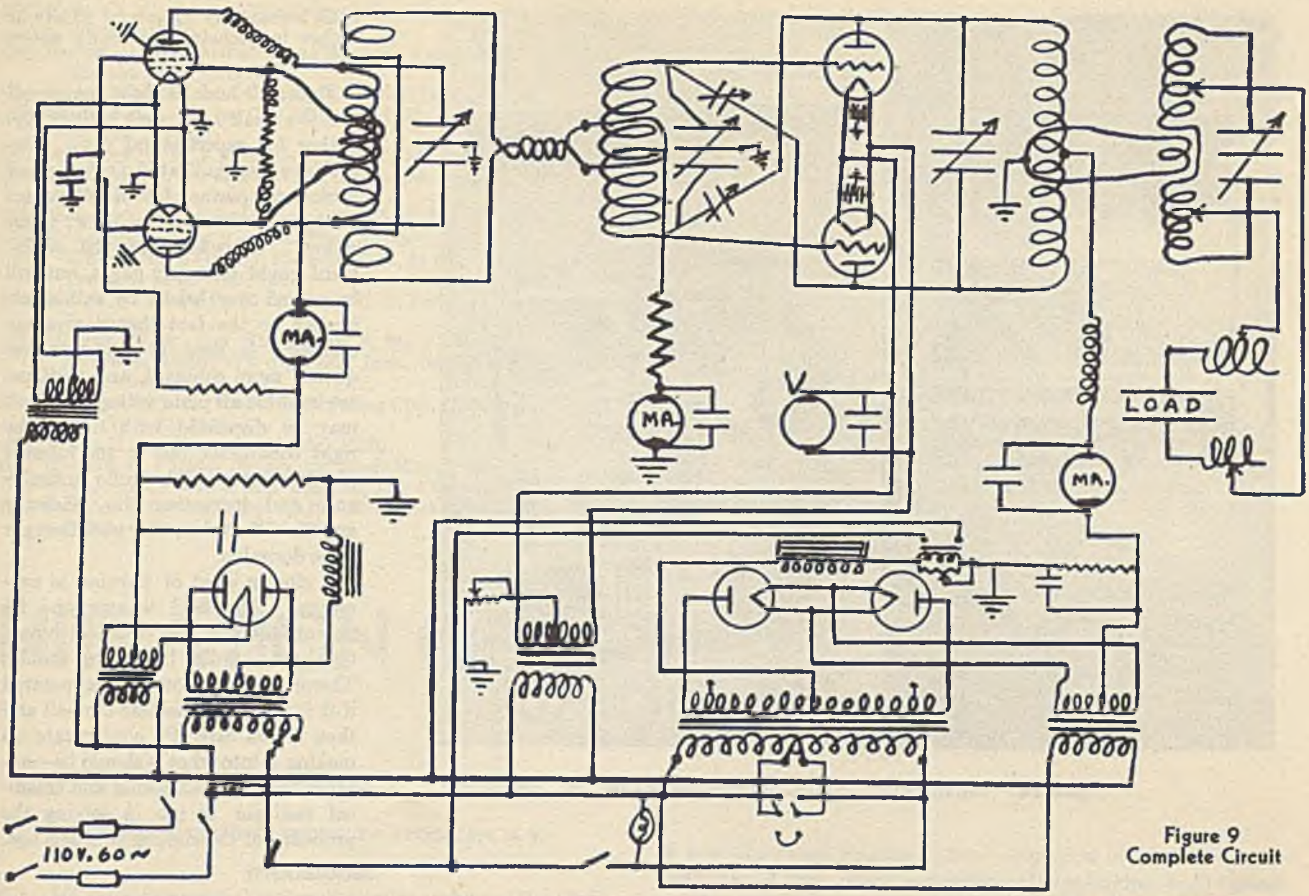


Figure 9
Complete Circuit

show the simplicity of equipment which can be used, aside from the high-frequency generator, some of this work was done in paper cups and the electrodes were placed parallel inside these containers (Figure 7*a*). Another setup for cooking resins and heating organic compounds is shown in Figure 7*b*. The electrodes are on the outside of glass tubes containing the load.

These applications illustrate two methods of heating which have been discussed by different workers. That is, should the electrodes be in contact with the load (Figure 7*a*) and a relatively low voltage be utilized, or should a high-voltage field be set up as in *b* and the electrodes be maintained at a slight distance from the load? Here again the best method for each specific job must be worked out on the basis of desired results at best efficiencies.

Wood or coal can be destructively distilled with RF power, and there are possibilities for radical developments in these industries. For instance, the products obtained by this type of heating are not necessarily the same as those obtained where local overheating is bound to occur. Another radical departure would be to send the powdered coal or wood, in the complete absence of oxygen, through a high-voltage electrostatic field and thus bring about the destructive distillation of the particles almost instantly by virtue of the heat generated within each particle and without heating the surrounding gas appreciably.

ADVANTAGES AND DISADVANTAGES

Some advantages and disadvantages of radio power are listed below, but are by no means complete:

ADVANTAGES. Temperatures are raised uniformly throughout mass.

Power input, or rate of heating, can be varied at will without regard for platen temperatures, etc.

Temperature of a reactive mixture can be more closely controlled.

Redistribution of moisture and casehardening in heating wood are lessened.

Equipment is less expensive in many cases.

Color possibilities are better as a result of less local overheating.

Reaction temperatures or "apparent" reaction temperatures may be lower.

The heating-up-to-temperature cycle is shorter.

Efficiency is increased on some jobs such as molding heavy sections.

Internal stresses in moldings are fewer.

Better designs of some equipment possible.

DISADVANTAGES. Possibilities and methods of application are not well understood.

Difficulties are sometimes experienced in getting the load in resonance with the generator.

Present cost of generating equipment is high.

Wider use of the process is the cure for disadvantages, and sometimes the last mentioned is overcome because of lower equipment costs at other stages in the process or more efficient utilization of power. A general idea of equipment costs may be had from Figure 8. They are based on actual RF power expected to reach the load, and should be subject to drastic reductions after the war when radio frequency power comes into more general use industrially.

POWER REQUIREMENTS

A general idea of the power required for a particular application may be obtained by calculating the B.t.u. per hour needed and then converting this into kilowatts. Manufacturers of equipment are currently

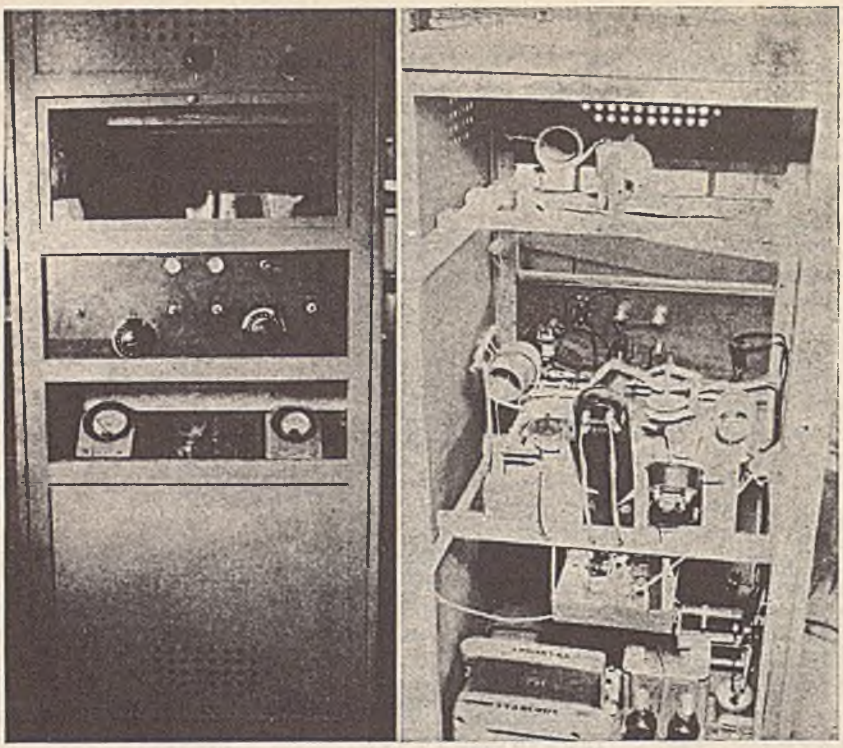


Figure 10. Experimental 1-Kw. Radio Frequency Unit

rating their equipment by output in B.t.u. per hour. The following simple equation can be useful on preliminary calculations:

$$\text{kw. needed} = \frac{\text{wt. (lb.)} \times \text{sp. heat} \times \text{temp. rise } (^\circ\text{F.})}{3413 \times \text{time (hr.)}}$$

This assumes that kilowatts are in RF power available for work. To calculate approximately the size of power line needed, it is necessary to double this figure. Over-all efficiencies in RF installations can well vary from 35 to 75%, depending on the job and conditions surrounding it, but are usually calculated at about 50% until better data are available.

Such calculations are based on raising an entire mass from starting temperature to another temperature which is considered necessary; the selective heating effect of RF power is ignored, as well as the possibility that the reaction may be completed at a lower "apparent" temperature than is considered feasible. Such possibilities are indicated in the gluing charts (Figure 6) and in other work. Other important factors are also ignored in these calculations because no data are available to calculate their effects. One of them is the dielectric constant of the material being treated. If it is such as to cause the RF to be "absorbed" readily, it appears to heat more efficiently. Another factor of importance is the frequency of the RF power best suited to the job; this point has had little fundamental study to date except as it is based on mechanical influences.

In general the choice of operating frequency appears to resolve in the following factors (at lower frequencies, 1 to 5 MC.):

1. Higher voltages required for penetrating a given load
2. More danger of flashover
3. More bulky tuning equipment
4. Easier tuning to the load
5. Less radiation losses
6. More efficient tubes available, especially at high power
7. Certain types of reactions are carried out efficiently but little is generally known of effects at higher frequencies, especially above 500 MC.

Figures 9 and 10 show the circuit and the small 1-kw. unit built by the author for experimental work. Experience has indicated that a wiser choice of power for development work is at least 5 to 7 kw. input power. Discussion of the equipment could fill many pages, but will be passed over briefly by calling attention to the fact that a separate oscillator is used to maintain frequency more constant, and rectifiers are used for all plate voltages. Both may be dispensed with under the right conditions, but in the interest of reducing possible radio interference and increasing the efficiency and life of the tubes, they were thought to be desirable.

A closing word of warning is necessary. The field is new and its potentialities in the chemical industry have hardly begun to unfold. Therefore let us not be disappointed if it is not an immediate cure-all and then let us carefully concentrate on making it into what it should be—another tool for the chemist and chemical engineer to use in solving the problems of the coming chemical age.

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NITRATION OF TOLUENE » » Continuous Partial Pressure Process Using Nitric Acid Alone

Donald F. Othmer and Hugo L. Kleinhans, Jr.

POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, N. Y.

▶ ▶ ▶ The partial pressure process is applied to nitration of toluene for the production of mononitrotoluene in a distillation unit using nitric acid alone. Reaction velocities, optimum conditions of concentrations of nitric acid, and ratio of toluene to nitric acid are considered. The success of this operation suggests the possibility of continuous nitration of toluene to mononitrotoluene by this process and the subsequent separation of the nitrotoluene in a pure form. Some of the advantages are discussed, such as the higher yields from toluene, the lower heat costs, the possibility of lower equipment costs, etc., of a continuous process, without the use of sulfuric acid.

IN THE usual commercial process of nitrating toluene (*2*), sulfuric acid mixed with nitric acid is used to unite with the water formed. The sulfuric acid takes up only a limited amount of water and various oxides of nitrogen give side reactions. Thus, the mixed acid cannot be used indefinitely. The spent acids are recovered by distillation.

A continuous method for nitrating benzene (*7*) and also toluene with nitric acid alone has been suggested (*4, 7, 8*). It depends on the removal of water formed by partial pressure distillation, as developed by Kokatnur (*3*). The reaction and water removal are carried out simultaneously in a fractionating apparatus. The water-toluene azeotropic mixture boils at 84.1° C.; thus, the water may be removed as formed, and nitric acid alone may be used since it is not being diluted. Only the mono-nitration of toluene is considered.

Most of the experiments reported were simple reactions of nitric acid and toluene under total reflux in an agitated flask. Runs in a fractionating column, condenser, and decanter were also made as a first step toward a continuous process.

NITRATION TECHNIQUE

In the reaction method used, an aqueous or acid layer and an organic or toluene layer are present. The amount of nitric acid in each layer was determined by titration.

Treatment of Crude Product. The product of nitration was washed with two equal volumes of water, with an equal volume of a 5% solution of sodium bicarbonate, and with two more equal volumes of water. The use of 1 liter of water and 250 cc. of sodium bicarbonate solution might be expected to dissolve and remove about 0.6 gram of mononitrotoluenes. This would approximate 0.3% of the organic layer.

Vacuum Distillation. The possible presence of other nitro compounds caused the rejection of analytical methods dependent on the reduction of the nitro group; the mononitrotoluenes were determined by vacuum distillation. Unless otherwise specified, "nitrotoluene" refers to the mono compound. A column might have been employed; but because of the wide divergence of the boiling points of nitrotoluene and toluene, it was felt that the error, due to incomplete drainage, would be larger than the error introduced by simple distillation.

The toluene was distilled off at atmospheric pressure to about 110° C. where the temperature rose abruptly. A water pump was then connected, and the pressure (about 20 mm.) was determined by a manometer and barometer. The receiver was cooled with running water, and an oil bath was used for heating during vacuum distillation. After the residual toluene had come over under vacuum, the receiving flask was changed. The toluene actually distilled at a much lower temperature, but the subsequent rise was so rapid that the thermometer usually rose to about 90° C. The first drop of nitrotoluene appeared at about 95°, and the distillation was complete when the temperature had risen to about 120° C. and then dropped suddenly. A deep red residue remained in the flask in all cases.

As a blank test, pure nitrotoluene was mixed with pure toluene to give mixtures containing 5, 7.33, and 10% nitrotoluene. The nitrotoluene was a mixture of isomers in the proportion 56% *o*-, 4% *m*-, and 40% *p*-nitrotoluene, which is approximately the ratio formed according to the results of various investigators (*1, 11*). The mixtures were vacuum-distilled, and the percentage of nitrotoluene shown was always somewhat lower than the true

value. The results were plotted as specific gravity against percentage nitrotoluene in Figure 1. Both the specific gravity of the known solutions and the percentage as determined by vacuum distillation were found to be linear relations with the composition.

The percentages from experimental runs (to be described) were plotted against specific gravity. The corrected values were determined from the upper line in Figure 2; its position was determined by adding the difference between the two lines of Figure 1.

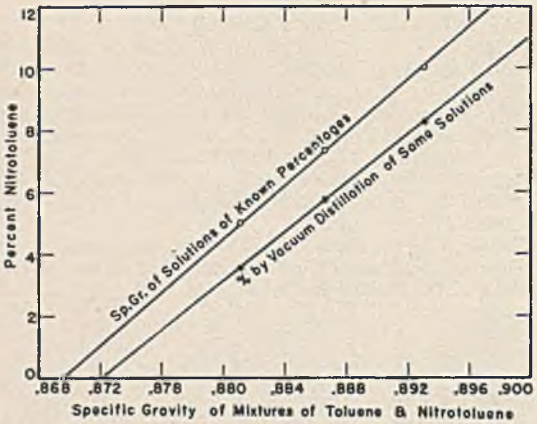

Figure 1. Results of Vacuum Distillation of Mixtures

Difference between ordinates of two lines represents a correction in analysis of mixtures by vacuum distillation technique used.

The specific gravity of toluene recovered from the blank runs during the atmospheric portion of the distillation was that of pure toluene. Thus, the error in not using a fractionating column for the atmospheric distillations was negligible.

Nitrating Apparatus. Batch runs were made in a 2-liter flask fitted with an agitator, dropping funnel, and reflux condenser. Heat was supplied by an oil bath. A stainless steel propeller-agitator was provided, with a shaft 9 inches long and a bearing for the shaft $5^{1}/_{2}$ inches long. The bearing and shaft were machined to close tolerances to prevent leakage. A condenser, 24 inches long with nine bulbs, was used and a thermometer was hung in the flask through the condenser. Glass connections were provided in all apparatus.

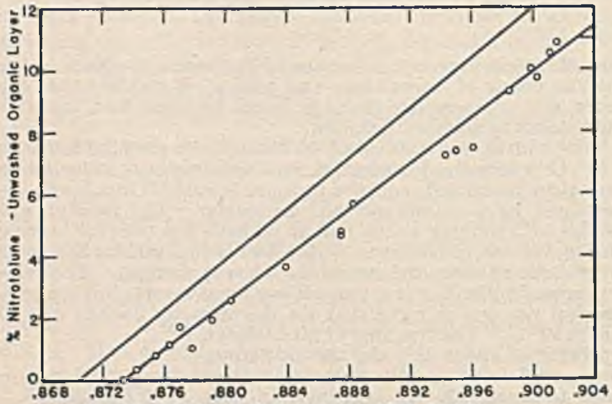

Figure 2. Relation between Specific Gravity and Percentage Nitrotoluene Determined by Vacuum Distillation (*lower curve*) and True Value of Percentage Nitrotoluene after Correction Determined from Figure 1 (*upper curve*)

Two different distilling columns were used for those runs where rectification was desired. One was 1 inch in diameter and 2 feet long, and the other was 2 inches in diameter and 5 feet long. Both were packed with $^{1}/_{4}$-inch Raschig rings. A Dean and Stark tube beneath the condenser served as decanter. It had a drain cock and was fitted with a thermometer.

TOTAL REFLUX WITHOUT COLUMN

The mixture of acid and toluene was heated to boiling. The agitator was started after boiling had begun. Boiling was continued a definite number of minutes and then the run was stopped; only one sample, the product, was taken for each run.

At the start, finish, and usually during the runs, red fumes were evident and were normally confined to the flask. In nearly all of the runs, white fumes escaped from the condenser. Their loss was not considered serious since it seemed to be small. However, attempts to make nitric acid balances showed that there had been a loss of acid in some cases; these fumes may have been partly responsible. Condensation was visible only in the lower three bulbs of the nine-bulb condenser. In one run 250 ml. of pure toluene were placed in the apparatus, and 25 ml. of 67% nitric acid were added. The mixture was gradually warmed by a water bath. Nitrogen oxides became apparent at 43° C. Appreciable oxidation must, therefore, take place at or below this temperature. This run was repeated with 25 ml. of distilled water. The temperature rose to 91° C. before oxides appeared. The product was washed with water and sodium bicarbonate solution and again with water. It was tested for nitrotoluene by reduction with titanous chloride; no signs of nitration were found. This does not agree with the fact that dilute nitric acid is a stronger oxidizing agent than stronger acid (*10*). The results of the runs show less loss of nitric acid when the weaker acids are used.

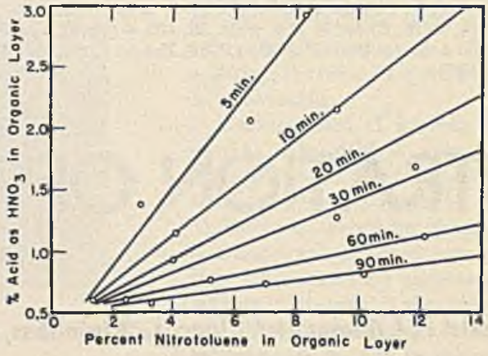

Figure 3. Relation of Nitric Acid to Nitrotoluene in Final Organic Layer for Various Time Intervals of Nitration

BATCH AND CONTINUOUS RUNS IN A COLUMN

Batch runs utilized total reflux; in the continuous runs the aqueous layer was removed in a Dean and Stark tube.

Frequently at the end of a run the toluene layer overhead was darker in color than the toluene layer in the pot. The water layer overhead was often red. A red substance, probably formed by side reactions, could be seen dissolving in the water layer of the Dean and Stark tube as the drops descended from the condenser above the tube. Red acid fumes sometimes escaped through the column and reflux condenser; they obscured the estimation on the column efficiency, which was based on the amount of acid that appeared overhead. The loss of these oxides may be desirable in carrying out this process. They have no place in the desired reactions but do enter into the side reactions.

Several runs were made to determine if all the acid could be kept from the top of the larger column. A 250-ml. portion of toluene was placed in the pot with 34.4 grams of 66.91% nitric acid and 250 ml. of distilled water. The water collected in the Dean and Stark tube was withdrawn continuously. The first 2.8 grams were neutral. After an hour there were about 25 ml. of aqueous layer in the pot and the water overhead showed 0.65% acid calculated as nitric. After $1^{1}/_{2}$ hours no more water was visible in the pot, and in 3 minutes the type of boiling changed.

Table I. Summary of Results

Run No.	HNO$_3$ Used		Toluene Used, Grams	Time, Min.	Organic Layer				Acid Layer in Pot at End of Run		% Mononitrotoluene		"Available" HNO$_3$, %	% Loss of HNO$_3$	% Loss of Total Material Charged[f]
	Grams	%[a]			Grams	Sp. gr., $d_{15.5}^{15.5}$ Before washing	After washing	% HNO$_3$ before washing[b]	Grams	% HNO$_3$[c]	Vacuum distn.[d]	Corrected[e]			
1	156.4	42.77	213.4	30	...	0.8763	0.8741[g]	..	98.8	41.84	0.34	1.54	4.72	34.7	...
2	156.4	42.77	214.4	60	212.7	0.8778	0.8754[g]	..	143.6	43.42	0.81	2.02	4.72	2.1	3.9
3	156.4	42.77	214.0	90	213.0	0.8796	0.8770[g]	..	145.0	42.53	1.74	3.05	4.72	1.4	3.3
4	100.0	50.00	214.4	30	217.5	0.8913	0.8875[g]	..	88.6	47.67	4.69	6.28	10.25	−1.7	2.6
5	100.0	50.00	214.4	60	217.9	0.8912	0.8875[g]	..	89.6	46.61	4.79	6.39	10.25	0.1	2.2
6	100.0	50.00	215.1	90	220.9	0.8971	0.8928[g]	0.75	95.7	42.53	5.32	6.97	10.25	1.1	−0.5
7	70.1	67.30	214.8	30	221.8	0.9008	0.8961[g]	1.28	57.0	48.53	7.49	9.30	19.31	15.2	2.1
8	70.1	67.30	214.0	60	219.9	0.9046	0.8995[g]	1.13	54.9	46.79	10.06	12.12	19.31	14.3	3.3
9	70.1	67.30	213.8	90	217.2	0.8947	0.8906[g]	0.82	52.6	40.47	8.25	10.15	19.31	48.6	5.0
10	37.0	75.36	214.0	30	223.3	0.9054	0.9003[g]	1.69	22.3	50.78	9.75	11.80	13.18	2.4	2.2
11	37.0	75.36	214.9	30	223.1	0.9061	0.9009[g]	..	23.2	50.90	6.72	8.50	13.18	16.0	2.2
12	37.0	75.36	214.6	60	220.3	0.8986	0.8943	..	22.9	47.73	7.23	9.03	13.18	20.4	3.3
13	37.0	75.36	214.8	90	221.4	0.8998	0.8950	..	21.8	48.26	7.39	9.20	13.18	22.1	3.4
14	32.2	87.19	215.0	30	222.9	0.9027	0.8993	..	15.6	51.34	7.83	10.20	15.28	23.1	3.5
15	32.2	87.19	215.0	60	223.5	0.9043	0.8984	..	16.5	47.38	9.28	11.78	15.28	20.4	2.9
16	32.2	87.19	214.8	90	221.0	0.9061	0.9011	..	15.9	45.70	10.53	12.63	15.28	21.0	4.1
17	62.8	42.51	215.5	45	214.0	0.8743	0.8733	..	58.3	41.79	0.00	1.20	1.73	0.2	2.2
18	50.0	52.50	214.8	30	214.4	0.8794	0.8778	..	45.6	47.13	1.04	2.30	6.38	3.4	1.8
19	49.2	49.87	215.1	60	214.9	0.8782	0.8763	0.62	43.4	45.53	1.16	2.40	5.23	4.4	2.3
20	49.2	49.87	215.5	90	215.0	0.8818	0.8791	0.58	43.9	43.28	1.96	3.29	5.23	4.2	2.2
21	38.5	64.29	214.9	30	218.0	0.8882	0.8865[g]	..	28.9	48.10	3.18	4.60	9.45	17.1	2.6
22	38.5	64.29	214.5	60	218.1	0.8874	0.8839	0.77	30.8	49.28	3.66	5.14	9.45	11.1	1.6
23	38.5	64.29	214.6	90	216.9	0.8928	0.8883	..	26.8	45.59	5.68	7.85	9.45	12.4	3.7
24	49.7	51.32	215.0	20	215.4	0.8788	0.8755	..	44.8	47.11	...	2.07[g]	5.75	3.5	1.7
25	49.7	51.32	215.8	10	217.0	0.8769	0.8736	0.62	46.9	47.69	...	1.31[g]	5.75	1.9	0.6
26	39.8	65.10	215.5	20	218.0	0.8842	0.8802	0.93	35.3	50.78	...	3.96[g]	10.09	7.6	0.8
27	39.8	65.10	215.3	10	221.5	0.8860	0.8805	1.15	34.6	50.82	...	4.08[g]	10.09	6.3	−0.4
28	39.8	65.10	215.9	5	218.8	0.8831	0.8776	1.39	34.5	53.13	...	2.91[g]	10.09	6.2	0.9
29	32.8	76.55	215.6	5	221.1	0.8938	0.8864	2.07	21.3	54.41	...	6.45[g]	12.07	9.5	2.4
30	28.7	87.57	216.3	5	225.7	0.9010	0.8909	2.93	15.0	60.45	...	8.26[g]	13.72	3.5	1.8
31	28.5	87.57	214.6	10	221.1	0.9015	0.8934	2.16	14.0	55.06	...	9.27[g]	13.63	12.2	3.3
33	28.5	87.57	214.8	30	223.5	0.9018	0.8953	2.02	14.5	52.43	...	10.05[g]	13.63	10.1	2.2
33	32.8	76.53	214.6	10	221.8	0.8943	0.8864	2.33	21.1	53.21	...	6.47[g]	12.06	8.4	1.8
34	28.4	91.85	216.8	60	225.3	0.9037	0.8981	..	15.5	48.36	...	11.19[g]	14.77	17.5	1.8

[a] (HNO_3 × 100)/(HNO_3 + H_2O). [b] (HNO_3 × 100)/organic layer. [c] (HNO_3 × 100)/aqueous layer.
[d] In unwashed organic layer. [e] In washed organic layer. [f] From material balance. [g] Data derived from graphs.

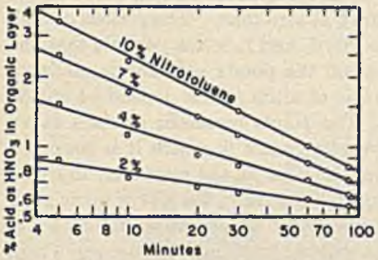

Figure 4. Logarithmic Cross Plot of Figure 3

The source of heat was removed. After $1^1/_4$ hour the reaction in the pot had not stopped. Bubbles were rising from the mixture, and there were copious fumes in the pot. No evidence of nitrogen oxides had appeared during the run. The liquid had been clear yellow throughout but now turned orange-red. The organic layer contained 6.58% nitrotoluene; and the total amount of nitric acid removed through the Dean and Stark tube was 0.18 gram.

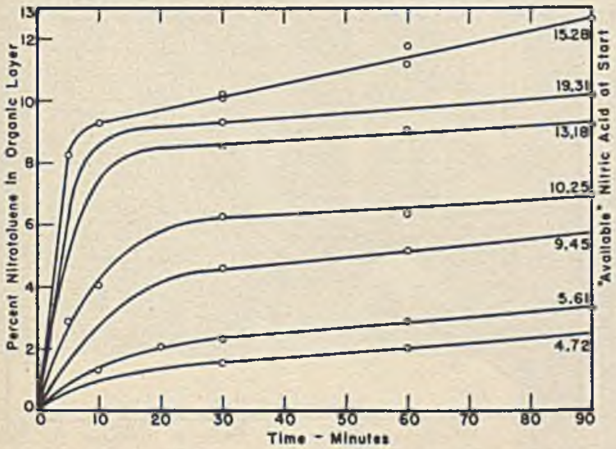

Figure 5. Nitrotoluene Formation as a Function of Reaction Time for Different Concentrations of "Available" Nitric Acid at Start of Nitration

This run shows that it is possible to retain all the acid in this process by a column of sufficient length. The figures for the strength of acid at the top of the column are not consistent; therefore the necessary height of the column is not known exactly. A sufficient quantity of water in the column is apparently necessary to prevent the acid from going overhead. This would adjust itself in continuous operation, and the amount of water withdrawn would be balanced against that formed in the reaction. In other column runs the concentration of the nitrotoluene in the organic layer was as high as 50%, an indication that a substantial part of the toluene may be readily nitrated continuously. The subsequent separation of this product would be done by distillation.

After conditions in the column are brought to a steady state, acid will be fed to the column in a continuous operation at a point where the acid strength corresponds. Water is then removed at the rate of addition of water in the acid, plus that formed by the reaction.

AFTER-REACTION AND PRODUCT FORMED

Reaction after Completion of Runs. In practically all of the experiments, action in the pot continued after heating had stopped and there was a large increase in the amount of red fumes. Bubbles continued to rise long after boiling had ceased, and the temperature dropped considerably. Even the runs in which there had been no aqueous layer in the pot showed this action; there was always some aqueous material in the column which drained into the pot when the heat source was removed. The extent of this action and its effect on the results were not explained. In continuous operation the nitric acid balance and probably the yield of product would be improved by the fact that this action would be eliminated.

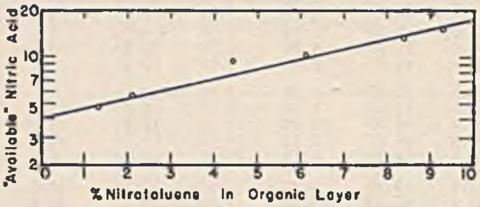

Figure 6. Nitrotoluene Formed during High Reaction Rate as a Function of Available Nitric Acid at Start of Nitration

Product. The organic layer fumed when brought into contact with the air and was always acid; 20 ml. were washed separately with water and sodium bicarbonate solution. In each case there was no change in volume. Since the specific gravity could be determined before and after washing, it was then possible to convert the percentage nitrotoluenes found to whichever basis was desirable.

RATE OF REACTION

The results (Table I) showed two basically different rates of nitration—a so-called low rate and high rate, since there was always an abrupt breaking point in the curve of nitrotoluene formed against time of reaction.

Figure 3 is a plot of nitric acid against nitrotoluene in the residual organic layer, for those runs where the percentage of nitric acid was determined before the organic layer was washed. The graph shows that runs containing most nitrotoluene, formed in a given length of time, also have an organic layer with a higher percentage of nitric acid. Figure 4 is a logarithmic plot of the percentage nitric acid in the organic layer against time, taken from Figure 3; the other parameter is the percentage of nitrotoluene in this layer. Figure 5 shows percentage nitrotoluene in the organic layer related to the time of reaction for different runs having constant amounts of "available" nitric acid at the start.

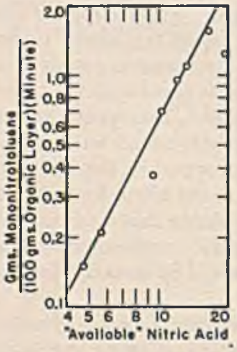

Figure 7. Initial Rate of Nitrotoluene Formation in High Reaction Rate Period as Function of Available Nitric Acid in Charge

A relation was sought between the nitric acid available for nitration and the percentage of nitrotoluene formed to the point of inception of the slow rate. Acid below about 42% concentration does not form nitrotoluene at the high reaction rate. This percentage was subtracted from the concentration of the original nitric acid and the difference multiplied by the grams of acid used. The percentage of nitrotoluene formed during the high rate of reaction was determined from Figure 5.

The data were first plotted, and the graph approached a straight line on semilog paper: Trial showed that, by reducing the amount subtracted to 39.75%, a straight line was obtained (Figure 6). This plot is a convenient means for determining the amount of nitrotoluene that can be formed when a definite amount of acid of a certain strength is used.

Whether 39.75% is the limiting value for the concentration of nitric acid that will nitrate under the conditions of these experiments is not indicated directly. That it is not far from such a limiting value for high reaction rates is shown by Figure 6, together with a consideration of the concentration of acid used. The amount of nitric acid available for the reaction determined by using 39.75% as the limiting value does not equal zero for zero concentration of nitrotoluene on Figure 6. Available nitric acid is thus used to denote the product of the grams of aqueous acid charged, M, multiplied by the difference of the concentration in percentage nitric acid used, C, and 39.75%:

$$\text{Available acid} = M\ (C - 39.75)$$

In every case the same amount of toluene (250 cc.) was used; otherwise it would be necessary to reduce this to available acid per unit of toluene.

The same amounts and concentrations of nitric acid were used to determine all points on any of the curves of Figure 5 during the time corresponding to the low rate of reaction. Those points on the curves for the high rate were obtained with the same amount of available acid. Determinations of the point on the high reaction rate portions of the curves were difficult. This can hardly be considered a reflection on the validity of using the "available" relation, since the agreement between points determined with all conditions identical was also poor. Figure 5 suggests that the periods of low rate may be due to continued nitration in the organic phase after the concentration in the aqueous phase has fallen to a point where nitration is no longer possible. That the rate of nitration in the organic phase was slower than in the inorganic one was inferred from the fact that the same is true in nitrating with mixed acid (*5*).

No explanation is offered for the fact that the uppermost curve on Figure 5 is different from the others during the low rate period. The points at 30 and 60 minutes were rechecked experimentally to minimize the probability of experimental error.

Figure 7 shows the rate of nitrotoluene formation, based on the slopes of the curves of Figure 5 at zero time. The periods of high reaction rate are more important, and it seems possible that the rate may be extended beyond the points actually determined.

Figure 8 shows that the loss of nitric acid is dependent on the strength of original acid. The points represent samples taken during the high range of reaction rates in which it is proposed to operate. The oxidation observed at the start and finish of the runs is probably an important factor in the loss of nitric acid. In a continuous operation the loss of nitric acid would probably be materially lower since this oxidation would not occur. There was much less evidence of oxidation during the runs. The formation of nitrogen oxides was taken as the criterion of oxidation.

The agitated still pot for the reaction, distilling column with appropriate feed inlets of toluene and nitric acid, condenser, and decanter with toluene reflux have been indicated as parts of a

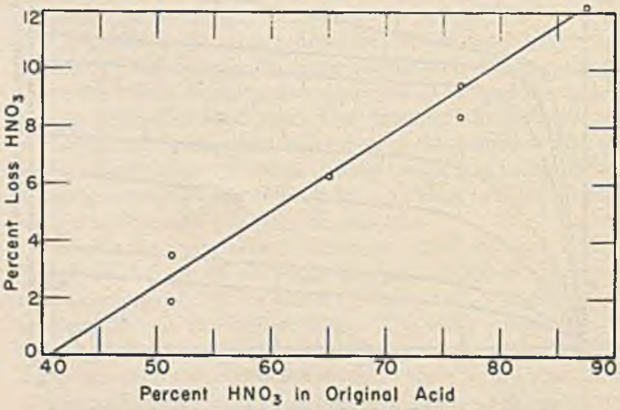

Figure 8. Loss of Nitric Acid as a Function of Percentage Nitric Acid in Original Charge

continuous process; in plant operation they would be constructed of suitable nickel-chromium steels or high-silicon iron. In addition, a continuous distilling column to separate the large excess of toluene (and residual nitric acid and water) from the nitrotoluene formed would be necessary; the complete flow sheet would be similar to that previously suggested for nitration of benzene (*9*).

CONCLUSIONS

Nitrotoluene may be made by the action on toluene of aqueous nitric acid alone, using the toluene itself as an entrainer to carry the water out of the reaction in a partial pressure distillation. The method of nitrating proposed can be operated as a continuous process. This type of operation will probably give lower costs and greater capacity and ease of operation than batch operation. Materials of plant construction will be more expensive than in the standard method using sulfuric acid.

Too concentrated nitric acid is to be avoided; there is, however, a limiting strength of acid below which no nitration will occur under prevailing conditions. The rate is controlled by the amount of acid above the limiting concentration below which nitration does not proceed. It is high enough so that a comparatively small unit operating under optimum conditions should give a satisfactory volume of production. The use of less concentrated nitric acid to avoid side reaction is supported by the deductions of Michael and Carlson (*6*). They state that water is basic in comparison with nitric acid and that the acid loses some of its negative chemical energy in aqueous solution. This, they believe, protects the nitro derivative to some extent. There are two opposing factors in the choice of nitric acid concentration to be used. Below about 40% HNO_3 no reaction will take place; an acid that is too concentrated will cause excessive loss of both toluene and nitric acid. A concentration between 40 and 50% appears optimum.

To avoid losses and hold the size of the apparatus to a minimum, conditions of operation should be chosen to fall within the range of high reaction rate. An excess of toluene must be used to ensure the presence of a constant-boiling water-toluene mixture in the column.

The extensive plant necessary for recovering the spent acids from the mixed acid process would be eliminated since the desired concentration of the nitric acid is always maintained by the distillation operation. In commercial operation any lower oxides of nitrogen formed could be recovered in a standard manner and added directly to the fresh acid entering the system.

The process using nitric acid alone would avoid the cooling and heating of the charge which is necessary in the mixed acid process; the temperature would always be under control through the automatic balance of the heat quantities in the column.

No comparative heat balances have been made, but they might well favor the present method, since the concentration of sulfuric acid in the older process requires considerable thermal energy.

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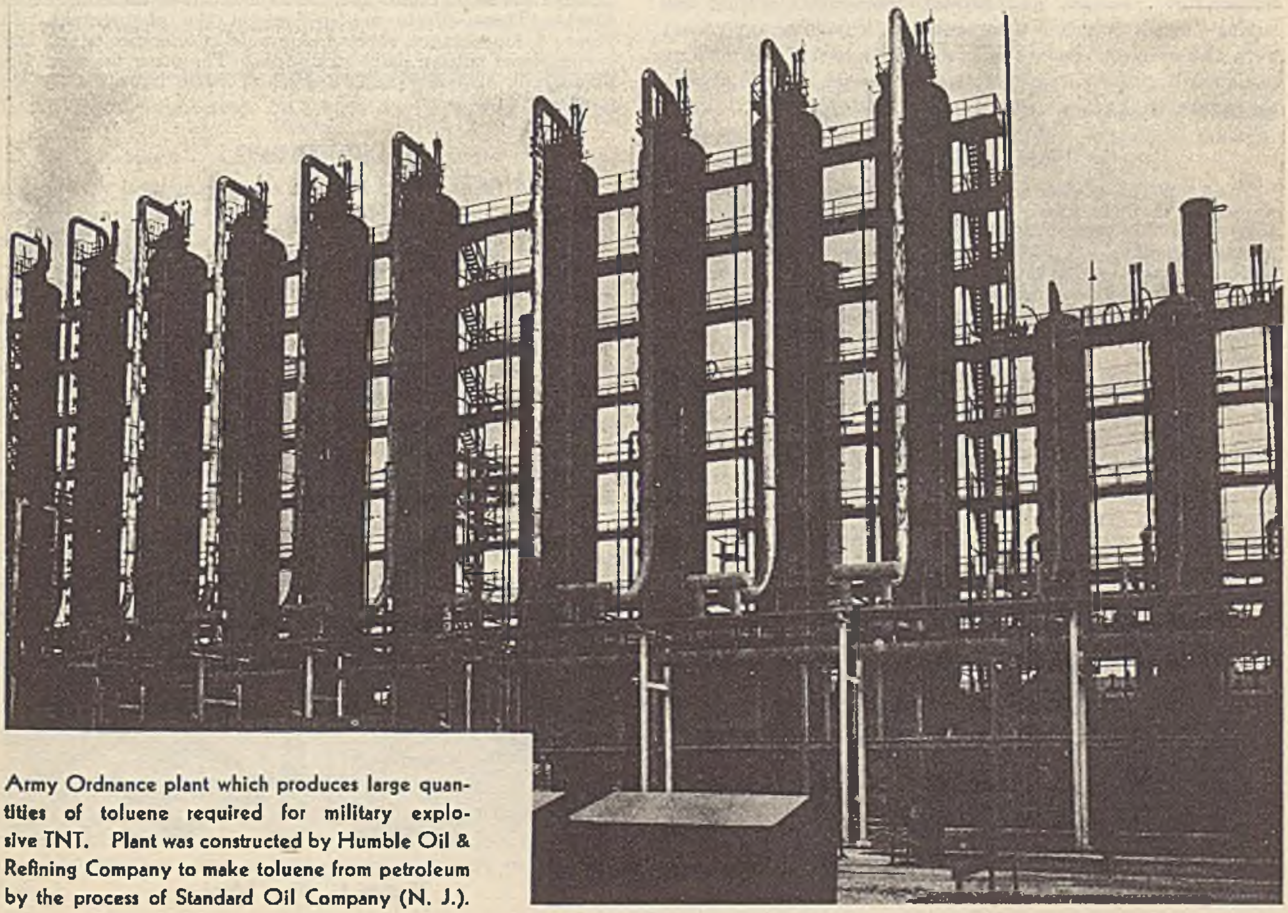
[End of Symposium]



Army Ordnance plant which produces large quantities of toluene required for military explosive TNT. Plant was constructed by Humble Oil & Refining Company to make toluene from petroleum by the process of Standard Oil Company (N. J.).

Factors in Molding
CELLULOSE DERIVATIVES

Strain in translucent cellulose acetate injection-molded or sheet-stock plastics appears related to plastics temperatures, pressures mold (or chase) temperatures, rates of filling mold (injection), and solvent content (sheet stock). Strain patterns as evidenced by placing the molded pieces between crossed Polaroid films have been photographed. High temperature and pressures produce pieces of minimum strain pattern, closest mold reproduction, and heaviest weight. Low rate of filling mold aids in forming bubble-free pieces. Side gating is more effective than corner gating in producing pieces relatively free of strain. Solvent content in block prior to baking, baking temperature, and cooling pressure are critical factors in achieving strain-free cellulose acetate sheet stock.

W. O. Bracken and F. E. Piech

HERCULES POWDER COMPANY, PARLIN, N. J.

ENGINEERING applications for cellulose derivative plastics are expanding for wartime uses. Changes in plastic formulations to meet these new requirements have necessitated modification of molding techniques for such materials.

As an approach to determining the effect of variations in molding, it was decided to study the varied strain patterns produced in heavy molded test pieces made under different molding conditions. It is widely believed that the properties of molded thermoplastics, especially with regard to water absorption and change of dimension in hot, humid climates, are largely dependent on the amount and nature of the strains present in the molded article. Strains produced in injection-molded transparent plastics based on cellulose acetate, through variation of molding temperature, pressure, and speed of filling the mold, were compared. Similar work has been reported by Delmonte and Dewar for light moldings (*2*). Strains produced in cellulose acetate sheet stock through variation in temperature, pressure, and solvent composition during the baking process (which is comparable to a molding procedure) were also studied. Such strains are easily seen if the molding is viewed by transmitted light through crossed Polaroid glasses, the sample being placed between the polarizing plates.

MATERIALS AND EQUIPMENT

Three types of cellulose acetate plastic, varying in substitution, were used in these tests. A PM type (53% combined acetic acid) and a WH type (57% combined acetic acid) were used for injection molding. A PM and an FM type (56.0% combined acetic acid) were used in the sheeter process. Basic formulations, as given in Table I, were made.

The injection molding powders were prepared by the solvent process and dried to a volatile content of about 0.25% before molding (*3*).

Sheet stock was made by duplicating, upon small equipment, the usual operations in the "celluloid"-type process—that is, preparing the paste, rolling it into slabs of controlled solvent content, baking the slabs in a chase until fused, and then cooling under pressure, slicing into sheets, curing to a low solvent content, and polishing between padded, heated planishing plates (*1*).

The equipment used for injection molding (*4*) included a 4-ounce Reed Prentice machine (10-A-4) and two molds. The injection machine had a 2-inch-diameter ram which developed pressure up to 19,000 pounds per square inch. The nozzle orifice was $^5/_{32}$ inch in diameter. The mold for the 5 × $^1/_2$ × $^1/_2$ inch bar contained a sprue orifice $2^9/_{16}$ inches long, tapering from $^9/_{32}$ to $^3/_{16}$ inch. The runner was $^3/_4$ inch long and $^1/_4$ inch deep. The gate size was $^3/_{16}$ inch wide × $^1/_8$ inch deep. The block mold had two 2 × 2 × $^1/_2$ inch cavities. One block was corner-gated to the full depth of the piece; the other cavity had a $^1/_{16}$-inch deep side gate extending across one wall (Figure 1). Both molds were cored. The complete shot weighed 94 grams. Plastic and mold temperatures were taken with a Cambridge pyrometer.

The sheeter equipment consisted of the following: a $4^1/_2$-gallon, chrome-plated, jacketed Baker-Perkins mixer; cored, chrome-plated 30-inch rolls; a 150-ton press (16 × 22 inch platens); and a sheeter or planer having a stationary knife and traveling table. Steam was the heating medium, and maximum temperature was 330° F. (150 pounds steam pressure).

A matched set of 6 × 6 inch Polaroid films to obtain polarized light was used for determining strain pattern in the transparent plastics. The molded blocks were examined qualitatively for stress distribution. These stresses are set up in the plastic during the sudden cooling under pressure of the material. Double refraction is induced in the plastic by such stresses. The light passing through the film (polarizer) between the light source and block is polarized and is in one plane of vibration. Because of double refraction it is divided in the plastic into two systems of transverse waves. The light passes from the block through the second film (analyzer) which shows the interference effects. These effects are evident in the photographs. In Figure 4, for instance, sheet *A* shows no interference effects and is considered substantially strain-free. The other pieces in the photograph exhibit various degrees of stress indicated by the shadings in the prints.

MOLDED BARS

Series *A* (bars 1–8) in Figure 2 shows structural variation in WH-type cellulose acetate plastic (57% combined acetic acid) caused by changes in plastic temperature, pressure, and rate of filling mold (Table II). Bar 1 (high temperature, high pressure, low rate) shows better strain pattern than does bar 8 (high temperature, high pressure, high rate). This indicates that a low rate of mold filling is desirable for heavy-section molding since sounder, less highly strained pieces are produced. Bars 5 and 7 show poor structural pattern resulting from insufficient temperature, regardless of variation in pressure or rate of fill. Bar 4 (high temperature, low pressure, low rate) shows a more diverse strain pattern than bar 1 and indicates that slightly too low a pressure for optimum strcuture was used. Bars 2, 3, and

Figure 1. Test Blocks

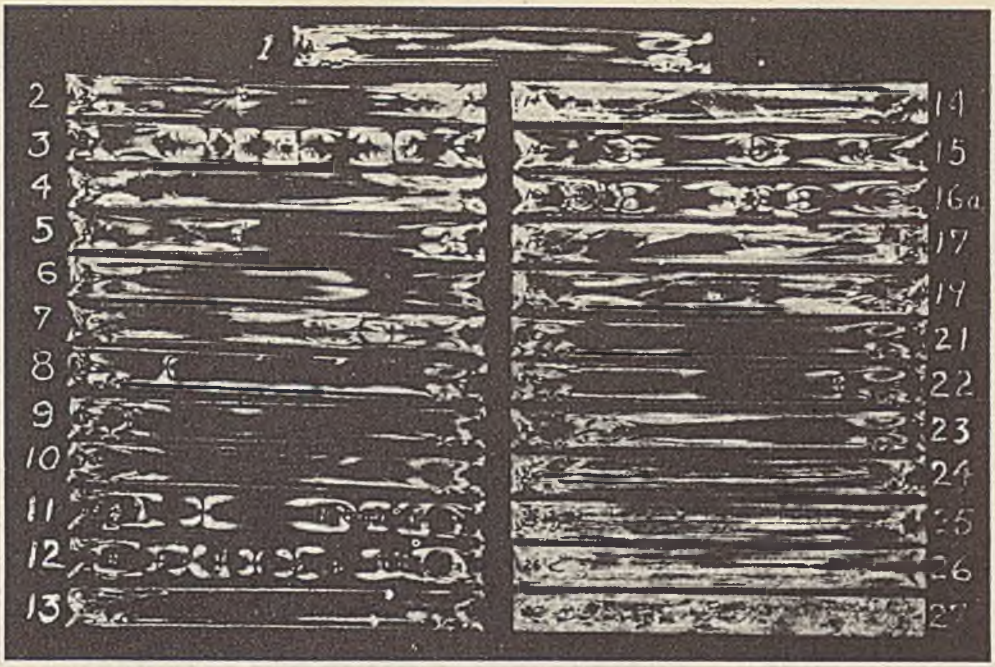


Figure 2. Test Bars in Polarized Light

6 show bubble formation caused by high rate of mold filling. The high degree of freedom from strain in bar 6 is attributed partly to the "working" of the plastic as it was rapidly forced into the mold. The presence of bubbles is a general result of high rate of flow in filling heavy pieces.

The variation in dimensions of the molded test pieces in this series with molding conditions is worthy of note. Table II indicates that it is necessary for the plastic to be molded under high temperature and high pressure in order to obtain best mold reproduction. This series alone shows mold shrinkages of 0.002 to 0.009 inch per inch, depending upon molding technique. The correlation between good strain pattern and close mold reproduction is significant. It indicates that high temperature, medium to high pressure, and low rate of fill are necessary for WH-type cellulose acetate plastics to produce the most sound, consistently reproducible pieces with optimum strain pattern.

TABLE I. FORMULATIONS OF CELLULOSE ACETATE PLASTICS TESTED

Component	Injection Molding, %		Sheet Stock, %	
	I	II	III	IV
Cellulose acetate FM-2	..	..	70	..
Cellulose acetate PM-3	68	..	..	70
Cellulose acetate WH-1	..	72	..	..
Diethyl phthalate	16	12	12	12
Dimethyl phthalate	16	12	10	10
Triphenyl phosphate	..	..	8	8
Dibutyl phthalate	..	4	..	..

Series *B* (bars 9–19) in Figure 2 shows agreement of strain pattern and dimensions with molding conditions for PM-type cellulose acetate plastics (53% combined acetic acid) similar to that found with WH-type plastics. Molding data for bars 9–19 are given in Table II. The point to be emphasized is that the PM-type cellulose acetate plastic will require, generally, higher pressures than the WH-type. This is due to the more volatile nature (higher plasticizer content) of these materials. Higher pressures upon the plastic after it has been slowly introduced into the mold prevent formation of bubbles.

Series *C* (bars 21–27) in Figure 2 shows progressive deterioration of structural strain pattern in WH-type cellulose acetate plastics with decrease in plastic temperature (Table II, bars 21–27). Bar 21 gives a desirable strain pattern in polarized light. As the temperature of the plastic decreases, mixed strain patterns appear (bar 24) until finally poor fusion and welding are evident in bars 26 and 27. The unaided eye would hardly be able to distinguish between samples molded under these varied conditions. Bar 21 had a high gloss and was free of "sink-marks". Absence of gloss was not apparent until bar 26 was formed.

The length of the molded bar decreased as the temperature of the plastic was lowered. A corresponding decrease in weight also took place. The maximum difference in weight between a piece showing good structure (bar 21) and one having the poorest (bar 27) amounted to more than 2%.

MOLDED BLOCKS

Figure 3 shows the effects of the molding variables listed above as well as the influence of mold temperature, cycle, and gating upon the structure of a 2 × 2 × $^1/_2$ inch, PM-type, cellulose acetate plastic block. Table III gives the molding data.

TABLE II. VARIATION IN MOLDING CONDITIONS FOR CELLULOSE ACETATE PLASTIC BARS

(Impact bar mold, 5.036 × 0.501 × 0.500 inch; cycle, 36–18–3 seconds)

Bar No.[a]	Temp., ° F. Head	Cylinder	Plastic	Pressure, Lb./Sq. In.	T.S.A. Timer, Sec.	Bar Size In.	Grams
			Series *A*				
II-1	400	380	360	19,000	$^1/_4$	5.024	..
II-2	370	350	330	19,000	5	5.010	..
II-3	400	380	360	10,000	5	5.002	..
II-4	400	380	360	10,000	$^1/_4$	5.002	..
II-5	370	350	330	10,000	$^1/_4$	5.014	..
II-6	370	350	330	10,000	5	4.992	..
II-7	370	350	330	19,000	$^1/_4$	5.010	..
II-8	400	380	360	19,000	5	5.025	..
			Series *B*				
I-9	410	390	370	19,000	$^1/_4$	5.018	..
I-10	410	390	370	19,000	5	5.018	..
I-11	410	390	370	10,000	$^1/_4$	4.997	..
I-12	410	390	370	10,000	5	4.995	..
I-13	380	390	340	19,000	$^1/_4$	5.017	..
I-14	380	390	340	19,000	5	5.012	..
I-15	380	390	340	10,000	$^1/_4$	4.998	..
I-16	380	390	340	10,000	5	4.993	..
I-17	350	330	310	19,000	$^1/_2$	5.008	..
I-19	350	330	310	19,000	5	5.018	..
			Series *C*				
II-21	410	390	370	19,000	$^1/_4$	5.017	25.366
II-22	..	..	Constant	19,000	$^1/_4$	5.023	25.300
II-23	..	..	decrease	19,000	$^1/_4$	5.018	25.244
II-24	..	..	in	19,000	$^1/_4$	5.013	25.120
II-25	..	..	temp.	19,000	$^1/_4$	5.010	25.004
II-26	..	..	to	19,000	$^1/_4$	4.988	24.831
II-27	..	..	290	19,000	$^1/_4$	4.984	24.829

[a] Roman numeral indicates formula in Table I.

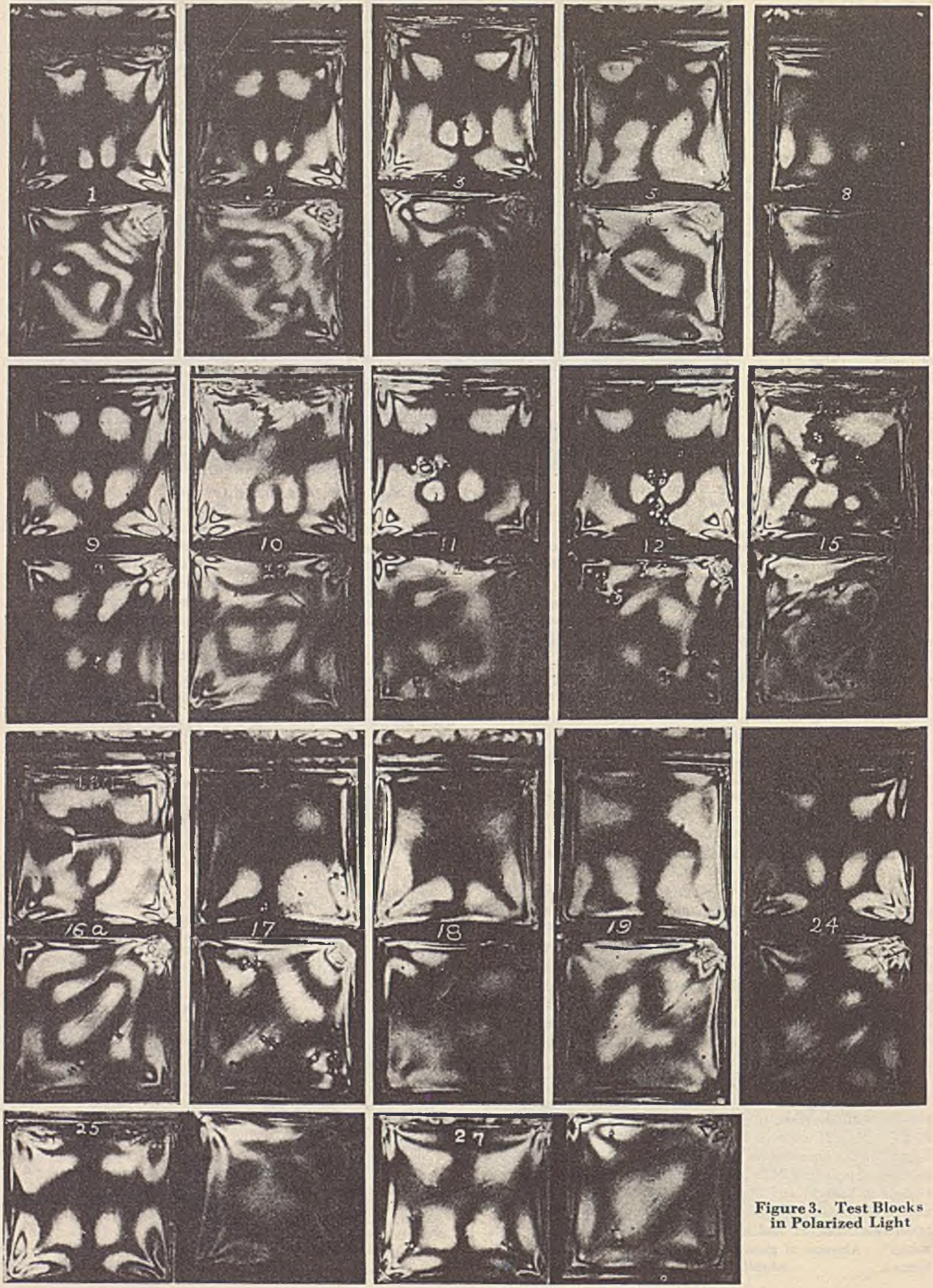


Figure 3. Test Blocks in Polarized Light

The type of gate has a pronounced effect upon strain patterns found in the finished molding. The corner-gated plastics show more general and more highly concentrated stress within the block. The side-gated pieces show, generally, an even dispersion of strain, usually to the edge of the piece. It is believed that the "surge" channel immediately before the gate is effective as a strain-release area for the plastic traveling from the nozzle to the cavity.

Blocks 1 through 8 were molded at slightly lower temperature than is desirable. This series indicates that low rate of fill, low injection pressure, and prolonged cooling in warm molds dissipate strain. Block 3 (cold mold, 60° F.) shows a greater concentration of stress at the gate than does block 1 (warm mold, 95° F.). Block 8 shows the favorable effects of a hot mold (210° F.). Such a mold temperature is not generally practical but was used in these tests to produce the trend obtained with increase in temperature. Block 5 (low temperature, low pressure, low rate of fill) points out the decrease of impressed strain produced by the latter two factors as compared with block 2 (high pressure and rate).

Blocks 9 through 19 were molded at normal molding temperature. Increase in average molding-cycle temperatures shows decrease of strain in molded pieces (blocks 18, 10, and 15). There are minimum pressures below which bubble formation occurs (blocks 11 and 12). Too high a mold temperature leads to bubble formation (blocks 17 and 18). Increased injection pressure shows increased stress pattern in cool molds (blocks 15 and 16*a*).

Blocks 24, 25, and 27 were molded at a temperature slightly above that necessary to obtain complete fusion. Such a condition with low injection pressure may be used with lower mold temperature to obtain structure equivalent to that obtained by normal injection and high mold temperature (compare block 27 with block 19). Blocks 24 and 25 indicate that high injection temperature and pressure, low rate of filling mold, and cool mold temperatures are effective in producing pieces free of severe stress concentrations.

Table III. Effect of Molding Variables on Test Blocks of Plastic I (2 × 2 × ½ Inch)

Block No.	Temperature, ° F. Nozzle	Cylinder	Plastic	Mold	Pressure, Lb./Sq. In.	T.S.A. Timer, Sec.	Cycle, Sec.
				Series *A*			
1	370	330	305	95	19,000	1/2	36-30-3
2	370	330	305	95	19,000	4	36-30-3
3	370	330	305	60	19,000	1/2	40-20-3
5	370	330	305	60	12,000	1/2	20-40-3
6	370	330	305	210	12,000	4	20-50-3
7	370	330	305	210	19,000	4	15-40-3
8	370	330	305	210	19,000	1/2	20-50-3
				Series *B*			
9	460	360	330	110	19,000	1/2	36-36-3
10	400	360	330	110	19,000	4	36-36-3
11	400	360	330	110	12,000	4	36-36-3
12	400	360	330	110	12,000	1/2	36-36-3
13	400	360	330	70	12,000	1/2	36-24-3
14	400	360	330	70	12,000	4	36-24-3
15	400	360	330	70	19,000	4	15-25-3
16*a*	400	360	330	70	19,000	1/4	36-30-3
				Series *C*			
17	400	360	330	210	19,000	1/4	36-18-3
18	400	360	330	210	19,000	4	15-35-3
19	400	360	330	210	12,000	4	20-35-3
24	430	400	360	80	19,000	1/2	30-30-3
25	430	400	360	110	19,000	1/2	36-18-3
27	430	400	360	110	12,000	4	36-18-3

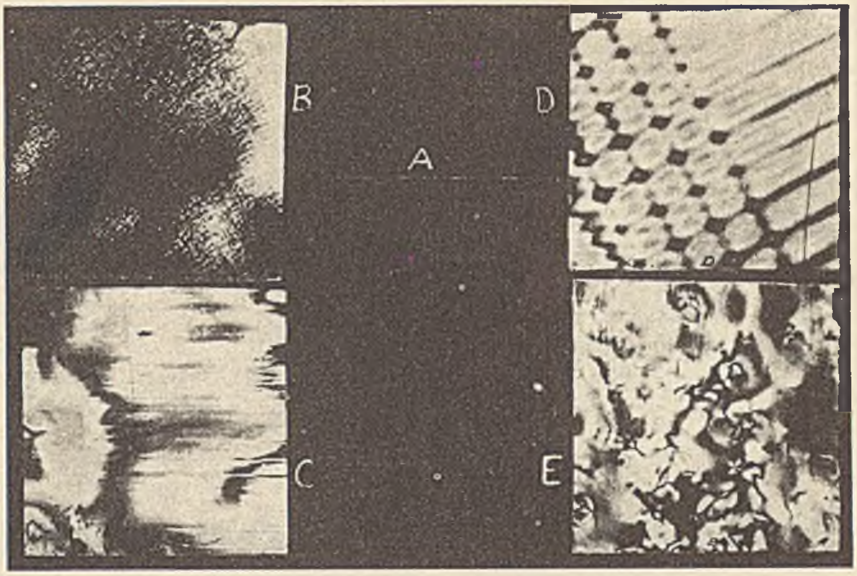


Figure 4. Sheet Stock in Polarized Light

Table IV. Experimental Conditions for Sheeting Manufacture

Cellulose Derivative	Viscosity, Sec.	Solvent in Rolled Slab, %	Baking Temp., ° F.	Pressure on Plastic, Lb./Sq. In. Baking	Cooling
Cellulose acetate PM-3 (53% acetic acid)	35	15	280	50-100	500-1000
Cellulose acetate FM-6 (56% acetic acid)	30	17	320	50-100	500-1000
Ethylcellulose G-type (45% ethoxyl)	100	20	320	50-100	600-1500

SHEET STOCK

Figure 4 shows the structure of five polished pieces of PM- and FM-type cellulose acetate sheet stock when seen between crossed Polaroids. To the unaided eye the sheets looked the same, but between Polaroids their wide differences in structure were evident. Sheet *A* has excellent structure, completely free of strain. This was a result of the following conditions: solvent content, 17%; baking temperature, 320° F.; baking time, 1 hour per inch thickness of block; baking pressure, 100 pounds per square inch; cooling pressure, 1000 pounds; cooling time, 1 hour per inch thickness.

Sheet *B* shows the granular effect of insufficient baking temperature and too low solvent content in the block. Sheet *C* shows sheeter lines (improperly honed blade) and impressed strain caused by incorrect polishing technique. Sheet *D* has stresses conforming to the outline of the block bed plate; these may be eliminated by increasing the block solvent content and baking temperature. Sheet *E* shows the so-called hammer effect which appears occasionally in sheet stock and has not been satisfactorily explained as yet.

Table IV gives the best experimental conditions yet found for producing cellulose acetate and ethylcellulose sheet stock free of the defects noted above.

SUMMARY

1. Injection temperatures of cellulose acetate plastics should be sufficiently high to obtain homogeneity in moldings. Lesser temperatures show poor fusion and a high degree of strain.

2. High-acetyl (57% combined acetic acid) cellulose acetate injection plastics require high temperature, high pressure, and

low rate of fill to produce heavy-sectioned pieces having minimum impressed strain.

3. High temperature and pressure are necessary to obtain closest mold reproduction. Mold shrinkage varied from 0.002 to 0.009 inch per inch and weights varied as much as 2% in $5 \times 1/2 \times 1/2$ inch bars by changing molding technique.
4. Low rate of filling mold aids in forming bubble-free pieces.
5. PM-type cellulose acetate plastics (53% combined acetic acid) generally require higher injection pressures than plastics of higher acetyl content to avoid bubble formation in thick pieces.
6. Side gating is more effective than corner gating in producing pieces relatively free of strain.
7. There are minimum pressures below which bubble formation consistently occurs in heavy moldings.
8. Increased mold temperature and longer periods in warm molds improve the strain structure of plastics.
9. Solvent content in the test block prior to baking (about 17%), baking temperature (320° F. approximately), and cooling pressure (500–1000 pounds per square inch) are critical factors in producing cellulose acetate sheet stock free of strain.

ACKNOWLEDGMENT

The assistance in preparing this paper by W. E. Gloor, C. A. Borton, and associates, and by J. S. Biddle in making the photographs, is gratefully acknowledged.

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Presented before the Division of Paint, Varnish, and Plastics Chemistry at the 106th Meeting of the American Chemical Society, Pittsburgh, Pa.

Ammonium Ferrous Phosphate » » » A PIGMENT FOR METAL PROTECTIVE PAINT FINISHES

In a search for new pigment materials to improve the performance of metal protective paints, the behavior of ammonium ferrous phosphate ($NH_4FePO_4.H_2O$) has been investigated. This is an insoluble, greenish compound possessing a platelike structure and a characteristic x-ray diffraction pattern. Evaluation of the product to date by various methods, including conventional panel tests, indicates that a definite improvement in performance can be obtained by its use in certain types of primer systems. Tests designed to demonstrate behavior under severe conditions of moisture condensation likewise indicate its value especially in ferrous metal primers of the zinc yellow type. The mechanism of the action of ammonium ferrous phosphate has not been positively established, but it probably functions both as an acid acceptor and oxygen acceptor and at the same time improves the impermeability of the film to water vapor.

A. M. Erskine, Godfrey Grimm, and S. C. Horning

PIGMENTS DEPARTMENT,
E. I. DU PONT DE NEMOURS & COMPANY, INC.,
NEWARK, N. J.

THE growing recognition in recent years of the desirability of improving metal protective systems has stimulated research in this field by the many industrial groups facing corrosion problems. Considering only one line of attack—namely, protection by organic coatings—intensive efforts have been made to develop and investigate improved products not only by manufacturers of paints, pigments, and vehicles, but likewise by organizations having a direct interest in the protection of metals.

Since such work has been concerned with both ferrous and nonferrous metals, each exposed under a wide variety of conditions, it is obvious that the problem is one of unusual complexity. Because of the magnitude of the field and the difficulties in evaluating research results, progress is relatively much slower than in other comparable branches of technology.

From the practical point of view the problem of developing primer paints for a given use requires consideration of three equally important factors—namely, the pigment system, the vehicle, and the finished primer. Considering only the pigmentation factor, certain points are worthy of comment.

While many primers are formulated satisfactorily for certain purposes with inert, noninhibiting pigments such as iron oxide, there has been a definite trend toward the use of products with positive rust-inhibitive properties—furnished, for example, by zinc yellow. This pigment is a complex basic salt containing, in addition to zinc and hexavalent chromium, a substantial percentage of potassium. The composition is represented approximately by the empirical formula $K_2O.4ZnO.4CrO_3.3H_2O$ (*1*). The use of this pigment has become well established in primers for nonferrous metals; during recent years it has been finding increased application in primers for steel, particularly in the newer and more durable rapid-drying vehicles. Its use in primers for steel has been favored not only by its rust inhibitive properties but also by its ease of grinding, good settling resistance, and stability in the package. It has a tendency toward water sensitivity due to its appreciable solubility; this property is manifested by a tendency to blister under certain exposure conditions and requires consideration when formulating the pigment in metal protective paints.

A value of 26.1% "water soluble material" was reported (*2*) on the basis of the A.S.T.M. test (D-126-36) which involves leaching a sample with a definite quantity of water. This figure is equivalent to a concentration of 0.261 gram per 100 ml. of solution and is in reasonable agreement with the results of experiments in this laboratory, in which the equilibrium solubility (i.e., the concentration of solution in equilibrium with an excess of solid phase) was determined by shaking a large excess of pigment with distilled water. No known quantitative relation exists between either leaching values or actual solubility, and the behavior of the pigment in a paint film under exposure conditions or when immersed in water.

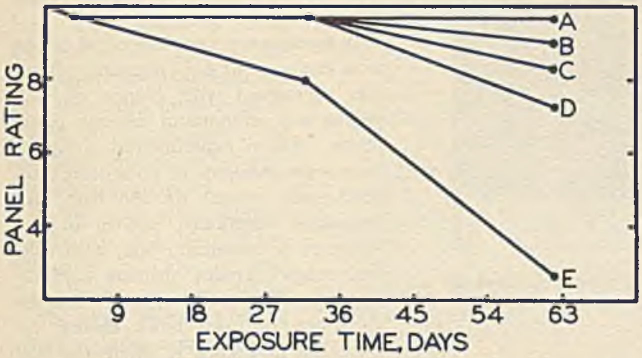

Figure 1. Effect of Ammonium Ferrous Phosphate in Primer Paints Exposed on Structural Steel Sheet (Mill Scale Intact)

A. Ammonium ferrous phosphate/zinc yellow, 30/70 (40% pigment volume)
B. Red lead, 100% (30% pigment volume)
C. Ammonium ferrous phosphate/zinc yellow, 20/80 (40% pigment volume)
D. Ammonium ferrous phosphate/zinc yellow, 10/90 (40% pigment volume)
E. Zinc yellow 100% (40% pigment volume)

Vehicle, raw linseed oil; *paint system*, one primer coat (about 0.2 mil thick), no top coat; *exposure*, miniature panel moisture condensation box

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EVALUATION OF METAL PROTECTIVE SYSTEMS

The evaluation of metal protective pigments and primer systems in general represents one of the most difficult fields of technical research, and progress is impeded to an unusual degree by pitfalls of many kinds. Indeed, it is unsafe to draw final conclusions pending long-time observations of performance in the field. The difficulty in devising testing techniques that will properly evaluate the different factors, such as effects of pigment and vehicle, condition of substratum, exposure conditions, pigment-binder ratio and other paint variables, film thickness, etc., under the array of conditions encountered in the study of this field is evident.

One type of test comprises the application of primer paints with suitable controls to portions of actual structures; such as bridges, tanks, or the like, under the conditions usually applicable in maintenance work. The structures are observed from time to time and the relative protective values noted and recorded, if desired, photographically. Exact control of all the factors influencing the results is difficult, and the time required to show up significant differences between the test systems may run into a matter of several years. Nevertheless, this procedure may yield valuable results and is widely used notwithstanding its limitations.

A second type of test comprises painting panels of convenient size and design and exposing them to various environments, usually including conditions tending to promote early failure. Great care is necessary, not only in making certain that the surfaces being painted are really comparable but also in maintaining equal film thickness and controlling conditions during application. It is this control of application conditions which makes tests of this type most useful. While somewhat artificial, panel tests are recognized as having definite value and are regularly used. Results are sometimes obtained more rapidly than in practical structure tests.

A more severe test (*4*), which at the same time duplicates certain extreme conditions encountered in service, involves applying the test paints as relatively thin films to small panels—e.g., 1 × 3 inch (2.5 × 7.6 cm.); they are exposed, usually without a topcoat, alternately to the ordinary atmosphere during the day and to conditions of positive water condensation at night. Failure by corrosion may occur in as short a time as 4–6 months, even with systems which behave satisfactorily in practice under ordinary conditions.

Either of the above types of panels can be graded on a scale in which 10 represents perfect condition, and 0 represents complete failure. The intervening figures give an approximate representation of the percentage of area corroded. These gradings are similar to those obtained with the A.S.T.M. Photographic Reference Standards (D-610-41T) for evaluating the degree of resistance to rusting with paints on iron or steel surfaces.

The results obtained by any of the above methods can be supplemented by specific tests for pigment or paint film properties which may be of interest—for example, solubility, pH values, film permeability, adhesion, electrode potential measurements with corrosion test cells, etc. Unfortunately, the correlation of these specific tests with behavior in the field is frequently puzzling and interpretation of the data is difficult.

AMMONIUM FERROUS PHOSPHATE AS A PIGMENT MATERIAL

A search of the literature for novel materials of possible interest as metal protective pigments, or as adjuvants to metal protective primer systems based on the pigments in current use, suggested the use of ammonium ferrous phosphate.

This compound, first prepared over a century ago (*3*), is described as an insoluble greenish material possessing a platelike structure. While stable at room temperature, it was found to be decomposed by heat, giving ammonia and a ferrous phosphate which, in turn, oxidized to the ferric compound. The composition, expressed in modern atomic units, was established as $NH_4FePO_4.H_2O$.

The basis for considering ammonium ferrous phosphate as a metal protective pigment can be indicated briefly as follows: Like other nominally insoluble salts, it does have some slight

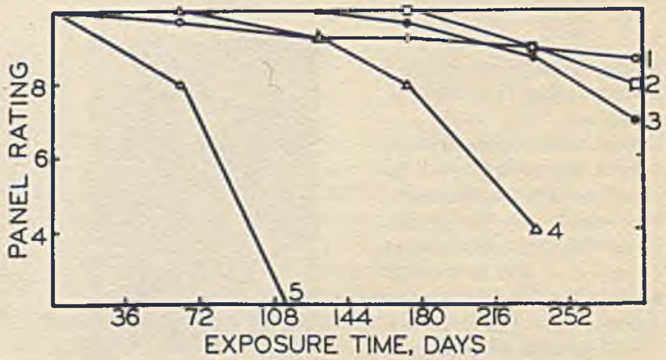


Figure 2. Effect of Ammonium Ferrous Phosphate in Primer Paints Exposed on Bright Auto Body Steel

1. Red lead in oil (30% pigment volume)
2. Ammonium ferrous phosphate/zinc yellow/iron oxide/extender, 22/53/10/15 (40% pigment volume)
3. Ammonium ferrous phosphate/zinc yellow/iron oxide/extender, 10/65/10/15 (40% pigment volume)
4. Zinc yellow/iron oxide/extender, 75/10/15 (40% pigment volume)
5. Iron oxide/extender, 85/15 (40 % pigment volume)

Vehicle: (1) Raw linseed oil; (2, 3, 4, 5) alkyd/raw linseed oil, 75/25
Paint System: Single thin (about 0.2-mil) primer coat, no top coat

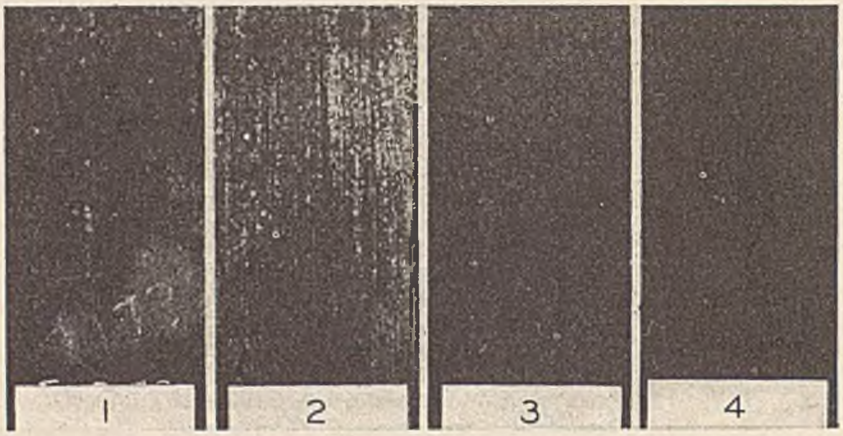
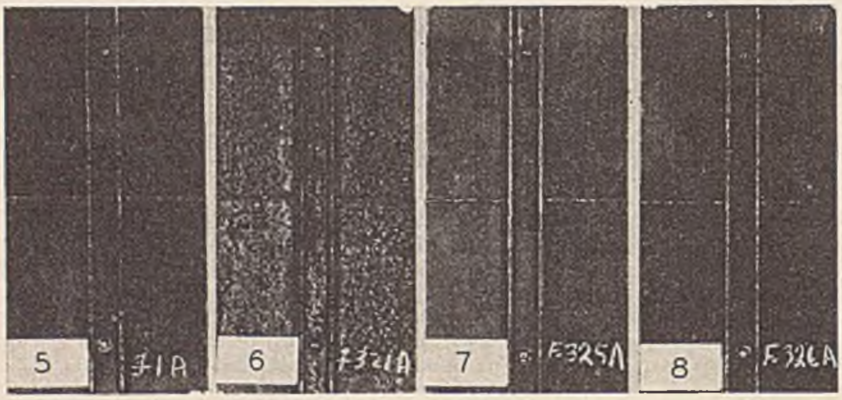


Figure 3. Topcoated Primer Films on Rusted Steel (*above*) and on Rusted Mill Scale Steel (*below*), Exposed 28 Months (45° South) in Florida

Primer Pigmentation
1, 5. Red lead, 100% (30% pigment volume)
2, 6. Zinc yellow/iron oxide/extender, 75/10/15 (40% pigment volume)
3, 7. Like 2 and 6, but 5 parts of zinc yellow replaced by ammonium ferrous phosphate
4, 8. Like 2 and 6, but 20 parts of zinc yellow replaced by ammonium ferrous phosphate

Primer Vehicle
1, 5. Raw linseed oil.
2, 3, 4 and 6, 7, 8. Alkyd/raw linseed oil, 50/50

Top Coat. Black iron oxide and carbon black in a 50-gallon spar varnish



solubility sufficient to give ammonium, ferrous, and phosphate ions, and ammonia could obviously be formed by hydrolysis or by reaction with alkaline materials which may be present in the film. It is known that corrosion of wet iron is retarded by the presence of ammonia. Ferrous ion would be expected not only to repress the solution of metallic iron by a mass action effect but should function as an "oxygen acceptor" in the system. Phosphate ion under certain conditions probably has a specific corrosion-inhibitive effect and, in any case, should have positive acid-accepting properties. The compound itself is sufficiently low in solubility to warrant evaluation as a component of the total pigmentation, particularly since its platelike character might conceivably impart impermeability and improved durability in a primer film.

In preliminary tests linseed oil paints were made up at 40% pigment volume and pigmented with blends of zinc yellow and ammonium ferrous phosphate. These experimental compositions were exposed on structural steel (mill scale intact) by the thin film technique mentioned above, in the moisture condensation box, with control single-pigment primers containing zinc yellow and red lead. The results can be seen most clearly by reference to Figure 1, where the condition of the panel is plotted against the days of exposure. Under these conditions the performance of zinc yellow was definitely improved by the presence of ammonium ferrous phosphate, and the degree of improvement increased as the proportion of ammonium ferrous phosphate was increased. The proportion for optimum performance in practical systems has not been definitely established. However, in the light of present knowledge, 100% ammonium ferrous phosphate is generally unsatisfactory.

It should be understood that the paints used in these tests are experimental compositions and do not necessarily represent the optimum formulations for the type of exposure or pigment used.

Figure 2 shows the results of similar tests using systems containing, in addition to the zinc yellow, iron

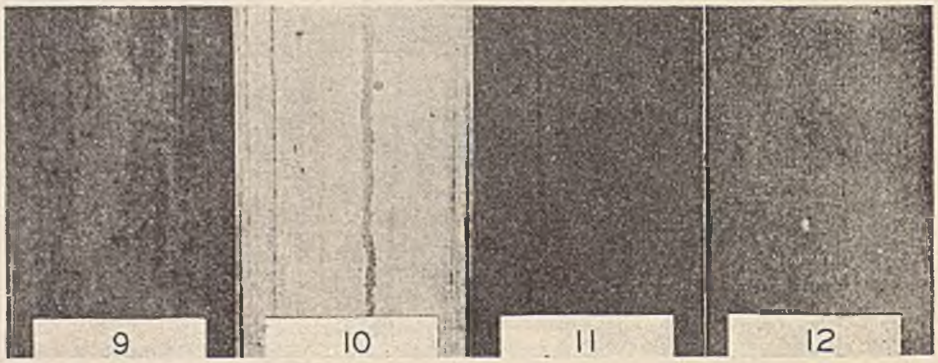


Figure 4. Untopcoated Primer Films on Clean Steel, Exposed 3 Years (45° South) in New Jersey

Pigmentation
9. Iron oxide/extender, 85/15 (40% pigment volume)
10. Red lead, 100% (30% pigment volume)
11. Zinc yellow/iron oxide/extender, 75/10/15 (40% pigment volume)
12. Like 11, but 20 parts zinc yellow replaced by ammonium ferrous phosphate

Vehicle
10. Raw linseed oil
9, 11 12. Alkyd/raw linseed oil, 50/50

oxide (for hiding) and extender. The vehicle was a blend of long-oil alkyd and linseed oil and the paints were applied to bright steel. An iron oxide primer was included as an additional control. This series of tests likewise showed marked improvement after the addition of ammonium ferrous phosphate, the improvement being more marked as the proportion was increased.

These tests were supplemented by the usual fence exposures in Florida and New Jersey. Primer paints of the type discussed in the previous paragraph were applied in the laboratory to both clean and rusty steel and exposed (45° South) at both locations with and without a topcoat. Figure 3 shows the condition of the prerusted Florida panels after 28-month exposure. Figure 4 presents panels from the same series of paints exposed without a topcoat for 3 years on clean steel in New Jersey. The zinc yellow control shows an improved performance over this substratum although a little rusting is evident in the brush marks. With ammonium ferrous phosphate present, a definite improvement can be seen.

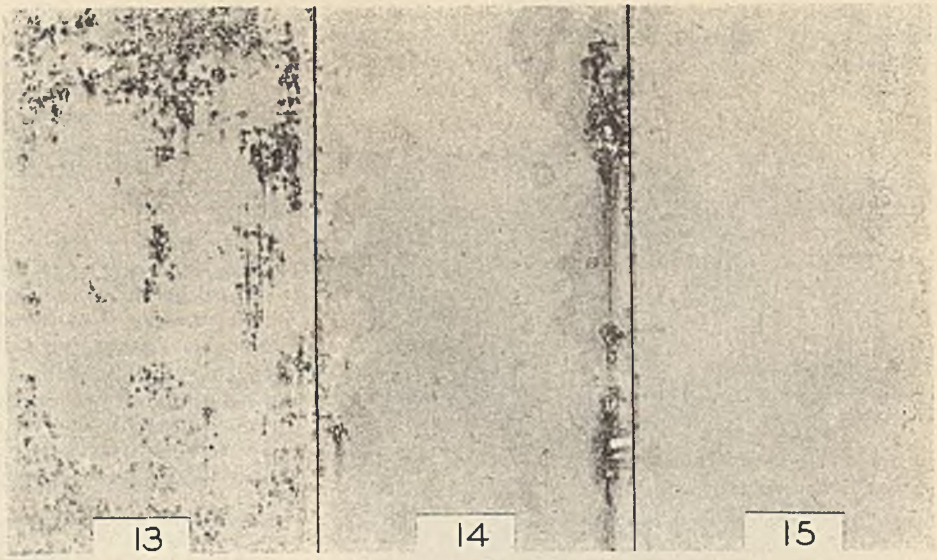


Figure 5. Topcoated Primer Films on Clean Steel, Exposed 9 Months at Mean Tide Level in Florida

Primer Pigmentation
13. Red lead, 100% (30% pigment volume)
14. Zinc yellow/sienna/titanium dioxide/extender, 55/5/15/25 (40% pigment volume)
15. Like 14, but 15 parts zinc yellow replaced by ammonium ferrous phosphate

Primer Vehicle
13. Raw linseed oil
14, 15. Phenolic/alkyd, 63/37

Top Coat. **Dark gray, 100% alkyd**

Figure 5 represents a still different type of test—namely, 9-month immersion at tide level in Florida. Red lead in oil is shown as a control. The second paint was of the Navy 52-P-18 (INT) type (phenolic/alkyd vehicle) with zinc yellow representing 55% of the total pigmentation. In the third panel part of the zinc yellow in the latter formula has been replaced by ammonium ferrous phosphate. All of the panels had a pigmented alkyd topcoat. Here again the introduction of ammonium ferrous phosphate has resulted in improved performance.

These results were considered sufficiently outstanding to warrant proceeding with more practical character tests to establish the merit of ammonium ferrous phosphate under field conditions. Numerous evaluation studies of this sort, including the behavior of ammonium ferrous phosphate with pigments other than zinc yellow, are underway; the results continue to show promise.

PREPARATION OF AMMONIUM FERROUS PHOSPHATE

Ammonium ferrous phosphate is prepared by the interaction of a ferrous salt with ammonium and phosphate ion—for example, by adding diammonium hydrogen phosphate. Formation of the compound apparently occurs in two distinct steps: the precipitation of ferrous hydrogen phosphate, and the conversion of the latter to the ammonium salt, $NH_4FePO_4.H_2O$. The former is a grayish flocculent precipitate; the latter is crystalline, and its flakelike particles give an opalescent appearance to the slurry.

The desired reactions occur over a fairly wide range of experimental conditions and are controlled largely by the factors of alkalinity, ammonium ion concentration, and conditions influencing oxidation of the iron. The safe maximum pH is about 8.5; above this, normal ferrous phosphate forms and is converted with difficulty, if at all, to the ammonium salt.

Chemical Properties. Unless unusual precautions are followed, a certain amount of the iron is oxidized to the ferric condition and appears in the product as hydrous ferric oxide, ferric phosphate, or possibly a double salt of the latter with ammonium phosphate. The purity of the product—i.e., the ammonium ferrous phosphate content, which ordinarily runs about 80–85%, can be determined most easily from the proportion of the total iron in the ferrous state. Material of even 70% purity (around 9% ferric iron) appears normal by functional tests. The following is a typical analysis:

	Analysis	Theory ($NH_4FePO_4.H_2O$)
Ammonium as NH_4	8.75%	9.64%
Total iron as Fe	29.39	29.90
Phosphate as PO_4	52.70	50.90
Water, by difference as H_2O	9.16	9.56
Total	100.00	100.00
Ferric iron as Fe	5.27	0
% $NH_4FePO_4.H_2O$	80.7	100.0

When heated above 100° C., ammonium ferrous phosphate is decomposed, the decomposition becoming more rapid as the temperature increases. At 160° C. it loses all of its ammonia in about 16 hours; at the same time, all of the iron is oxidized and appears as ferric phosphate. There is some evidence of decomposition below 100° C., but it is very slow.

Ammonium ferrous phosphate is slowly hydrolyzed in water and is rapidly decomposed in alkaline solutions with the formation of ammonia. In this latter case, a black residue is left, probably a hydrated ferrous oxide (*3*). The pH of an aqueous suspension is about 8.

Physical Properties. Ammonium ferrous phosphate is a somewhat bulky, grayish-green solid with a specific gravity of 2.5. It is quite insoluble, 100 ml. of a saturated solution at 25° C. containing 0.02 gram. Microscopic and electron micrograph studies show it to consist of thin irregular plates ranging in diameter from 0.02 to 37 microns, and in thickness up to 0.3 micron (Figure 6). Its complete particle size distribution has not been determined.

The refractive index of ammonium ferrous phosphate is approximately 1.6. Between crossed Nicols only part of the material appears anisotropic, and it shows oblique extinction. It is probable that the whole of the material is anisotropic, but because of the platelike habit, detection of this is not possible. X-ray diffraction data point to the existence of a crystalline compound having a characteristic structure independent of the mode of preparation. The diffraction pattern is shown in Figure 6 for a sample prepared under nitrogen and dried in a vacuum, and data on interplanar spacings are presented in Table I. They have been compared with spacings for the other compounds which might be present and appear to be unique.

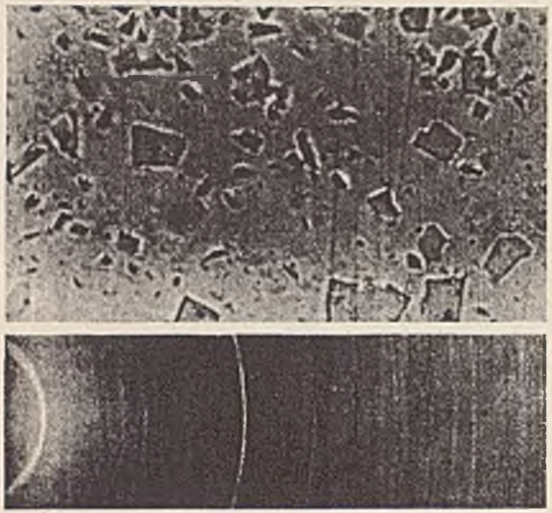


Figure 6. (*Above*) Ammonium Ferrous Phosphate Dispersed in a Semialkyd Vehicle (× 1000); (*Below*) X-Ray Diffraction Pattern of Ammonium Ferrous Phosphate (Copper Radiation, Nickel and Aluminum Filter)

ACTION IN PAINT FILMS

No complete explanation for the improved behavior of primers containing ammonium ferrous phosphate can be given at this time, and it would be imprudent to postulate the mechanism of its behavior. Nevertheless, it is of interest to record preliminary observations and to suggest possible factors of speculative interest.

Ammonium ferrous phosphate, unlike chromate pigments such as zinc yellow, does not appear to have a specific passivating action, according to evidence available at present. The latter factor, however, may have definite importance under certain conditions; for example, it may modify the effect of more active passivating pigments.

The flake structure of ammonium ferrous phosphate was mentioned above, and is not only evident during precipitation but can also be seen readily in a paint under the microscope (Figure 6). Flake pigments have a well established place in the formulation of metal protective paints; while leafing is less marked than with mica or aluminum, for example, this property may at least partly contribute to the enhanced performance which has been given by the addition of ammonium ferrous phosphate.

Film impermeability to water and water vapor plays a large part in the protection obtained under some experimental conditions. It is probably related to the flake structure and leafing mentioned above, but will obviously also be affected in great degree by the vehicle component. It is likewise a function of interdependent factors contributed by both pigment and vehicle—for example, reactivity or character of the film as determined by the pigment/binder ratio. Whatever the explanation, impermeability measurements on detached films have shown an improvement in this property to result when ammonium ferrous phosphate is added to certain systems.

Again, water sensitivity as evidenced by blistering, loss of adhesion, etc., represents a complex set of phenomena and the final result is due to no one cause. Several tests have indicated ammonium ferrous phosphate to decrease water sensitivity to a significant degree, and further research along this line is warranted.

Mention should be made of the role of acid-accepting materials in relation to corrosion occurring under a paint film due to acids liberated during drying of the paints or carried through the films during exposure to industrial atmospheres. While not so active as the more soluble zinc yellow, ammonium ferrous phosphate has been shown to act as a solid-phase buffer and its beneficial action in some cases is probably due to this fact. Its particular advantage may be that the equilibrium pH value obtained with it is at a relatively high level, compared with other substances used in this way as acid acceptors.

TABLE I. X-RAY DIFFRACTION INTERPLANAR SPACING OF AMMONIUM FERROUS PHOSPHATE

Å.	Intensity	Å.	Intensity
8.83	Very strong	1.895	Medium
4.76	Medium	1.870	Weak
4.42	Very weak	1.833	Very weak
4.23	Medium	1.793	Weak
3.65	Very weak	1.771	Weak
3.38	Medium	1.739	Very weak
3.25	Very weak	1.692	Medium
2.93	Very weak	1.626	Medium
2.83	Very strong	1.553	Very weak
2.51	Medium	1.511	Very weak
2.43	Weak	1.498	Weak
2.35	Weak	1.426	Very weak
2.30	Strong	1.415	Weak.
2.14	Weak	1.373	Very weak
2.12	Very weak	1.262	Very weak
2.07	Weak		

There is little direct experimental evidence as yet bearing on the influence of ammonium ferrous phosphate considered simply as a ferrous salt. The possible function of ferrous ion as an inhibitor of anodic corrosion of iron was mentioned above and may serve at least to explain the observed facts partially. Furthermore, the relative ease with which ferrous salts are oxidized suggests that they may have value simply as oxygen acceptors.

Moisture, acidity, and oxygen have been recognized as the three most important factors contributing to corrosion. Ammonium ferrous phosphate may be unique in supplying, in a single compound, the properties required to minimize their influence—namely, impermeability, acid acceptance, and oxygen acceptance. The validity of this hypothesis must obviously be tested by further research. It is hoped that a clear-cut answer will be afforded, not only by practical evaluations now in progress, but also by more basic studies on the influence of ammonium ferrous phosphate on paint film properties.

ACKNOWLEDGMENT

Appreciation is expressed to members of the research staff of this laboratory for assistance in various phases of the work. Acknowledgment is also made to the Experimental Station of the Chemical Department, E. I. du Pont de Nemours & Company, Inc., for the development of special testing methods.

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Presented before the Division of Paint, Varnish, and Plastics Chemistry at the 106th Meeting of the American Chemical Society, Pittsburgh, Pa.

Physical Structure of Phenoplasts

The rate of net-work formation, when cured phenolic films are swollen in acetone, is helpful in investigating phenoplasts in advanced states of cure. This technique has been applied in an investigation of the effect of catalyst concentration, reactant ratios, temperature of initial reaction, and temperature of cure on the degree of cure in the final hardened resin. The existing concepts of resin structure are reviewed in the light of this additional experimental evidence. A modified concept of phenoplast structure which more closely conforms with the experimental facts is proposed.

R. A. Barkhuff, Jr., and T. S. Carswell

MONSANTO CHEMICAL COMPANY, SPRINGFIELD, MASS.

FOR many years the chemist has been familiar with the resinous products resulting from the condensations of aldehydes with phenols. He is equally familiar with the dominant position which phenoplasts have assumed in the synthetic resin field since their introduction in the first decade of this century. Despite their favorable economic position, relatively little is known about the chemical nature and the physical structure of the thermosetting resins in general and the phenoplasts in particular. This situation has resulted from two factors: (*a*) The immediate requirements of industry, in the past, have been satisfied without the necessity of a great deal of fundamental research. (*b*) The cured resinoid does not permit usual methods of investigation, such as viscosity or osmotic measurements in solution and x-ray diffraction patterns.

Despite these difficulties, investigators such as Bender, Raschig, Granger, Megson, Koebner, and Zinke, to name only a few, have made important contributions to our knowledge of the organic chemistry of the condensation products. Investigations into the physical structure of these resinoids have been more fragmentary but have led to the isogel theory of Houwink and others and to the sphero-colloid theory, which was recently elaborated by Stäger.

ISOGEL THEORY

The initial reaction between phenols and aldehydes leads to the formation of small, two-dimensional products joined by methylene linkages. Through further polycondensations, the molecules grow in size in two or three dimensions until they reach the ill-defined range termed "colloidal". At this point, after dehydration, the resin is in the state usually referred to as isocolloidal. This state, in essence, is composed of condensed molecules having a rather limited range of particle size. These are dispersed in a medium of their lower homologs; the condensing agent or catalyst is often viewed as the stabilizing medium.

Under the influence of heat this dispersed phase grows in size at the expense of the dispersing medium until a critical point is reached at which gelation takes place. According to the theory of Houwink and others, once the gel point is reached, the material is considered to be an isogel which is composed of infinitely large macromolecules which form a spongelike skeleton throughout the mass. Trapped in the capillaries and pores of the sponge are the unreacted ingredients and resin particles of a lower degree of condensation. This portion is a more mobile, viscous material which is often referred to as *Harzbrei*. The spongelike skeleton portion of the structure becomes increasingly predominant as condensation progresses. With further condensation the *Harzbrei* becomes more closely identified with the sponge skeleton until ultimately the greater majority of the available linkages are employed in the tight three-dimensional network. However, this ultimate state of cure is apparently seldom reached in the molding of commercial phenolic resins.

Many of the mechanical properties of the phenoplasts seem to support the isogel structure. The elastic nature of the resin is attributed to the rigid macromolecular skeleton, whereas its viscous flow characteristics are attributed to the *Harzbrei*.

Flory (*2*) and Stockmeyer (*10*) presented one of the strongest arguments for the isogel structure in their ability to predict the gel point for three-dimensional glyptal-type resins from a statistical study of the reaction mechanism. However, as will be seen later, such a postulated mechanism does not appear capable of accounting for all of the experimental facts in this complex phenolic system.

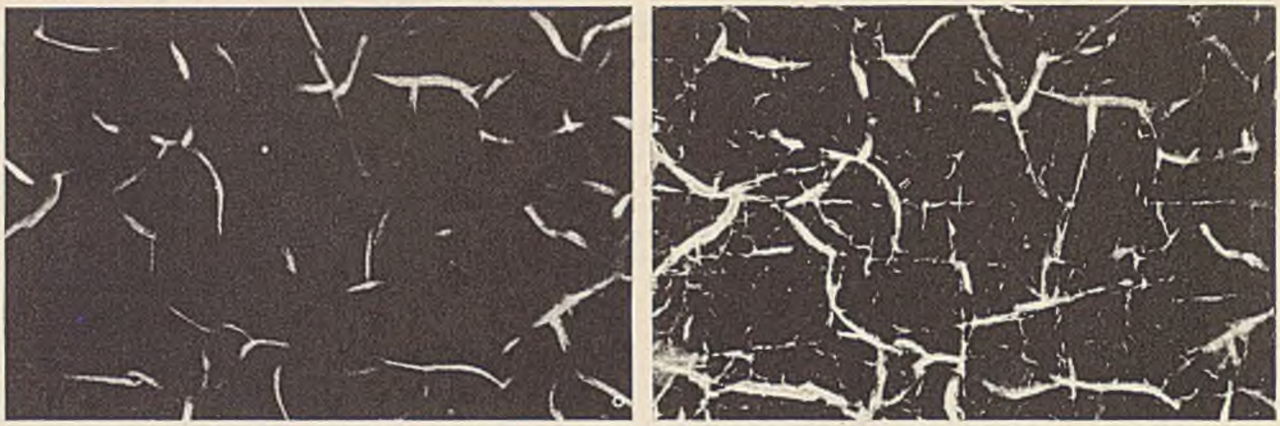
Hetenyi (*3*) provided evidence for this type of structure, based on its elastic behavior. He found that slightly cured sections of thermosetting resins, when subjected to stresses at 110° C. and then slowly cooled, retain their elastic deformation on the removal of the load. Such a test piece may then be sawed and viewed in polarized light. An isochromatic fringe pattern, corresponding to an elastic state of stress, may then be observed. He explains this phenomenon on the basis of a gelatinous three-dimensional network, which acts elastically, and an internal viscous phase. At elevated temperatures this viscous phase is quite fluid, but, upon cooling, the viscosity increases until at room temperature it is so great that it prevents the deformed elastic network from returning to its original shape. This is but one of the many arguments supporting the sponge structure for these thermosetting resins.

Houwink's studies (*6*) on high elasticity observed in B-stage phenolic resins form another line of evidence for the sponge structure. Houwink showed further (*5*) that the tensile strength increases as cure proceeds and as the elastic skeleton grows. It is well known that the tensile strength of such resins never approaches that calculated from either primary or secondary valence bonds; this has been demonstrated by the work of Houwink (*5*) and de Boer (*1*). This discrepancy is often explained by the presence of *Locherstellen*—that is, gaps in the primary bond structure which serve as flaws at which stress-concentrations build up.

SPHERO-COLLOID THEORY

Another school of thought holds that a somewhat opposite structure exists. The more highly polymerized three-dimensional network forms small clumps, or sphero-colloids, which are surrounded by a continuous phase of the lower-molecular-weight viscous *Harzbrei*. According to this viewpoint, the isocolloid structure is retained throughout the curing of the resin and is to be found in the final cured mass. In this theory there is no need to assume that the isocolloidal particles are fully linked by primary valence bonds to give a rigid sponge skeleton. Gelation is assumed to be the result of association and interpenetration of the molecules.

Stäger and co-workers (*7, 8, 9*), in an effort to elucidate further the structure of the phenoplasts, conducted an extensive investigation of broad significance during 1935–40. Swelling phenomena resulting from the action of solvents on the cured phenoplasts were especially studied in this work, and an attempt was made to correlate the observations with the mechanical properties of the phenoplasts. Stäger interprets his results as



A. Interior pattern *B.* Surface pattern photographed under a layer of acetone

Figure 1. Patterns of Phenol-Formaldehyde Resin (1 to 1 Molar Ratio) Made with Barium Hydroxide as Catalyst (× 106)

supporting the sphero-colloid theory, in that the solvent selectively attacks the less cured portions of the phenoplast and reveals definite grain boundaries, similar to those found in metal alloys or the cross section of pith wood.

OUTLINE OF PRESENT WORK

The purpose of this work was to study further the swelling phenomenon described by Stäger and the application of this technique to phenoplast structure. Stäger prepared a series of alkaline catalyzed or one-stage phenoplasts from formaldehyde and phenol or mixed cresols. Cast disks were cured from the A-stage resins, and from these disks thin films (0.02 to 0.04 mm. thick) were prepared by a modification of the grinding technique of Weigel (*11*). These films were then swollen in acetone and examined under the microscope in polarized light. A network appeared as shown in Figure 1*A*, which Stäger interpreted as representing grain boundaries.

Our first experimental technique closely followed that of Stäger. Resins were cast in shallow metal pans, and thin sheets were ground off and polished. They were then swollen in acetone and examined under the microscope. Networks (Figure 1*A*) were observed as described by Stäger. This technique proved laborious for a large number of specimens, and a simple method was developed which apparently gives the same result. A film of liquid resin was spread on a glass microscope slide, cured, and polished on the top surface to the same thickness as used by Stäger.

The resins were prepared from pure phenol and formaldehyde, using basic catalysts as summarized in Table I. The molar ratio of phenol to formaldehyde was varied from 1:1 to 1:1.5. Various basic catalysts were used, such as sodium hydroxide, ammonia, calcium hydroxide, and barium hydroxide. In an effort to limit the number of variables, which is essential in a fundamental series of experiments, the preparation of these resins was greatly simplified. Investigators should, therefore, be cautioned against comparing these resins directly with resins prepared under normal operating conditions, where many more variables may exist. A typical method for the preparation of the liquid resin was as follows: 94 grams of phenol and 81 grams of formalin (37% CH_2O) were mixed with 2 grams of sodium hydroxide ($^1/_{20}$ mole). The mixture was agitated under reflux (100° C.) for 15 minutes. The mass was cooled to 50° C. and water was removed under a pressure of 30 mm. The temperature during dehydration rose from 50° to 90° C. and permitted the reduction of the water content to less than 1%. The velocity of formaldehyde addition is at a maximum during the refluxing period, but the over-all reaction time is the sum of this refluxing period and the dehydration period which required approximately 2 hours. Although no controls were maintained on the formaldehyde consumptions during the course of the reaction, the resins so prepared with each catalyst were judged to be relatively comparable in their extent of reaction. Subsequent work in which the formaldehyde consumption was followed would indicate this to be true. The resulting resin was spread on slides as indicated above.

Table I. Resins Prepared for Investigation

Resin	Moles CH_2O/ Mole Phenol	Catalyst, Mole	Reaction Conditions Hr.	Reaction Conditions ° C.
a	1	1/20 NaOH	$^1/_4$	100
b	1	1/50 NaOH	$^1/_2$	100
c	1	1/200 NaOH	$^3/_4$	100
d	1.5	1/20 NaOH	$^1/_4$	100
e	1	1/50 $Ba(OH)_2$	2	100
f	1	1/50 $Ba(OH)_2$	3	90
g	1	1/50 $Ba(OH)_2$	4	80
h	1	1/20 NH_3	$1^1/_4$	100
i	1.25	1/20 NH_3	$1^1/_4$	100
j	1.50	1/20 NH_3	$1^1/_4$	100
k	1	1/20 $Ca(OH)_2$	1	100

The resin-coated slides were heated at 78°, 100°, and 125° C. for various periods to cure the resin. The tops of the resulting cured films were polished with graded emery papers followed by a paste of pumice in mineral oil. The film thickness was checked with a micrometer.

The cured films were treated with anhydrous acetone for various periods and examined intermittently under the microscope to determine the degree to which swelling and network development had proceeded. In the microscopic examination no advantage was found by using polarized light. Better results were obtained with dark-field illumination—the technique used in this paper.

Two separate types of swelling patterns are obtained, one apparently lying at the surface of the resin film, the other at the interior. These two types can be differentiated by careful focusing. Figure 1, photomicrographs at different focal depths of the same resin film, illustrates these two series of patterns. The resin was prepared from an equimolar ratio of phenol to formaldehyde, with $^1/_{50}$ mole of barium hydroxide as catalyst. The film was cured 14 hours at 100° C. and swollen 30 minutes in acetone. Similar series of patterns were observed with the other resins studied, under the various conditions of cure employed.

The finer of these patterns (*B*), which develops on the surface, normally appears first during the acetone treatment. This pattern cannot be observed in polarized light or when the film surface has been allowed to dry. It is visible best under dark-field illumination and only when the surface is in contact with a liquid whose refractive index differs from that of the resin. When the film has a low degree of cure, the resin grains within this surface network swell during prolonged contact with acetone; the network pattern disappears but reappears again when the excess of swelling agent is allowed to evaporate. With a more completely cured film, the grains do not swell sufficiently

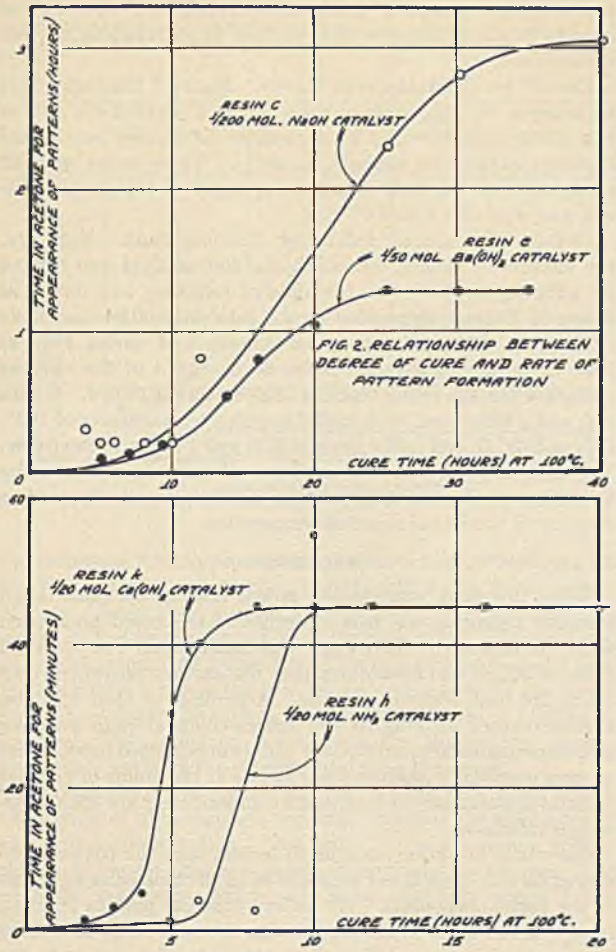


FIG. 2. RELATIONSHIP BETWEEN DEGREE OF CURE AND RATE OF PATTERN FORMATION

to cause the pattern to disappear. Since this type of pattern is more difficult to observe, it was not studied so extensively as the coarser interior pattern.

The coarser pattern which appears in a plane below the surface is clearly shown in both *A* and *B* (Figure 1); it is more clearly defined in *A* because the surface network has been eliminated by careful focusing. This pattern is clearly visible in polarized light as well as by dark-field illumination, and can be detected faintly by ordinary transmitted light. This pattern forms during the acetone treatment and, once formed, is permanent. During acetone treatment, strains develop which are visible in polarized light, but these strain patterns correlate in no way with the swelling pattern illustrated in *A*. The interior resin pattern seems to represent cracks in the resin mass.

RATE OF PATTERN FORMATION

Effect of Degree of Cure. Early in this work it was noted that the swelling time required to bring out the pattern varied directly with the extent of cure. Irrespective of the significance of the pattern as regards resin structure, the swelling pattern offers a useful tool for studying the advanced cure of the phenoplasts. In all of the subsequent work, only the coarse swelling pattern is referred to.

Figure 2 illustrates the interrelation between degree of cure and rate of pattern formation for four resins prepared with different catalysts. In each case, the resin was prepared with an equimolar ratio of phenol and formaldehyde (*c*, *e*, *h*, and *k*, Table I), and cured for various times at 100° C. Figure 2 is presented as typical of the type of results which may be obtained by this technique, but the resins are not necessarily comparable. In each case the curves have three characteristic portions:

1. An initial level portion which is characteristic of all resins. Here the resin is only slightly advanced and in transition through the so-called B-stage of cure. Swelling takes place rapidly in this region. In the early portions gelation rather than pattern formation may result.
2. A second portion of steep slope preceded by a rather sharp change in slope. This break appears to represent completion of the B-stage and initiation of the C-stage, in which three-dimensional cross linking predominates. That the change in slope does represent a critical stage in the curing reaction is supported by the correlation between the break and the "dry rubber" discussed below. The ascending linear section represents the progression of cross linking into a hard three-dimensional resin.
3. A third virtually level portion preceded by a second change in slope which appears to represent substantial completion of the curing reaction. Beyond this point the swelling time required for pattern formation is practically independent of the time of cure.

Dry Rubber. In the technology of phenoplast manufacture, a useful test for speed of cure of a resin is the so-called dry rubber test; 0.2 gram of the resin is placed on a hot plate at 150° C. and worked about with a spatula until the resin passes through a rubbery condition into an infusible mass. The number of seconds of heating required is called the "dry rubber".

In the preceding paragraphs it was pointed out that the first break in the curves of Figure 2 appears to represent completion of the B-stage and initiation of the C-stage. The dry rubber is a similar criterion of cure; hence if the first change of slope really does represent such a state, it would correlate with the dry rubber. The data plotted in Figure 3 shows that such a correlation does exist for the resins previously described. In addition, this curve contains points for two other resins, *a* and *d* (Table I).

Effect of Curing Temperature. It is well known that the rate of cure increases as the curing temperature is increased. Figure 4 shows the relation between rate of pattern formation, time of cure, and temperature of cure. All of these curves are for resin *c*. An increase in temperature causes a marked in-

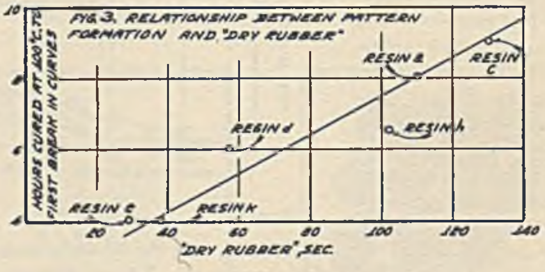


FIG. 3. RELATIONSHIP BETWEEN PATTERN FORMATION AND "DRY RUBBER"

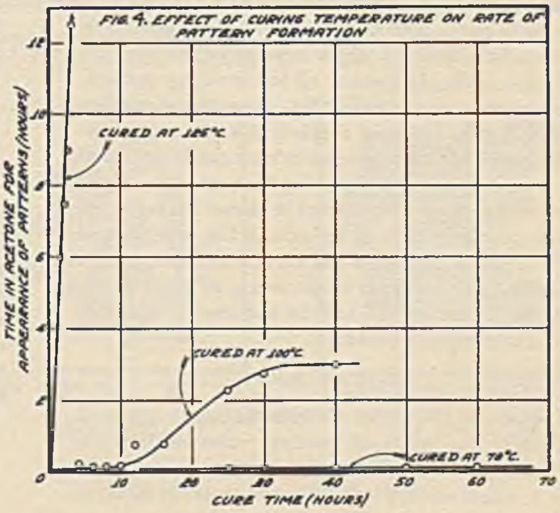


FIG. 4. EFFECT OF CURING TEMPERATURE ON RATE OF PATTERN FORMATION

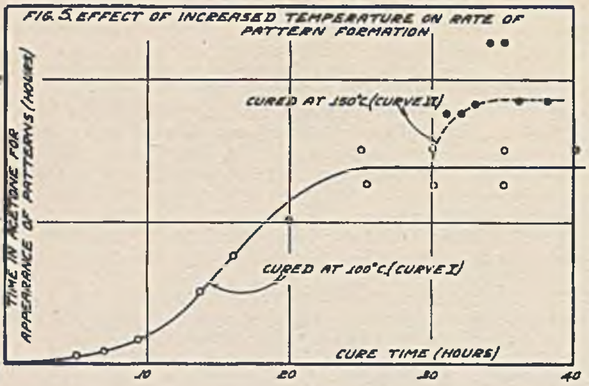


FIG. 5. EFFECT OF INCREASED TEMPERATURE ON RATE OF PATTERN FORMATION

crease in the degree of cure of the resin. At very low temperatures, such as 78° C., cure appears to advance to only a slight degree. Similar experiments have been carried out for as long as 240 hours without showing any change of slope which would indicate a rapid advance of cure.

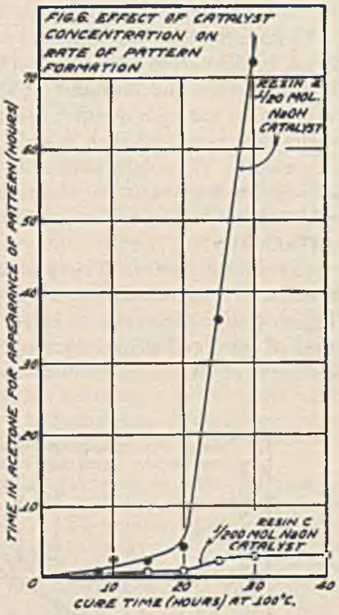


FIG. 6. EFFECT OF CATALYST CONCENTRATION ON RATE OF PATTERN FORMATION

Another effect of temperature on degree of cure, as brought out by the rate of pattern formation, is shown in Figure 5. When the time required for development of the swelling pattern is plotted against cure time for any given temperature, the last portion of the curve becomes virtually level, an indication that no further progression of cure takes place. To determine the effect of increase in temperature on cure at this stage, resin *e* was heated at 100° C. for 40 hours, and the swelling time was determined at various periods (curve I). The experiment was repeated, but the temperature was raised to 150° C. after heating for 30 hours at 100° C. (curve II). The increase in temperature caused a slight increase in the time required for the formation of the swelling pattern. This appears to indicate that, once the maximum degree of cure has been reached at a given temperature, a slight further increase in cure can be achieved by a further increase in curing temperature. However, comparison with Figure 4 shows that the increase in cure obtained by raising the temperature after the level section of the curve has been reached at a low temperature is by no means so great as the increase in cure which can be obtained by initially curing at a high temperature.

RATE OF CURE

Effect of Catalyst Concentration. Figure 6 illustrates the effect of catalyst concentration on the rate of cure. The curves represent resins *a* and *c*, cured at 100° C. The increase in catalyst concentration markedly increased the hardness of cure, at least in so far as the rate of formation of the swelling pattern is concerned.

Effect of Formaldehyde Ratio. Figure 7 illustrates that an increase in formaldehyde ratio causes a marked increase in rate of cure, as shown by time required for development of the swelling pattern, for resins *h*, *i*, and *j*. These resins were all catalyzed with $^1/_{20}$ mole of ammonia, based on the phenol present, and were cured at 100° C.

Effect of Initial Reaction Temperature. Normally, the mixture of phenol, formaldehyde, and catalyst was reacted by refluxing at 100° C.; the time of refluxing was varied as shown in Table I, depending on the catalyst and formaldehyde ratio used. Figure 8 represents the effect of curing time at 100° C. on the time required for development of the swelling pattern when the initial reaction temperature is varied. Resins *e*, *f*, and *g* were used, with initial reaction temperatures of 100°, 90°, and 80° C. and reflux times of 2, 3, and 4 hours, respectively. The data indicate that the hardness of cure, as indicated by formation of the swelling pattern, increases markedly with a decrease in the initial reaction temperature.

DISCUSSION

When this work was started, it was hoped that some direct evidence regarding the true structure of the cured phenoplast could be obtained. This hope was based upon the apparent belief of Stäger and co-workers that the acetone treatment does make the resin structure visible. According to their theories, acetone causes swelling of the sphero-colloidal resin particles and thus creates internal stresses visible in polarized light; these stresses eventually produce shear failure at the points of greatest structural weakness—that is, in the comparatively low-molecular-weight interfaces.

Our work, however, leads us to believe that the patterns observed furnish little direct evidence as to the molecular structure of the cured phenoplast. We believe that the pattern revealed in acetone is due to cracks produced in the resin structure during acetone treatment, and that this pattern is related only to the general state of cure. In interpreting the structure of the resin, the nature of the pattern itself is not so important as the time required for its development.

Stäger showed (*8*) and our work confirms the fact that the areas enclosed by the swelling pattern are of considerable magnitude (from 1×10^{-3} to 3×10^{-4} sq. mm.). If these represented sphero-colloidal particles, each of which is a single molecule, the number of phenol-alcohol units would have to be very great, in the neighborhood of 10^{12}.

Neither the type of swelling pattern nor the time required for its development furnish any direct evidence favoring either the isogel or the sphero-colloidal theory. However, the swell-

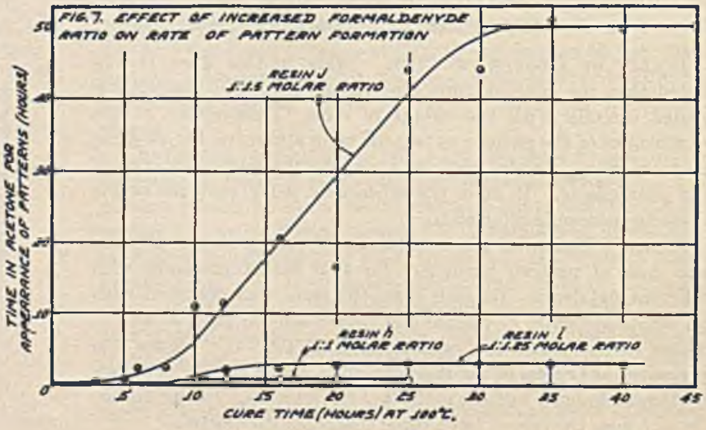


FIG. 7. EFFECT OF INCREASED FORMALDEHYDE RATIO ON RATE OF PATTERN FORMATION

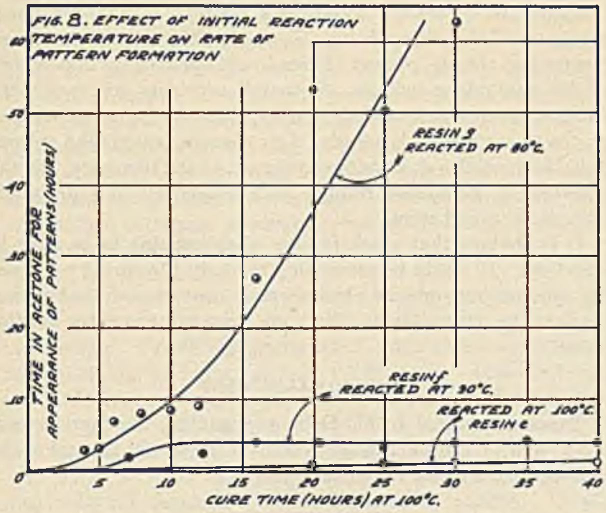
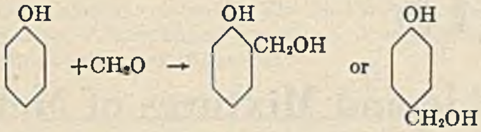


FIG. 8. EFFECT OF INITIAL REACTION TEMPERATURE ON RATE OF PATTERN FORMATION

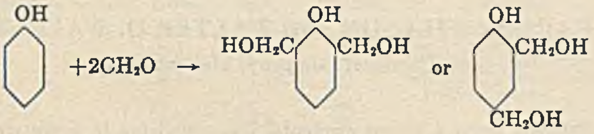
ing technique does appear to be a valuable tool for studying the kinetics of the curing process, particularly in the lower degrees of cure. From these studies, some indirect conclusions may be drawn concerning the structure of the resin and the development of cross linking. As pointed out in the experimental work, the factors which increase the rate of the curing process also result in a higher degree of cure as revealed by the rate of swelling in acetone. The following mechanism for the curing process reasonably explains the experimental data presented.

In considering the mechanism which may take place during the curing of a phenoplast, we must consider the chemistry of the initial condensation. The latter is by no means simple, and it is known that a number of products are formed. For example, the condensation may be divided into stages I and II as follows:

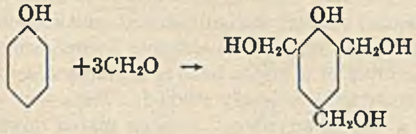
IA. Formation of the two monoalcohols:



IB. Formation of dialcohols of which the two isomers are possible:



IC. Possible formation of trialcohols:



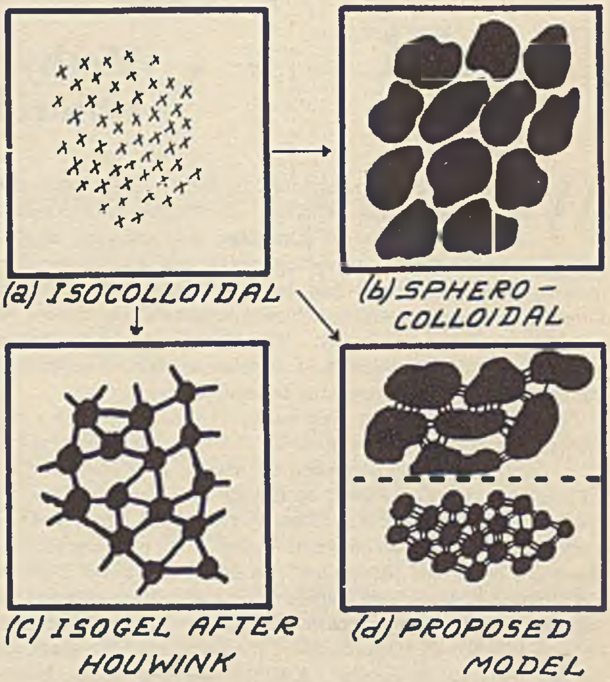
All of these are competing reactions, and IA is never predominent unless a large excess of phenol is present.

II. Polycondensation of any of the above with one another or with free phenol to form large molecules with the elimination of water or formaldehyde. It is evident that, when equimolar ratios of phenol and formaldehyde are used, and when reactions IA and IB both take place, some free phenol must be present.

It is apparent that not only the chemical nature of the polycondensation products may vary, but also their geometry in respect to the positions in the ring at which methylene bridging may take place. It is evident that any conditions which affect the ratio of initial reaction products, as shown by stage I, will affect the nature of the final cure. It is also true that any conditions which affect the chemical or spatial nature of the polycondensation (II) will also affect the nature of the final cure.

In the initial stages of phenoplast condensation, relatively small molecules are formed and dispersed throughout a mass of the lower homologs. These molecules form the nuclei of the isocolloidal state and may be diagrammatically represented by the X's in Figure 9*a*. The number and configuration of these nuclei are influenced by the initial reaction temperature, the amount of catalyst, the ratio of reactants, and other environmental factors. It must be noted that the phenoplast condensation, by its very nature, leads to highly branched macromolecules; the latter probably have a more or less spherical form, and differ in this respect from the long-chain molecules which are present in addition polymerizations and in polyester condensations. As the reaction proceeds, the nuclei grow at the expense of the less polymerized portions and occasionally by union of the nuclei. This process continues until steric considerations and the amount of available reactants remaining terminate the growth. At this point, which corresponds to the completion of the B-stage of resin formation, a structure similar to the sphero-colloid picture is visualized (Figure 9*b*). Under certain conditions of reaction the nuclei form slowly and attain relatively large size. This may be compared to the process of crystallization where large crystals are obtained when a relatively small number of nuclei are present.

With further curing, C-stage resin formation takes place (the ascending portion of the curves), and cross linking between the macromolecules is the predominant reaction. Since most of the methylol groups are consumed in the formation of the three-dimensional macromolecules, there will be a deficiency of reactants in the interface capable of forming methylene bridges. These bridges will then be formed primarily through methylol groups already present on the macromolecules. The bridges formed in this C-stage of resin structure will be limited in number by steric considerations and by available reactive positions containing methylol groups. It is evident that the methylene



(a) ISOCOLLOIDAL

(b) SPHERO-COLLOIDAL

(c) ISOGEL AFTER HOUWINK

(d) PROPOSED MODEL

Figure 9. Diagrammatic States of Resin Cure According to Various Viewpoints

bridges formed with large micelles will be relatively few in number as represented in the upper half of Figure 9*d*.

Figure 5 presents one of the strongest arguments against the isogel structure. It would be reasonable to assume under the isogel theory that the final temperature of curing would be the only controlling factor in the degree of cure. Actually, comparison of Figures 4 and 5 shows that some other factor is entering the picture. On the basis of the postulated mechanism, this can be explained by the cross linking of the macromolecules. In transition through the B-stage of resin formation the size of the macromolecules is fixed. At 100° C. a certain number of sterically unhindered bonds cross linking the macromolecules are formed. As Figure 5 shows, the increase in temperature to 150° C. results in further cross linking through a few sterically hindered reactive positions to form a resin of slightly higher cure.

It is evident that increasing the formaldehyde ratio will result in a greater number of methylol groups available for bridging in the final stages of cure. The result is a resin of higher degree of cure (Figure 7).

In general, any factor which promotes the formation of numerous nuclei will favor increased bridging and a higher degree of cure. For example, in addition to an increased formaldehyde ratio, increase in catalyst concentration and in temperature of cure will increase the rate of nucleus formation. This increased rate of nucleus formation will be reflected in the structure by a smaller macromolecular size as shown in the lower half of Figure 9*d*. These smaller macromolecules result in closer packing and give a thinner interface of the lower polymerized material between the sphero-colloids. The higher degree of packing permits formation of a greater number of methylene bridges. These trends are reflected in more highly cured resins as Figures 4, 6, and 7 show.

At the moment it is difficult to explain the effect of initial reaction temperature on the final cure as shown in Figure 8. Probably many of the variables present in this complex system must be considered before drawing a conclusion.

Figure 9*c* represents Houwink's concept (*4*) of the isogel structure of the phenoplasts. The only difference between this theory and the one presented here lies in the relative importance of the methylene bridges. Houwink considers the methylene bridges to represent a major portion of the structure, giving rise to the elastic sponge network. Our concept regards the sphero-colloidal particles as a major component of the structure, and the interlinking methylene bridges as a secondary but important part of the cured resin.

It is obvious that much further work remains to be done in this field. It would be interesting to study the curing processes for various pure phenol alcohols and other cross-linked resins, such as the aminoplasts. We hope eventually to carry out this work.

ACKNOWLEDGMENT

The assistance of L. M. Debing in guiding the experimental work, and of Turner Alfrey and H. K. Nason in preparing the manuscript, is gratefully acknowledged.

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Presented before the Division of Paint, Varnish, and Plastics Chemistry at the 106th Meeting of the American Chemical Society, Pittsburgh, Pa.

FLAMMABILITY LIMITS IN AIR . . . Methyl Chloride and Mixtures of Methyl Chloride with Dichlorodifluoromethane

KARL S. WILLSON AND WALTER O. WALKER
Ansul Chemical Company, Marinette, Wis.

WIDE variations in the limits of flammability for methyl chloride have been reported. Spark and flame ignitions in different types of apparatus give different limiting values according to some investigators (*3*, *6*). Extinctive effect in some related mixtures has been determined (*3*, *4*, *5*), although the methyl chloride–dichlorodifluoromethane system has not been reported previously. The desirability of a comprehensive survey of the effect of various sources of ignition on mixtures in the same apparatus became apparent.

The explosion chamber used consisted essentially of a cylindrical $^1/_8$-inch steel vessel of about 7.5-liter capacity attached to a heavy base and equipped as shown in Figure 1. The $^1/_4$-inch steel cover lay loosely on the top of the cylinder, and the seal was made by a soft wax (Flexowax C, Glyco Products Company). A pivoted framework of $^1/_4$-inch iron rod, anchored at the front, prevented throwing of the lid beyond about 2 inches.

For spark ignition tests a spark plug with points extended was supplied with power by a spark coil, using two dry cells in series, or by a 15,000-volt 18-milliampere transformer. The spark gap was normally about $^1/_8$ inch. A 3-inch length of resistance wire, coiled, was shorted across the points of the spark plug for the red-hot wire tests. The wire, of the type used in the ordinary 550-watt radiant heater elements, was connected in series with such an element in a 110-volt circuit.

Lighted cigars and cigarets, attached to a tube, were thrust into the chamber through the ignition port, and suction was alternately applied and removed to simulate normal smoking conditions. The firing of a match head is a practical source of ignition apparently not previously studied. Tests were carried out by sliding a "strike-anywhere" wooden match down the glass tube so that the head rested on the resistance wire. On closing the resistance-wire electrical circuit, the head was ignited by the hot wire. Flame test results depended on the method of ignition, as described later.

To prepare the desired gas mixture, a suitable vacuum was drawn in the chamber and test gas was admitted to the desired pressure. Air was added to restore atmospheric pressure, and the sample was mixed by the fan which was stopped before ignition was attempted. The volume percentage of the gas was calculated by dividing the pressure of the test gas by the barome-

Current shortages of dichlorodifluoromethane (Freon 12) and the advantageous solvent and other properties of methyl chloride have led to the consideration of methyl chloride–dichlorodifluoromethane mixtures where dichlorodifluoromethane had previously been used alone. Flammability limits in air of such mixtures are important and have been determined. The effects of the type of ignition on these mixtures and on pure methyl chloride have been studied.

ter reading. Pressure readings were made at 1-mm. intervals, corresponding to approximately 0.1% steps. Tests involving dichlorodifluoromethane were made by using a fixed quantity of methyl chloride and varying the dichlorodifluoromethane content to establish the particular limiting mixture.

To establish limit values, mixtures were tested which extended into both the flammable and nonflammable regions. In general, a mixture was secured which was definitely explosive. A variation of 1 mm. in gas pressure gave a mixture which might or might not explode, depending apparently on minor variations. A further change of 1 mm. in pressure gave a mixture which did not explode. This latter value was taken as the limit and hence the values in this paper are actually the "safe" limits.

Near the limits in some instances, particularly with intense sources of ignition such as the 15,000-volt spark or the igniting match, rising waves of flame or flaring at the source occurred without detonating the mixtures. These points were listed as the limiting values only if the flaming or flaring was small in extent.

METHYL CHLORIDE–AIR

Flammable limits determined for the sources of ignition described above are given in Table I and illustrated in Figure 2 in connection with other tests. For spark ignition the intensity of the spark is a factor. When the 2-volt spark coil was used with the points very close together to give a spark of low intensity, no ignition was obtained. The cited values are for a spark gap of about 1/8 inch, but some variation in the limit was noted, depending on the spark adjustment.

TABLE I. FLAMMABLE LIMITS OF METHYL CHLORIDE IN AIR

Ignition Source	Limit, % by Vol. Lower	Limit, % by Vol. Upper	Citation	Remarks
Spark	9.3	16.3	[a]	2-volt spark coil
	9.1	....	[a]	6-volt spark coil
	7.6	19.1	[a]	15,000-volt transformer
	8.25	18.70	(3)	6-volt spark coil, 4.5-amp. primary current
	10	15	(6)	....
	8.9	15.5	(2)	....
	8.1	17.2	(7)	....
Cigar, cigaret	No ignition		[a]	....
White-hot wire	10	15	(6)	....
Red-hot wire	No ignition		[a]	....
	No ignition		(6)	....
Igniting match	8.0	18.9	[a]	....
Flame	10.75	17.40	(3)	Long tube
	10	15	(6)	.....
	7.9	18.9[b]	[a]	Approx. max. values[b]
Unknown	8.2	19.7	(1)	....

[a] This report.
[b] Widest limits.

With glowing cigars or cigarets, no ignition occurred. Red hot resistance wire likewise failed to detonate the mixtures and hence probably did not appreciably affect the limits established for the igniting matches. With mixtures near the upper limit, some difficulty was encountered in securing consistent results with matches; the mixture tended to "quench" the ignition of the match which, in some cases, burned sputteringly without appreciable flame.

Flame ignition tests presented unexpected results. For mixtures containing less than about 13% methyl chloride, detonation of the charge usually occurred when a lighted match or splint was applied at the ignition port. In some instances the warmed gases issuing through the port tended to blow out the flame and give false results. Application of gentle suction to the apparatus at the instant of applying the flame in order to suck the flame into the chamber was of value in establishing the approximate lower limits. In some instances near the lower limiting values, a tongue of flame rose along the wall above the port or flashed horizontally witohut detonating the entire charge.

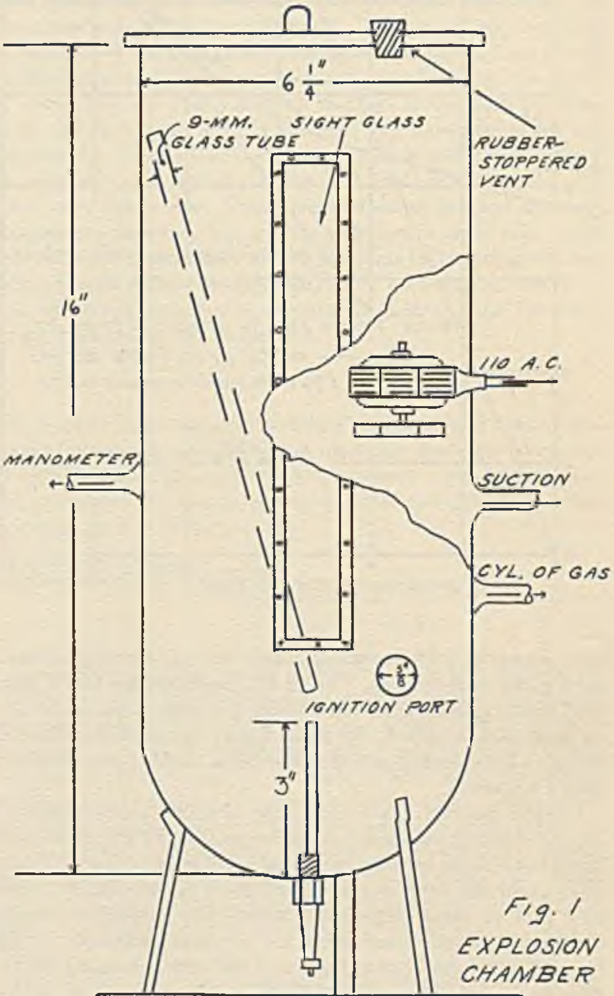

Fig. 1
EXPLOSION CHAMBER

For mixtures above about 13%, more complex results were secured. A burning match or splint applied at the ignition port did not detonate the mixture, although if it was introduced through the port without being extinguished, detonation occurred. Likewise, if the flame was sucked into the chamber, detonation resulted.

On the other hand, if the vent was opened in the lid of the chamber and a match then applied to the ignition port as it was opened, an envelope of flame was formed (outside of the vessel) which gradually diminished. When the flame had receded to the port, a flash back with detonation of the residual mixture resulted in most instances, and the time of burning before flash

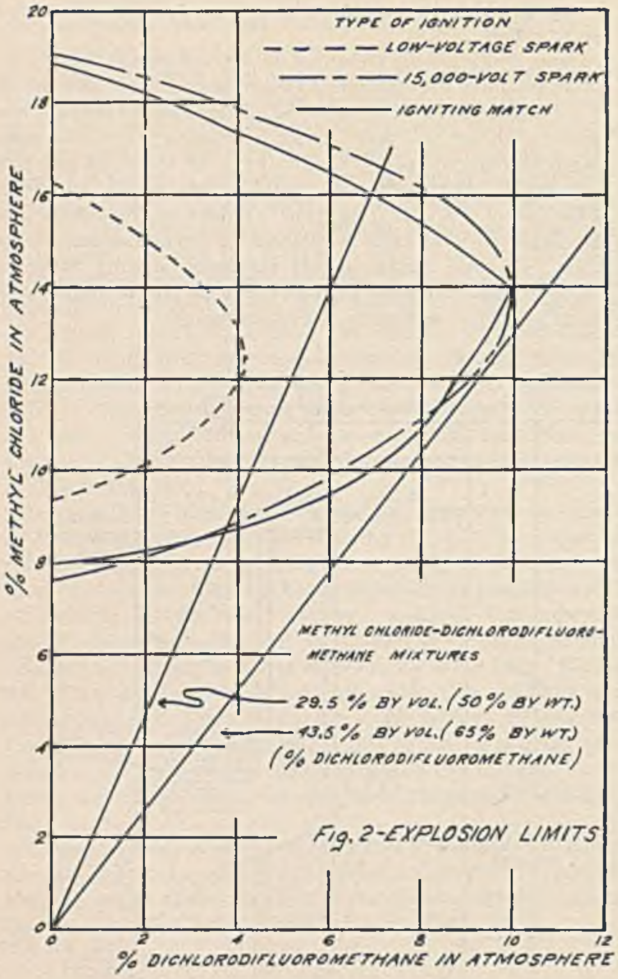

Fig. 2-EXPLOSION LIMITS

back increased with increasing concentration of methyl chloride for a given vent opening. At 18.5% concentration and a small vent opening, burning of the mixture occurred at the orifice and no flash back occurred, the flame finally being extinguished although a flame sucked into the chamber in another test detonated such a mixture.

Methyl chloride has a slow rate of flame propagation (*8*). Issuing slowly from a tube, it can be ignited and will continue to burn, but a slight increase in flow rate will tend to blow the flame away from the tube and extinguishment occurs readily. This slow rate of flame propagation is probably largely responsible for the phenomena described in the previous paragraph; it was found that the envelope of flame and the time of burning prior to flash back could be decreased by decreasing the size of the top vent and hence the flow of gas from the ignition port. The rate of burning is also probably greater at the lower concentrations since detonations are much less violent near the upper limit.

Because of the effects noted and the difficulties of securing exactly reproducible conditions, approximate values only could be secured and it is probably best to report these limits only as being slightly within those reported for the 15,000-volt spark. These approximate limits are by far the broadest yet reported for flame ignition.

METHYL CHLORIDE-DICHLORODIFLUOROMETHANE-AIR

Flammable limits were determined for these mixtures. Consistent and duplicable results were secured for the ignition sources cited in Figure 2. The 2-volt spark coil test limits fall within the other two types. With low voltage, quenching of the spark occurred; in some instances a spark gap setting which gave a good spark in air did not give a spark at all or only an occasional flash when the mixture was present. Good sparks were secured beyond the limiting values at all points cited. With the 15,000-volt spark, no difficulty was encountered due to quenching.

With the igniting matches, quenching of ignition was evident; the match head often burned sputteringly without appreciable flame. Limiting values cited represent mixtures tested where normal ignition occurred.

Flame tests with dichlorodifluoromethane mixtures were unsatisfactory, apparently as a result of complexities caused by the extinctive effect of the dichlorodifluoromethane as well as those previously described for methyl chloride-air mixtures at the limiting values. Because of the impossibility of securing duplicable results or results which were of significance, only a few tests were made; but all such tests showed limiting values to be appreciably inside the limiting curve for the 15,000-volt spark.

At 13.2% methyl chloride, the limiting value for ignition when the flame was sucked into the chamber was approximately 9.3% dichlorodifluoromethane. At 11.2% methyl chloride the limit was approximately 6.6% dichlorodifluoromethane under the same conditions, although a similar mixture flowing from the ignition port after the top vent was opened could not be ignited with a match.

This type of phenomenon had previously been noted when a mixture was tested consisting of approximately 50% by weight (29.5% by volume) of dichlorodifluoromethane in methyl chloride contained in a cylinder. The composition of this mixture is shown in Figure 2. As expected, this mixture could not be detonated by the 2-volt spark coil when present in any concentration in air in the explosion vessel. On the other hand, although this mixture was clearly inside the flammable range for flame ignition, it could not be ignited to give a self-sustaining flame when issuing slowly from a tube or when used as fuel for a Bunsen burner.

SUMMARY

1. For methyl chloride-air mixtures, 7.6% by volume methyl chloride is the lowest flammable limit thus far reported; 19.1% methyl chloride by volume is appreciably less than the upper limit value of 19.7% previously reported, the source of which is unknown.

2. Mixtures of methyl chloride and air are nonflammable if they contain 10% by volume or more of dichlorodifluoromethane.

3. Mixtures containing 56.5% by volume (35.0% by weight) or less of methyl chloride in dichlorodifluoromethane are nonflammable when mixed with air in any quantity.

4. A spark operating from a 15,000-volt transformer gave the widest flammability limits secured except in minor instances, and is judged to be the most dependable source of ignition. Flame ignition tests gave variable results and are unreliable practically, at least for mixtures containing methyl chloride. Igniting matches gave limits similar to those secured with the 15,000-volt spark with slightly wider limits in a portion of the dichlorodifluoromethane curve. Burning cigars and cigarets and red-hot resistance wire did not ignite methyl chloride-air mixtures.

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Preparation of Methyl Acetoxypropionate

REACTION OF LACTIC ACID WITH METHYL ACETATE

C. E. REHBERG,
W. A. FAUCETTE,
AND C. H. FISHER

Eastern Regional Research Laboratory,
U. S. Department of Agriculture, Philadelphia, Pa.

Lactic acid can be made in almost unlimited quantities by fermentation of abundant, low-cost carbohydrates. A one-step method is described for transforming lactic acid into methyl acetoxypropionate. The reaction between lactic acid of various concentrations and methyl acetate is studied under different conditions to determine the effect of variables on the yield of methyl acetoxypropionate. Both methyl lactate and methyl acetoxypropionate are produced. Under some conditions 63.6 and 28.4% yields, respectively, of methyl lactate and methyl acetoxypropionate were obtained. This preparation of methyl acetoxypropionate requires less acetic anhydride or ketene than the customary method, which consists in treating methyl lactate with either acetic anhydride or ketene. Physical and chemical properties of methyl lactate and its azeotrope with water are described.

EFFICIENT and inexpensive methods of converting lactic acid (*27, 28, 29*) into its diester, methyl α-acetoxypropionate (I), are highly desirable since on pyrolysis methyl α-acetoxypropionate yields methyl acrylate and acetic acid (*5, 12, 21, 22, 29*). The preparation of methyl acrylate, an important synthetic rubber (*1, 6, 9, 10, 23, 24, 30, 35*) and resin (*16*) intermediate, by pyrolysis of the acetyl derivative (I) of methyl lactate, is attractive because lactic acid can be made at low cost by fermentation of several abundant carbohydrates:

$$\mathrm{HOCH(CH_3)COOH + CH_3COOCH_3 \longrightarrow \underset{(I)}{CH_3COOCH(CH_3)COOCH_3} + H_2O}$$

$$\mathrm{\underset{(I)}{CH_3COOCH(CH_3)COOCH_3} \xrightarrow{\text{pyrolysis}} CH_3COOH + CH_2{:}CHCOOCH_3}$$

Methyl acetoxypropionate is usually made by the two separate operations of esterifying lactic acid (*11, 13, 26, 28, 34*) with methanol and acetylating the resulting methyl lactate with acetic anhydride (*5, 29*), ketene (*7*), or acetyl chloride (*18*). The reaction of lactic acid with methyl acetate was studied in the present work because it seemed probable that lactic acid would be converted into methyl acetoxypropionate in one operation. At the beginning of the study it appeared that the direct transformation of lactic acid into methyl acetoxypropionate in this manner would have the following advantages: (*a*) One step of previous syntheses would be eliminated and thereby reduce the cost of manufacture; (*b*) less equipment would be required; (*c*) corrosion of equipment would be less troublesome; and (*d*) the use of acetic anhydride, ketene, or acetyl chloride would not be required.

The reaction of lactic acid with methyl acetate is of interest also because it involves an unusual type of ester interchange; i.e., one of the reactants is bifunctional and can enter into both alcoholysis and acidolysis reactions. The reaction between lactic acid and methyl acetate is more complex than would be realized on first consideration because the usual grades and concentrations of lactic acid consist of a mixture (*2, 3, 33*) of monomeric lactic acid, water, and condensation products of lactic acid, such as lactyllactic acid, $\mathrm{HOCH(CH_3)COOCH(CH_3)COOH}$. Isolation of the products was found to be rather difficult because of the presence of several components, one of which (methyl lactate) hydrolyzes easily and distills azeotropically with water.

Powers (*19*) reported that ethyl acetoxypropionate was obtained by treating lactic acid with ethyl acetate, but he did not give yields or the concurrent formation of ethyl lactate.

PROPERTIES OF METHYL LACTATE

In the earlier stages of the investigation the yields of methyl lactate varied widely, and the experiments could be reproduced only with difficulty. To determine whether these erratic results were due to condensation or hydrolysis reactions during distillation, a study of the stability of methyl lactate under various conditions was made. Possible side reactions considered were hydrolysis to lactic acid and methanol, conversion into its condensation polymers (II), and decomposition into acetaldehyde, carbon monoxide, and methanol:

$$\mathrm{\mathit{n}HOCH(CH_3)COOCH_3 \longrightarrow \underset{(II)}{H[OCH(CH_3)CO]_{\mathit{n}}OCH_3} + (\mathit{n}-1)CH_3OH}$$

CONDENSATION REACTIONS. Methyl lactate was refluxed for 3 hours with anhydrous zinc sulfate, calcium sulfate, sodium sulfate, sodium acetate, sulfuric acid, and lactic acid (100% concentration). Methyl lactate was not appreciably affected by this treatment in the presence of the salts or lactic acid, but sulfuric acid was highly active in promoting condensation. On distillation of the reaction mixture obtained from one drop of sulfuric acid and 75 ml. of methyl lactate, there were obtained methanol 46 ml. of methyl lactate and 20 ml. of viscous distillation residue (probably methyl esters of linear condensation products of lactic acid). Presumably other strong acids would have a similar effect.

HYDROLYSIS. Considerable hydrolysis occurs when methyl lactate containing water is distilled at atmospheric pressure, even in the absence of catalysts. The lactic acid produced by the hydrolysis was recovered as distillation residue, which probably consisted of lactic acid condensation polymers (*2, 3, 33*). Mineral acids catalyzed the hydrolysis most effectively. The effect of buffers was not studied thoroughly, but the addition of an alkaline agent, such as sodium acetate, retarded hydrolysis even in the apparent absence of mineral acid. As was to be expected, hydrolysis was negligible when the distillation was carried out under reduced pressure (approximately 50 mm.) in the absence of catalysts.

WATER-METHYL LACTATE AZEOTROPE. Prior to publication of Weisberg and Stimpson's patent (*34*), it was observed that water and methyl lactate distill as a constant-boiling mixture whose composition varies with the distillation pressure. Determination of the composition of the azeotrope was complicated

Table I. Densities of Methyl Lactate

Source	0° C.	10.7° C.	13° C.	15° C.	19° C.	20° C.	26° C.	30° C.
Equation 1	1.1162	1.1046	1.1013	1.0989	1.0943	1.0932	1.0862	1.0818
(*25*)	1.1180	..	..	..	1.0898	..	..	..
(*36*)	..	1.1037	..	..	..	..	1.0857	..
(*31*)	..	..	1.100	..	..	..	..	..
(*8*)	..	..	..	1.097	..	1.093	..	..
(*32*)	..	..	..	..	..	1.0895	..	1.0785
(*20*)	..	..	..	..	..	1.0925	..	..
Present work	..	..	..	..	..	1.0928	..	1.0825

by hydrolysis of methyl lactate, but it was found that under atmospheric pressure the azeotrope contains 25 to 30% methyl lactate and distills at 99° to 99.5° C. When distilled at 38–39° under a pressure of 50–52 mm., the azeotrope contained 12 to 15% of methyl lactate.

Benzene and methyl lactate did not distill azeotropically, and benzene, water, and methyl lactate did not form a constant-boiling ternary mixture. Hence benzene is suitable for removing water from methyl lactate by distilling the benzene-water binary azeotrope. Methyl lactate can also be recovered from aqueous solution by extraction with benzene, ether, or other suitable solvent.

Physical Constants. The density data of Patterson and coworkers (*17*, *18*), which were determined at temperatures from −74° to 125° C., are defined satisfactorily by Equation 1:

$$\text{density} = (967.34 - t°\text{ C.})/866.67 \qquad (1)$$

Other density data are recorded in Table I.

Refractive index data (n_D^t) determined in this laboratory with the redistilled methyl lactate referred to in Table I are: 1.4183 (10° C.), 1.4162 (15°), 1.4141 (20°), 1.41263 (23.5°), and 1.4120 (25°). The following refractive indices have been reported: 1.413 at 20°, Godchot and Vieles (*14*); 1.4149 at 19°, Burkard and Kahovec (*4*); 1.4132 at 25°, Smith and Claborn (*26*).

The molecular refraction of our sample, calculated from the refractive index of 1.4141 and density of 1.0928, was 23.82 instead of the theoretical value of 23.85. The relation between temperature and the refractive indices determined in the present work is given by Equation 2:

$$n_D^t = 1.4225 - 0.00042\,t \qquad (2)$$

Several boiling points of methyl lactate, observed in this laboratory, are plotted against pressure in Figure 1.

EXPERIMENTAL PROCEDURE

Commercial lactic acid samples of 80 and 100% concentration, which were edible and almost colorless, were used. The concentrations were verified by neutralization and saponification of a known quantity of sample with standard solutions of sodium hydroxide.

Concentrations of lactic acid above 100% were obtained by the dehydration of 80 or 100% acid. This can be effected by refluxing the acid with an entraining agent (*33*) such as benzene, which removes water azeotropically, or by heating the acid in a vacuum to distill both the "free water" and that formed by self-esterification (*2*, *3*, *11*). The acid used in experiments 21, 36, and 37 was dehydrated with benzene and without catalyst. It was a clear, transparent, brown, very viscous, resinlike material, the concentration of which was calculated from its saponification equivalent. That used in experiments 23, 24, and 25 was prepared with benzene and with sulfuric acid as a catalyst; its concentration was calculated from the amount of water removed from the 100% acid used as starting material.

High-pressure bombs designed for hydrogenation work were used for the ester-interchange experiments. They were electrically heated, and the temperatures were controlled and recorded automatically. In experiments 17, 18, and 22, a 183-cc. unlined stainless steel bomb was used; in experiments 8, 27, 28, 36, and 37, a 2240-cc. bomb with Pyrex liner was used; in all other experiments a 1270-cc. bomb with brass liner was used. The two larger bombs were made of high-carbon manganese steel. The two smaller bombs were rocked continuously during the heating periods; no agitation was used with the larger one. Agitation produced no detectable effect on the yields. Mild corrosion of the bombs was observed at 180° C., which became more pronounced at higher temperatures or when acetic acid was included in the charge. The pressures developed in the 180° and 220° C. experiments were 250 to 275 and 475 to 500 pounds per square inch, respectively.

The reaction mixtures were carefully distilled through efficient columns, usually a twenty-plate Lecky-Ewell still (*15*). A Vigreux column, 15 mm. in diameter and 800 mm. long, gave results agreeing closely with those from the more efficient still, although the purity of the various fractions was much lower. Very careful and efficient fractionation is required for good separation of the components: (1) methyl lactate–water azeotrope, boiling point 99.5° C.; (2) acetic acid, 118°; (3) methyl lactate, 144–5°; and (4) methyl α-acetoxypropionate, 171–2°. In some experiments the entire distillation was conducted at atmospheric pressure; in others the pressure was reduced to about 50 mm. when fraction 1 was reached. Operation at reduced pressure has the advantages that less methyl lactate is removed in fraction 1 and also less lactate is lost by hydrolysis and condensation. In either case it is essential to neutralize the acid catalyst before distillation, a slight excess of sodium acetate being used for this purpose in the present work.

INTERACTION OF LACTIC ACID AND METHYL ACETATE

Although a considerable quantity of methyl acetoxypropionate was formed by the reaction of lactic acid with methyl acetate, the principal product was methyl lactate. The reproducibility of the results, which was not entirely satisfactory, is indicated by experiments 1 to 8, Table II. Possibly the lack of reproducibility can be attributed to the use of relatively small quantities of reagents and the catalytic effect of the bomb or liner walls on the reaction. Experiments in which larger amounts of reagents were used are more significant, partly because smaller quantities were used early in the investigation when some of the difficulties encountered were not fully appreciated.

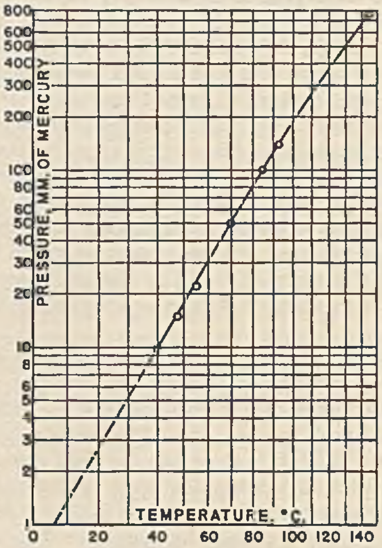

Figure 1. Vapor Pressure of Methyl Lactate

The total yields of esters obtained with methyl acetate (Table II) were as high as the yields of methyl lactate observed in the direct esterification of lactic acid with methanol. Considerable quantities of methyl acetoxypropionate and moderately high yields of methyl lactate were obtained when 1 mole of lactic acid was heated with 12 moles of methyl acetate at 180° C. for 4 hours (in the presence of a small amount of catalyst). The yields of methyl lactate and methyl acetoxypropionate observed under these conditions (63.6 and 28.4%, respectively) were obtained in experiment 27, in which larger amounts of the reactants were

Table II. Reaction of Lactic Acid with Methyl Acetate

Expt. No.	Lactic Acid		Ratio, Ester: Acid	Catalyst	Additional Reactants, Moles	Time, Hr.	Temp., ° C.	Conversion, %		
	Concn., %	Moles						Into methyl lactate	Into methyl acetoxy-propionate	Combined esters
1	100	0.67	6	H_2SO_4, 5 drops	None	4	180	43.2	17.9	61.1
2	100	0.67	6	Same	None	4	180	38.4	10.1	48.5
3	100	0.67	6	Same	None	4	180	53.6	12.4	66.0
4	100	0.67	6	Same	None	4	180	50.2	11.7	61.9
5	100	0.67	6	Same	None	4	180	51.5	14.0	65.5
6	100	0.67	6	Same	None	4	180	50.3	22.4	72.7
7	100	0.67	6	Same	None	4	180	60	17.3	77.3
8	100	2.0	6	H_2SO_4, 10 drops	None	4	180	55.0	24.7	79.7
9	100	0.67	6	Toluenesulfonic acid, 1 g.	None	4	180	43.4	11.1	54.5
10	100	0.67	6	Toluenesulfonic acid, 1 g.; H_2SO_4, 2 drops	None	4	180	46.5	23.0	69.5
11	100	0.67	6	H_2SO_4, 5 drops	None	2	180	41.5	3.4	44.9
12	100	0.67	6	Same	None	5.5	180	64.5	14.5	79.0
13	100	0.67	6	Same	None	8	180	64.5	17.3	81.8
14	100	0.67	6	Same	None	45	180	48.8	28.5	77.3
15	100	0.67	6	Same	None	4	150	50.2	0.0	50.2
16	100	0.67	6	Same	None	4	212	43.2	22.4	65.6
17	100	0.245	5.3	H_3PO_4, 1 ml.	None	3.5	260	49.0	13.3	62.3
18	100	0.5	2	Toluenesulfonic acid, 1 g.	None	4	180	34.4	11.5	45.9
19	100	1.00	2	H_2SO_4, 5 drops	None	4	220	27.2	12.7	39.9
20	100	1.00	3	Same	None	4	220	54.3	15.7	70.0
21	118	1.00	3	Same	None	7	140	29.8	5.2	35.0
22	100	0.3	4	Toluenesulfonic acid, 1 g.	None	4	180	22.7	15.8	38.5
23	120	1.0	4	Same	None	4	180	16.8	7.4	24.2
24	120	1.0	4	Same	None	4	180	10.4	0	10.4
25	120	1.0	4	H_2SO_4, 5 drops	None	4	180	1.8	0	1.8
26	80	0.75	4	Same	None	4	180	47.4	7.0	54.4
27	100	1.0	12	H_2SO_4, 10 drops	None	4	180	63.6	28.4	92.0
28	80	2.0	6	Same	None	4	180	64.4	11.2	75.6
29	118	1.0	2	H_2SO_4, 5 drops	Acetic acid, 1	7	140	6.1	3.2	9.3
30	100	1.0	3	Same	Same	7.5	210	36.7	15.7	52.4
31[a]	100	0.67	6	Same	Same	8	210	39.2	21.3	60.5
32[a]	100	0.67	6	Same	Same	8	210	36	..	..
33	100	0.67	6	Same	Acetic anhydride, 0.33	4	180	31.3	16.3	47.6
34	100	0.67	6	Same	Methyl lactate, 0.5	4	180	14.2	16.8	31.0
35	100	2.00	6	H_2SO_4, 10 drops	Methanol, 4	4	180	75.5	7.9	83.4
36	117	2.0	0	Same	Methanol, 12; acetic acid, 12	4	180	46.7	3.7	50.4
37	117	2.0	5	Same	Methanol, 2; acetic acid, 2	4	180	44.7	10.0	54.7

[a] A bulky white solid, possibly lactide, was obtained.

used. Examination of the results obtained in experiments 18, 22, 8, and 27 indicates that the formation of esters at 180° is favored by the use of increased proportions of methyl acetate.

Operating under the conditions of experiment 27 would give a total conversion of 92.0%, of which 38% by weight is methyl acetoxypropionate. Although the use of methyl acetate, as exemplified by experiment 27, would not eliminate entirely the use of acetic anhydride or ketene, the quantity of these acetylating agents required would be less. Probably a large proportion of the distillation residues obtained in experiments 1 to 8 could be converted into methyl lactate by treatment with methanol or into lactic acid by hydrolysis.

The results of experiments 8, 9, 10, 17, 18, 19, 22, 24, 25, and 26 may be used to compare sulfuric acid, phosphoric acid, and *p*-toluenesulfonic acid as catalysts, but definite conclusions do not appear warranted. Since *p*-toluenesulfonic acid is used in larger quantities, however, it can be concluded tentatively that sulfuric acid is preferable on a weight and cost basis.

It appears from experiments 8, 11, 12, 13, and 14 that the yields of esters increase with time of reaction (at 180° C.) up to approximately 4 hours, and that the use of longer periods has little effect on the total yield of esters.

Comparison of experiments 15 and 16 suggests that methyl lactate is formed at relatively low temperatures but that the formation of methyl acetoxypropionate is favored by more drastic conditions.

Experiments 22 to 25 show that 100% lactic acid gives higher yields of esters than polylactic acid under the same conditions. It appears from experiments 25, 26, and 28 that 80% lactic acid also is preferable to polylactic acid.

Judging from experiments 29 to 37, the value of using certain third components seems questionable. Acetic acid and acetic anhydride were used to determine whether increased yields of methyl acetoxypropionate would result. The purpose of using methyl lactate (experiment 34) was to ascertain the feasibility of recycling the methyl lactate in order to obtain a higher ultimate yield of methyl acetoxypropionate. The effect of using methanol (experiment 35) was to lower the yield of methyl acetoxypropionate.

It might be expected that polylactic acid, methanol, and acetic acid would react to give results comparable to those obtained by treating lactic acid with methyl acetate. Experiments 36 and 37 show that acetic acid and methanol cannot be substituted satisfactorily in this manner for methyl acetate when the mixture is heated at 180° C. for 4 hours. Possibly the same equilibrium mixture would result under more drastic conditions.

Several conclusions on the mechanism of the reactions involved seem warranted. When monomeric lactic acid and methyl acetate are the reactants, the following reactions, along with others, are to be anticipated:

$$\mathrm{HOCH(CH_3)COOH + CH_3COOCH_3 \rightleftharpoons HOCH(CH_3)COOCH_3 + CH_3COOH} \quad (3)$$

$$\mathrm{HOCH(CH_3)COOH + CH_3COOCH_3 \rightleftharpoons CH_3COOCH\,(CH_3)COOH + CH_3OH} \quad (4)$$

$$\mathrm{HOCH(CH_3)COOCH_3 + CH_3COOCH \rightleftharpoons CH_3COOCH(CH_3)COOCH_3 + CH_3OH} \quad (5)$$

$$\mathrm{HOCH(CH_3)COOCH_3 + CH_3COOH \rightleftharpoons CH_3COOCH(CH_3)COOCH_3 + H_2O} \quad (6)$$

$$\mathrm{CH_3COOCH(CH_3)COOH + CH_3COOCH_3 \rightleftharpoons CH_3COOCH(CH_3)COOCH_3 + CH_3COOH} \quad (7)$$

$$\mathrm{CH_3COOCH(CH_3)COOH + CH_3OH \rightleftharpoons CH_3COOCH(CH_3)COOCH_3 + H_2O} \quad (8)$$

Inasmuch as lactic acid, a secondary alcohol, would be expected to react sluggishly in alcoholysis reactions (Equation 4) and methyl lactate was the principal product, probably reaction 3 predominated over reaction 4. Acetoxypropionic acid was present in negligible or small quantities, and therefore it seems likely that it was not formed in significant amounts or that it was transformed readily (via reaction 7 or 8) into methyl acetoxypropionate. Since all the methyl acetate reactions (Equations 3, 4, 5, and 7) are beneficial, the importance of using large proportions of this ester is clear. Inasmuch as the use of acetic acid with methyl acetate was not helpful (experiments 29 to 32), probably reaction 6 plays a minor role. Acetic acid would be actually detrimental if its presence caused reactions 3 and 7 to be reversed.

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PRESENTED as part of the Symposium on Lactic Acid and Derived Products before the Division of Industrial and Engineering Chemistry at the 106th Meeting of the AMERICAN CHEMICAL SOCIETY, Pittsburgh, Pa.

(Preparation of Methyl Acetoxypropionate)

PREPARATION FROM LACTIC ACID, ACETIC ACID, AND METHANOL

E. M. FILACHIONE AND C. H. FISHER

The conversion of lactic acid into methyl α-acetoxypropionate without the use of acetic anhydride, ketene, or acetyl chloride is described. Acetoxypropionic acid is formed satisfactorily when lactic acid, acetic acid, an entraining agent such as benzene, and an esterification catalyst such as sulfuric acid, are refluxed so that water is removed. Acetoxypropionic acid is transformed into its methyl ester by treatment with either methanol or methyl acetate. The best means for esterifying acetoxypropionic acid consists in passing this acid and methanol vapor countercurrently through a packed tower maintained at 70° to 130° C. The manufacture of methyl α-acetoxypropionate by this method would be particularly advantageous under wartime conditions as it would not require the construction of plants to convert acetic acid into acetic anhydride or ketene.

IN 1935 Burns, Jones, and Ritchie (*3*, *8*) first demonstrated that methyl acrylate, a valuable synthetic rubber (*9*, *10*, *13*, *15*) and resin (*7*) intermediate, can be made in high yields by the pyrolysis (*5*, *12*) of methyl α-acetoxypropionate; it has now become desirable to have efficient and low-cost methods for preparing this diester from lactic acid. An attractive continuous method (*4*), which comprised the conversion of lactic acid into methyl lactate followed by acetylation with acetic anhydride or ketene, was described recently; but this method requires either acetic anhydride or ketene, which are more expensive than acetic acid. The use of acetic acid as the acetylating agent would have the advantages of lowering the cost of methyl acetoxypropionate (assuming comparable yields) and eliminating the need of plant facilities to convert acetic acid into acetic anhydride or ketene. The desirability of using acetic acid as the acetylating agent is increased by the fact that acetic acid as well as methyl acrylate is produced by the pyrolysis of methyl acetoxypropionate:

$$\underset{\text{(I)}}{\mathrm{CH_3COOCH(CH_3)COOCH_3}} \xrightarrow{500^\circ\text{ C.}} \mathrm{CH_3COOH} + \mathrm{CH_2{:}CHCOOCH_3} \quad (1)$$

At least two approaches to the problem of preparing methyl acetoxypropionate with acetic acid as the acetylating agent can be followed. By the first, methyl lactate is prepared by esterification of lactic acid, and the methyl lactate is acetylated with acetic acid. The second approach comprises the acetylation of lactic acid with acetic acid, followed by esterification of the acetoxypropionic acid (II). Preliminary experiments showed that, although some of the desired diester (I) is obtained, methyl acetate is formed readily when methyl lactate is treated with acetic acid. Since this side reaction cannot occur when lactic acid is acetylated, the possibility of transforming lactic acid into methyl acetoxypropionate by the second route (Equations 2 and 3) was investigated:

$$\mathrm{CH_3COOH} + \mathrm{HOCH(CH_3)COOH} \longrightarrow \underset{\text{(II)}}{\mathrm{CH_3COOCH(CH_3)COOH}} + \mathrm{H_2O} \quad (2)$$

$$\underset{\text{(II)}}{\mathrm{CH_3COOCH(CH_3)COOH}} + \mathrm{CH_3OH} \longrightarrow \underset{\text{(I)}}{\mathrm{CH_3COOCH(CH_3)COOCH_3}} + \mathrm{H_2O} \quad (3)$$

TABLE I. PREPARATION OF ACETOXYPROPIONIC ACID FROM LACTIC[a] AND ACETIC ACIDS

Expt. No.	Lactic Acid, Moles	Acetic Acid, Moles	Ratio, Acetic: Lactic	Entraining Agent, Ml.	Catalyst, Ml.	Time of Reflux, Hr.	Yield of Acetoxypropionic Acid, %
147	1.0	8.75	8.58[b]	Benzene, 150	H_2SO_4, 1	5.3	55
212	1.0	6.0	6[c]	Benzene, 200	Same	5.5	71.5
215	1.0	16.6	16[c]	Same	Same	10.	74
218	1.0	16.6	16[c]	Same	Same	6.5	78.4
139	6.0	18.0	2.6[b]	Benzene, 300	H_2SO_4, 1.5	25.5	68
314	4.0	8.0	1.7[b]	Benzene, 200	H_2SO_4, 1	15.3	40
316	4.0	12.0	2.4[b]	Same	Same	14.5	55
317	4.0	16.0	3.3[b]	Same	Same	19.5	61
319	4.0	20.0	4.1[b]	Same	Same	18.3	70
321	4.0	24.0	5.0[b]	Same	Same	12.8	67
323	4.0	28.0	6.0[b]	Same	Same	21.0	77
325	4.0	32.0	6.8[b]	Same	Same	14.3	71
173	4.0	20.0	4.0	Same	Same	15.0	61
333	1.0	16.6	15.4[b]	Same	H_2SO_4, 0.25	15.4	60
322	4.0	28.0	7[c]	Isopropyl acetate, 200	H_2SO_4, 1	9.3	67

[a] 80% lactic acid solution was used except in experiment 147, in which 100% acid was used.

[b] Correction made for amount of acetic acid removed with water by entraining agent.

[c] Approximate.

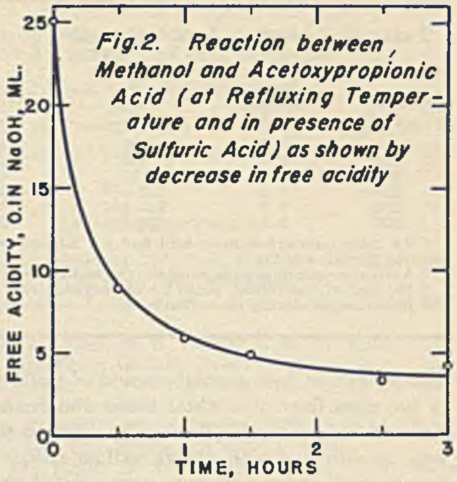

Fig. 2. Reaction between Methanol and Acetoxypropionic Acid (at Refluxing Temperature and in presence of Sulfuric Acid) as shown by decrease in free acidity

The acetyl derivative of lactic acid (II) has been prepared by the reaction of lactic acid with acetic anhydride (*2*, *11*) and with acetyl chloride (*1*, *6*), but apparently no previous attempts to acetylate lactic acid with acetic acid have been described.

REACTION OF ACETIC ACID WITH LACTIC ACID

Since lactic acid has a carboxylic acid group as well as an alcohol group, at least two reactions can occur when a mixture of lactic acid and acetic acid is heated and the water of esterification is removed. In the desired reaction, the alcoholic hydroxyl group of lactic acid reacts with the acetic acid to form acetoxypropionic acid. The alcoholic hydroxyl group also reacts with the lactic acid carboxyl group, forming lactyllactic acid (where $x = 2$) and similar linear condensation products (*14*) of lactic acid:

$$HO[CH(CH_3)COO]_x H \qquad (III)$$

Probably the linear condensation products (III) of lactic acid react with acetic acid in two ways. The acetic acid may acetylate the terminal alcoholic hydroxyl group, or it may decrease the chain length of the linear condensation products by acidolysis. Since all the reactions with acetic acid lead to the formation of acetoxypropionic acid, it would be expected that an excess of acetic acid would be helpful. Experience has borne out this expectation.

A commercial, edible grade of 80% lactic acid, which was almost colorless, was used in most of the acetylation experiments. The lactic acid was acetylated by refluxing a mixture of lactic acid, acetic acid, an entraining agent such as benzene, and a small amount of an esterification catalyst such as sulfuric acid, condensing the vapors, and returning the benzene layer to the reaction mixture (in a modified Dean and Stark tube). The reaction was considered complete when approximately one mole of water had been removed for each mole of lactic acid in the reaction mixture. After the mineral acid had been neutralized with anhydrous sodium acetate (usually 4 grams of sodium acetate per ml. of sulfuric acid), the acetoxypropionic acid was distilled under reduced pressure.

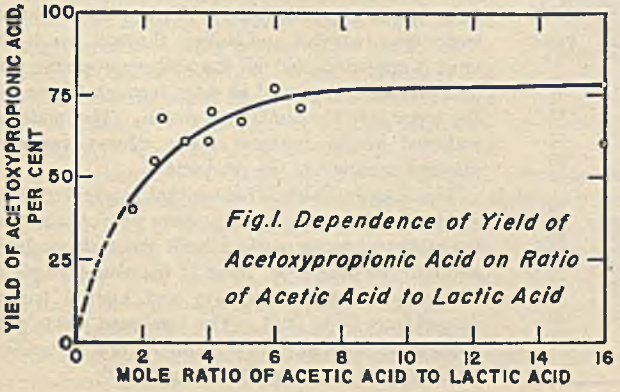

Fig. 1. Dependence of Yield of Acetoxypropionic Acid on Ratio of Acetic Acid to Lactic Acid

The results of the acetylation experiments show that acetoxypropionic acid can be made satisfactorily and in high yields by the reaction of acetic acid with lactic acid. The amount of lactic acid converted into acetoxypropionic acid varied with the amount of acetic acid used. The yield of acetoxypropionic acid was approximately 80% when a considerable excess of acetic acid was used (Table I). The dependence of yield upon the ratio of acetic acid to lactic acid is shown in Figure 1. The brown, viscous distillation residues, which probably consist mainly of acetylated condensation products of lactic acid, should be useful as a starting material in making monomeric lactic acid, methyl lactate, or acetoxypropionic acid.

Since both acetic and lactic acids are inexpensive and potentially available in large quantities, acetoxypropionic acid could be made on a large scale at low cost. As ordinarily prepared, this acid is a moderately viscous fluid that supercools easily and is difficult to crystallize unless seeded. When crystallized, the acid is a low-melting solid (*2*). It distills at 75° C. (0.2 mm.), 90° (1 mm.), and 165° to 172° (75 mm.).

REACTION OF ACETIC ACID WITH POLYLACTIC ACID

Acetoxypropionic acid was prepared also by the acidolysis of polylactic acid (III) with acetic acid. The linear condensation polymer of lactic acid was prepared by dehydrating, under 20 mm. pressure, 200 grams of 100% lactic acid containing 2 grams of *p*-toluenesulfonic acid. Water was distilled from this mixture (final temperature of reaction mixture, 150° C.) for several hours; the total distillate, mainly water, was 38.5 grams (approximately 96% dehydration). The distillation residue was then treated with 1000 grams of glacial acetic acid, and the resulting mixture was refluxed for 9.5 hours. After the addition of 3 grams of sodium acetate the mixture was distilled. The yield of acetoxypropionic acid was 26%. The results of this experiment indicate that the esterification of the alcoholic hydroxyl group is more rapid than the acidolysis of the ester group.

REACTION OF ACETOXYPROPIONIC ACID WITH METHYL ACETATE

Because of the high vapor pressure of methyl acetate, the reaction of methyl acetate with acetoxypropionic acid was studied in a closed system. A mixture of acetoxypropionic acid,

Table II. Methyl Acetoxypropionate from Acetoxypropionic Acid and Methyl Acetate[a]

Expt. No.	Methyl Acetate, Moles	Temp., ° C.	Methyl Acetoxypropionate Conversion, %[b]	Methyl Acetoxypropionate Yield, %[c]
214	1.25	100	33	61
219	2.5	100	33	77
223	2.5	125	40[d]	66[d]
225	2.5	120–130	35	74
226	2.5	140–150	60	84
227	2.5	120–126	54	81

[a] 0.5 mole acetoxypropionic acid and 0.5 ml. concentrated H_2SO_4 used; reaction period, 4 hours.
[b] Acetoxypropionic acid converted into methyl ester.
[c] Per cent of theoretical, based on acetoxypropionic acid destroyed.
[d] Bomb leaked during the experiment.

methyl acetate, and a small amount of sulfuric acid was placed in the glass liner of a metal bomb and heated for 4 hours at different temperatures (Table II). The contents of the bomb were then treated with enough sodium acetate to neutralize the sulfuric acid, and the products were isolated by distillation under reduced pressure.

The highest yield of methyl acetoxypropionate obtained by the reaction of acetoxypropionic acid with methyl acetate was 84% (Table II). Acetic acid also was isolated. The most extreme experimental conditions used (140° to 150° C. for 4 hours) were not drastic. This reaction, which does not require acetic anhydride or ketene, could be employed to prepare methyl acetoxypropionate.

ESTERIFICATION OF ACETOXYPROPIONIC ACID AND METHANOL

Because of the importance of the reaction, the esterification of acetoxypropionic acid and methanol was studied extensively under various conditions. In some of the experiments, mixtures of the two reactants were heated in the liquid phase and then distilled to determine the nature and amounts of the products. In other experiments the esterification was effected by passing methanol vapor and acetoxypropionic acid countercurrently through a packed tower under atmospheric or reduced pressures.

The liquid-phase esterifications were carried out by refluxing a mixture of 0.5 mole of acetoxypropionic acid, 2.5 moles of methanol, and 0.5 ml. of sulfuric acid. At the end of the reaction period the sulfuric acid was neutralized with sodium acetate (2 grams), and the products were isolated by distillation. The course of the reaction was followed by titration of small samples of the reaction mixture to determine the free acidity. The results (Figure 2) show that the free acidity almost reaches its minimum value in 2 hours. High yields of methyl acetoxypropionate were not obtained because of the formation of methyl lactate and methyl acetate. The yields, respectively, of methyl acetoxypropionate, methyl lactate, and methyl acetate were 34, 43, and 36% after 1 hour of refluxing, and 21, 52, and 48% after 3 hours. In both instances the combined yields of the lactic esters were more than 70%. Probably the distillation residues contained polylactic acid (III) or esters of polylactic acid, which should be of some value as a source of monomeric lactic acid, methyl lactate, or acetoxypropionic acid.

Much higher yields were obtained when the esterification was carried out with methanol vapor in a packed tower under nonequilibrium conditions. Slightly different techniques were used at atmospheric and at 100 mm. pressure.

Under a pressure of approximately 100 mm., a mixture of acetoxypropionic acid, methanol, and sulfuric acid was added dropwise into the top of a Pyrex tower (1 × 48 inches) packed with 1/4-inch porcelain Berl saddles and was electrically heated. The temperature of the column was controlled and recorded automatically. Methanol was passed into a heated vaporizing flask, and the vapor issuing from this flask was passed into the bottom of the packed tower. The methanol vapor was passed through the tower as long as acetoxypropionic acid was being passed into the column and until the dry appearance of the packing indicated that all the acetoxypropionic acid had reacted. The vapors withdrawn from the top of the tower, which consisted of methanol, methyl acetoxypropionate, and other volatile products, were passed into the center of a steam-jacketed distillation column packed with small Berl saddles. The methanol and water vapors that passed through this stripping still were condensed. The products of higher boiling points, which were collected at the bottom of the distilling column, were redistilled in a vacuum to determine the amounts of methyl lactate and methyl acetoxypropionate obtained. Yields of methyl acetoxypropionate as high as 72–75% were obtained at temperatures of 80°–100° C. Methyl lactate also was produced (Table III).

When acetoxypropionic acid was esterified with methanol vapor in the packed tower under atmospheric pressure, the procedure was slightly modified. As before, methanol vapor and acetoxypropionic acid were passed countercurrently through the tower, and the vapors withdrawn from the top of the tower were passed into the center of the steam-jacketed distilling column. The methanol distilling from the top of the column was condensed and returned through a liquid seal to the heated vaporizing flask. When the esterification was carried out at temperatures below 108° C., the material collected at the bottom of the distilling column contained water and some methyl lactate and methyl acetoxypropionate, but most of the esters passed downward through the esterification tower and were collected in a flask at the base. The contents of the flasks located at the bottom of both the distillation and esterification columns were distilled under reduced pressure to determine the yields of methyl lactate and methyl acetoxypropionate (Table III).

When esterification was carried out in the packed tower under atmospheric pressure and at temperatures above approximately 108° C., the methanol vapor was recycled and passed through the tower until it appeared that all the acetoxypropionic acid had reacted and passed as ester through the top of the tower into the distilling column. The material collected at the bottom of the column was then distilled to separate the products.

The data in Table III show that moderately high yields of methyl acetoxypropionate were obtained by the methanol vapor method, both under atmospheric and reduced pressures. Most of the combined yields of methyl acetoxypropionate and methyl lactate ranged from 80 to 90%. The combined yields were moderately high even in the absence of an esterification catalyst (experiments 311 and 312).

Table III. Methyl Lactate and Acetoxypropionate Produced by Reaction of Acetoxypropionic Acid with Methanol Vapor in a Packed Tower

Expt. No.	Acetoxypropionic Acid, Mole	H_2SO_4, Ml.	Temp., ° C.	Pressure, Mm.	Time, Hr.	Methyl Lactate		Methyl Acetoxypropionate	
						Conversion, %[a]	Yield, %[b]	Conversion, %[a]	Yield, %[b]
296	0.5	0.25	97–101	90–110	1.33	..	22	..	58
297	0.5	0.10	95–102	90–110	1.2	..	10	..	72
307	1.0	0.20	82–87	90–110	3.8	..	11	..	75
308	1.0	0.20	93–98	78–95	2.6	..	17	..	72
309	1.0	0.20	98–118	95–130	2.1	..	9	..	72
310	1.0	0.20	115–122	70–110	1.3	..	8	..	65
311	1.0	None	115–122	85–105	6.5	5	8	33	51
295	0.5	0.25	122–135	Atm.	1.8	..	47	..	34
312	1.0	None	128–133	Atm.	3.0	15	24	39	62
313	1.0	0.02	128–136	Atm.	2.0	21	25	46	55
324	1.0	0.05	74–79	Atm.	0.5	3	7	20	50
326	1.0	0.05	82–88	Atm.	0.7	6	10	35	60
327	1.0	0.05	ca. 95	Atm.	0.6	6	11	28	54
328	1.0	0.05	101–108	Atm.	0.7	10	19	31	60
329	1.0	0.05	74–79	Atm.	2.5	7	14	35	71

[a] Per cent of acetoxypropionic acid converted.
[b] Per cent of theoretical, on basis of acetoxypropionic acid destroyed.

DISCUSSION OF RESULTS

The production of methyl acetoxypropionate from lactic acid, acetic acid, and methanol by the methods described here have the advantage of not requiring the use of acetic anhydride or ketene, but the yields are not so high as those obtained by conversion of lactic acid into methyl lactate followed by acetylation with acetic anhydride, as described in the preceding paper. To afford a comparison of the relative merits of the two methods, the materials costs of methyl acetoxypropionate prepared by the two methods were calculated. The prices assumed for the intermediate chemicals may not have been exactly correct, but the same prices were used for both methods and therefore the calculated material costs should be adequate for a preliminary comparison. In making the calculations, the cost of sulfuric acid used as catalyst was not included, and it was assumed that an over-all yield of 85% acetoxypropionic acid could be obtained from lactic acid by treatment of the distillation residues with acetic acid. The other yields assumed in estimating relative costs were: 75% methyl acetoxypropionate and 10% methyl lactate in the esterification of acetoxypropionic acid, 90% methyl lactate in the esterification of lactic acid, and 96% methyl acetoxypropionate in the acetylation of methyl lactate. All yields were calculated on the basis of unrecovered starting materials.

The calculated cost of materials indicated that the acetoxypropionic acid method of making methyl acetoxypropionate is somewhat more expensive (approximately 2 cents per pound) than the previously described methyl lactate method (*4*). The acetoxypropionic acid method, however, has the advantage of not requiring plants for the manufacture of acetic anhydride or ketene. Owing to the shortage of alloys and other construction materials, this advantage would be highly important under wartime conditions if large quantities of methyl acrylate were manufactured by the pyrolysis of methyl acetoxypropionate.

ACKNOWLEDGMENT

The assistance and cooperation of other members of the Carbohydrate Division of this laboratory are gratefully acknowledged.

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Presented as part of the Symposium on Lactic Acid and Derived Products before the Division of Industrial and Engineering Chemistry at the 106th Meeting of the American Chemical Society, Pittsburgh, Pa.

CLASSIFICATION of TOBACCO

Nicotine-Nornicotine Method

C. V. BOWEN and W. F. BARTHEL
Bureau of Entomology and Plant Quarantine,
U. S. Department of Agriculture, Beltsville, Md.

The melting points of the picrates of known mixtures of nicotine and nornicotine indicate that the melting point of the steam-volatile alkaloid picrate may be used as a means of classifying tobaccos as to alkaloidal type. According to the upper limit of the melting point spread, the tobacco is classified as nicotine type (melting point above 211° C.), mixed nicotine-nornicotine type (melting point 198–211° C.), and nornicotine type (melting point below 198° C.). Six tobaccos of known nicotine and nornicotine content were tested for melting point of mixed picrates, and they were found to agree with the classification.

THE recent discovery of the widespread occurrence of nornicotine in tobaccos (*2*) brings up the need for their rapid classification according to the predominant alkaloid. Markwood and Barthel (*4*) made such a classification based on the melting points of the picrate of the benzene-soluble alkaloids. Thus, tobaccos giving picrate melting points above 215° C. were classified as nicotine type, those giving melting points between 175° and 200° C. as nornicotine type, and those between 190° and 215° C. as mixed type. No composition limits corresponding to these melting point limits were given. Furthermore, it is now known that some tobaccos contain other benzene-soluble basic materials which influence the picrate melting point. The work has therefore been continued to establish a rough correlation between composition and melting point for known mixtures of nicotine and nornicotine and to check the classification scheme adopted against the melting points of picrates obtained from analyzed samples of tobacco.

RELATION BETWEEN PICRATE MELTING POINT AND COMPOSITION

Known mixtures of standard nicotine and nornicotine solutions were treated with aqueous picric acid solution to obtain mixtures of the coprecipitated picrates. The standard solution of nicotine was prepared from a sample that had been vacuum-distilled, treated with nitrous acid to remove any secondary amines, and then steam-distilled from an aqueous alkaline solution. The nornicotine used in the standard solutions was identical with that

TABLE I. MELTING POINT SPREAD OF PICRATES OF KNOWN MIXTURES OF NICOTINE AND NORNICOTINE

Nicotine, %	Nornicotine, %	M.P. Spread (Cor.), ° C.	Nicotine, %	Nornicotine, %	M.P. Spread (Cor.), ° C.
0	100	186.9–189.6	45.3	54.7	175.5–204.1
5.2	94.8	167.8–180.4	52.5	47.5	180.0–206.2
10.6	89.4	180.3–184.1	62.4	37.6	192.0–208.3
13.7	86.3	177.8–184.6	68.9	31.1	194.5–211.7
15.7	84.3	175.3–183.1	81.6	18.4	204.9–217.5
20.8	79.2	178.4–182.6	89.9	10.1	213.0–219.9
30.0	70.0	178.4–182.5	100	0	218.7–224.8
35.6	64.4	177.4–199.9			

used by Markwood (*3*), which had been obtained from the Robinson Medium Broadleaf strain of Maryland tobacco, and formed a picrate melting at 190–191° C. The absence of nicotine was established by treating a sample with nitrous acid and by steam distilling the aqueous solution after making it basic to phenolphthalein. Upon heating in a capillary tube, each mixture of the alkaloid picrates so obtained melted, not sharply but over a temperature range that varied with the composition. This range or spread, from the temperature of first noticeable softening to that of disappearance of the last crystal, is shown in Table I and Figure 1. The latter point was much more reproducible and will be referred to as the upper limit of the melting point spread.

Figure 1 shows that the upper limits of the melting point spread of mixtures rich in nicotine fall on a straight line; those of mixtures rich in nornicotine are approximately alike and definitely lower than the lowest temperature reached by this line. Evidently a eutectic mixture exists. Since this abrupt change in the character of the curve occurs naturally at a composition of two thirds nornicotine and one third nicotine, it furnishes a convenient composition limit for nornicotine-type tobaccos. By analogy, the composition two thirds nicotine and one third nornicotine can be selected as the limit for nicotine-type tobaccos. The fairly rapid change of melting point with composition makes the differentiation easy and definite between a mixture rich in nicotine, and one not so rich. These upper limits of melting point spread of the nicotine-nornicotine picrates serve as a basis for classifying the tobaccos melting below 198° C. as nornicotine type, those melting above 211° as nicotine type, and those melting between these temperatures as mixed type.

ALKALOID PICRATE MELTING POINTS OF ANALYZED TOBACCOS

Previous analyses (*2*) of several tobaccos for nicotine and nornicotine were compared with the melting points of the alkaloid picrates, as determined both by the benzene-extraction method of Markwood and Barthel (*4*) and by the proposed steam-distillation method (Table II).

According to the Markwood and Barthel classification, based on melting point spread, it is obvious that if their data for tobacco samples had been plotted, the melting point spread would in all cases have fallen within areas *A*, *B*, and *C* in Figure 2. Although this was satisfactory by their procedure for the tobaccos studied, it is evident that samples with part of their spread in area *D* will be encountered—namely, Maryland-Connecticut Broadleaf. Certain known solutions also gave values lying outside the ranges prescribed in their classification. The use of only the upper limit of the melting point spread makes allowance for all possible mixtures.

The presence of benzene-soluble basic material, such as the nonsteam-volatile alkaloid in Maryland-Connecticut Broadleaf, precludes the use of benzene extraction of the alkaloids. Since nicotine and nornicotine are volatile with steam, a steam distillation into dilute hydrochloric acid and subsequent concentration of the distillate eliminates the use of benzene and shortens the time required. This method is briefly described as follows:

Mix a 2-gram sample of tobacco with 10 grams of sodium chloride and 10 ml. of sodium hydroxide solution (30% by weight) and steam distill into 3 ml. of hydrochloric acid. With the use of an improved steam distillation apparatus (*1*) the distillation can be completed within 30 minutes. Make the distillate just acid to phenolphthalein, evaporate to a small volume, filter into a small flask, neutralize with sodium hydroxide solution, add 25 ml. of saturated aqueous picric acid solution, and evaporate to 30 ml. Allow to stand to crystallize. If no crystals form, a larger sample of tobacco should be taken for the determination.

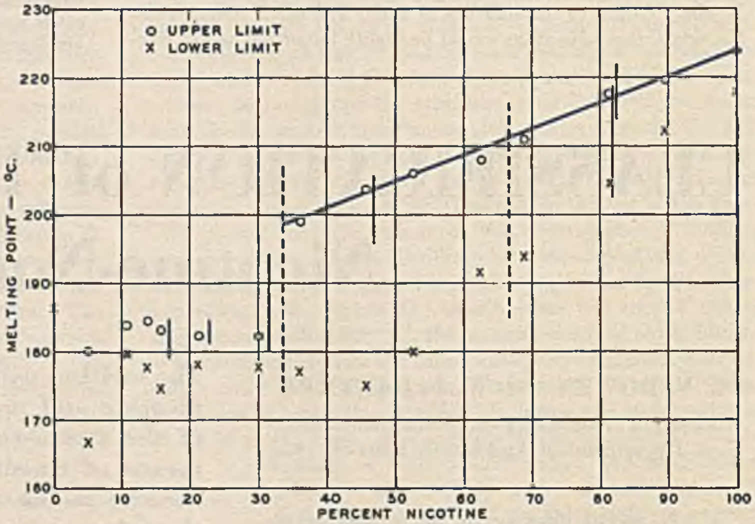

Figure 1. Melting Point Spread of Picrates of Known Mixtures of Nicotine and Nornicotine

Solid vertical lines show the melting point spread of analyzed samples of tobacco; broken lines show the composition range of each class of tobacco.

TABLE II. RELATION BETWEEN NICOTINE-NORNICOTINE CONTENT AND ALKALOID PICRATE MELTING POINT OF CERTAIN TOBACCOS

Tobacco[a]	Analysis, %		Nornicotine in Nicotine-Nornicotine Mixt., %	M.P. Spread (Cor.), ° C.		Classification Type
	Nicotine	Nornicotine		Benzene extn.	Steam distn.	
Nicotiana tobacum						
Robinson Maryland Medium Broadleaf, sample 1	0.34	1.71	83.4	184.6–185.6	179.4–184.6	Nornicotine
Cash, flue-cured	0.70	2.40	77.4	173.2–183.6	181.6–184.6	Nornicotine
Robinson Maryland Medium Broadleaf, sample 2	0.98	2.16	8.86	179.4–196.1	180.4–194.1	Nornicotine
Burley, Halley	1.23	1.41	53.4	192.0–124.0	196.1–205.6	Mixed
Maryland-Connecticut Broadleaf	2.22	0.49	18.1	215.6–220.9[b]	202.5–218.9	Nicotine
Nicotiana rustica	4.57	0.99	17.8	215.1–219.3	214.0–221.9	Nicotine

[a] Sample 1 was the source of nornicotine used in the standard solution; in the other samples the steam-volatile secondary-amine alkaloid was identified as nornicotine by methylation.

[b] Due to an additional alkaloid (approx. 0.2%), not steam volatile, having a melting point spread of 237.1–237.6° C.

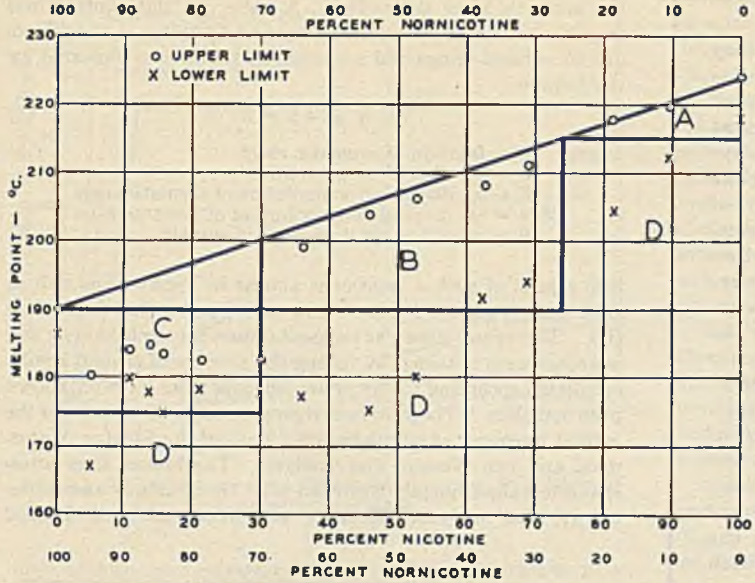

Figure 2. Area of Melting Point Spread According to the Markwood and Barthel Classification in Relation to Data for Known Mixtures in Figure 1

The melting point is taken without recrystallization, which would tend to eliminate the minor alkaloid. The presence of picric acid accounts for the spread in the melting points of pure nicotine picrate and pure nornicotine picrate (Table I).

Although the picrate melting point is not intended to be a quantitative procedure, the close agreement between the percentage composition and the melting point of the steam-volatile alkaloid picrate obtained from tobacco with the values obtained from the known solutions is striking.

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OXIDATION OF LUBRICATING OILS

Effect of Natural Sulfur Compounds and of Peroxides

G. H. DENISON, JR.
Standard Oil Company of California, San Francisco, Calif.

IN ACTUAL service the oxidation of a lubricating oil takes place in highly complicated systems. For example, in an internal combustion engine, catalysis by metal surfaces and metal soaps as well as complex variations in temperature and oil-air agitation throughout the oil stream markedly affect stability. To investigate the mechanism of oxidation in such a complicated system without adequate knowledge of the oxidation in simple systems does not appear sound. The aim of the present paper is to aid in establishing a basic mechanism of oil oxidation under as simple conditions as feasible; when adequate knowledge has been obtained, effect of service variables and catalysts may be dealt with as perturbations on the reactions taking place in simple systems.

Before lubricating oil oxidation can be discussed, a picture of oil constitution must be established. A finished lubricating oil consists of a multitude of different hydrocarbons, which make up from 80 to 98% of the stock. In addition, there are 2 to 20% sulfur compounds, 0.08 to 0.3% nitrogen compounds and some oxygen compounds. These materials may so perturb the oxidation of one another as to mask completely any similarity of the oxidation mechanism to those of the pure, low-molecular-weight compounds in the literature.

The resistance of oil to deterioration varies with the source of the crude and the treatment it receives. Simultaneously, with this variation in stability, the oil varies both in its major fraction, hydrocarbons, and in the small percentage of nonhydrocarbons present, such as sulfur compounds. The most obvious point of attack in studying composition, at least for oxidation research, consists in determining whether the hydrocarbons or the nonhydrocarbons control the oxidation characteristics.

HYDROCARBON FRACTION

There are two general methods by which the composition of a mixture such as lubricating oil can be determined or, more literally, approximated. These methods might be termed "analytic" and "synthetic". In the analytic method the mixture is separated by physical and chemical processes into its components, which are analyzed and compared with known substances. In the case of lubricating oils this process is exceedingly difficult because of the complexity of the mixture. The synthetic method employs the procedure of preparing compounds similar to those expected to be present in the mixture and comparing the properties of the synthesized substances and their blends with those of the lubricating oil. This method is simpler than the analytical method, but definite proof of composition is never established. Both of these methods have been applied by Mikeska (7) and by many others.

In applying the analytic method to the present problem, the technique adopted at the National Bureau of Standards was followed and the finished lubricating oil separated into narrow fractions by solvent extraction in a Fenske column, as described by Mair and Schicktanz (5).

The hydrocarbon fraction of refined lubricating oils is shown to consist of naphthenes in admixture with homologs of benzene and naphthalene. By removing natural sulfur compounds without appreciably affecting other constituents, this hydrocarbon fraction is shown to possess negligible resistance to oxidation. Thus, the few per cent of natural sulfur compounds present in a finished lubricating oil appear to determine the oxidation characteristics. This control of stability is interpreted as resulting from the fact that the hydrocarbon fraction oxidizes at a rate controlled by the concentration of organic peroxides, and the latter are reduced by reaction with the natural sulfur-containing inhibitors residual in the refined lubricating stock. In addition to controlling the rate of oxidation of an oil, the organic peroxides determine the rate of corrosion of bearing metals. Such corrosion is shown to result from the ability of peroxides to convert metal into metal oxide, the latter subsequently dissolving by reaction with acidic constituents developed during oxidation.

Each fraction was analyzed as follows: The ring analysis devised by Vlugter, Waterman, and van Westen (*8*) was employed to estimate the percentage of different types of hydrocarbon groups (paraffinic, naphthenic, and aromatic) present in the base oils and in the fractions produced by the solvent treatment. Since many types of aromatic nuclei are possible in a lubricating oil, and inasmuch as the type of aromatic nucleus will affect stability, a classification of aromatic fractions was desirable. For this purpose a chart published by Mair, Willingham, and Streiff (*6*) was used. They correlated the number of carbon atoms per molecule with the specific dispersion of a large number of hydrocarbons, and were able thereby to classify unknown aromatic bodies. The result of such an analysis on an S. A. E. 30 oil (A, Table I), prepared by moderate refinement of a California naphthenic crude, is shown in Table II. Since the quantity of each fraction decreased as the extraction progressed, it was necessary after removal of the first six to combine the succeeding fractions into pairs; thus fraction 7 was in reality fraction 7 plus fraction 8. As was to be expected, the successive fractions decreased in specific dispersion and per cent aromatic rings.

To use directly the specific dispersion chart of Mair, Willingham, and Streiff, the number of carbon atoms per molecule for each fraction was approximated by dividing the molecular weight by 13.5. Plotting these specific dispersion values for the extracts did not furnish much information on composition. The points on such a plot started close to the alkyl naphthalene line and followed down to that of almost pure naphthenes. Such behavior results from the fact that, as a result of variation in molecular weight and in the nature of the paraffin side chains, the various extracts are necessarily blends of aromatics and nonaromatics rather than pure alkyl aromatics.

Considerably more information on the nature of the extract fractions is obtained if the per cent aromatic rings and specific dispersion are used to calculate the specific dispersion contribution of the aromatic rings themselves. A value for this contribution may be estimated by assuming linear additivity of the effects due to aromatic rings and nonaromatic residues as indicated by the formula:

$$aY + 98.4\,b = S \qquad (1)$$

where a = fraction of aromatic rings
b = fraction of nonaromatics
Y = sp. dispersion contribution of aromatic rings
98.4 = sp. dispersion contribution of nonaromatics
S = measured sp. dispersion of sample

The results of such a treatment appear in Figure 1, as well as similar analyses of a Pennsylvania oil (B) and a Gulf Coastal oil (C). The values shown as horizontal lines for naphthalenes and benzenes were obtained by taking the average of several results calculated according to the above formula from data on known pure homologs. The solid lines represent the original data for the extract fractions, as calculated on a basis of the Vlugter, Waterman, and van Westen ring analysis. The broken lines correspond to values roughly corrected to fit the Deanesly and Carleton (*1*) ring analysis. That the aromatics present in finished lubricating oils of various origins are fundamentally benzene and naphthalene homologs appears evident. Therefore to evaluate the stability of the hydrocarbon fraction of a lubricating oil, a study of the stability of blends of naphthalene, benzene, and naphthene hydrocarbons should suffice.

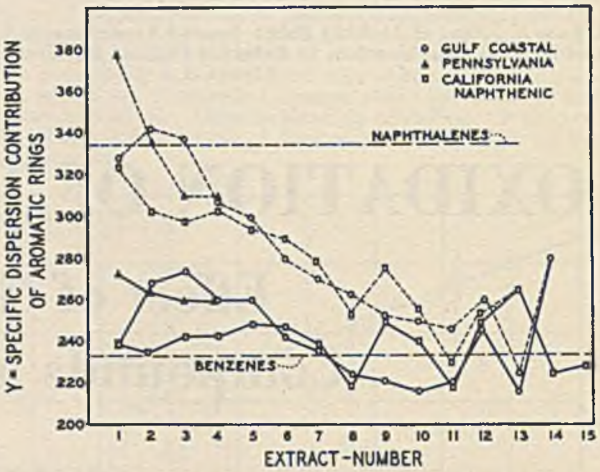

Figure 1. Characterization of Aromatic Fractions from Lubricating Oils

The oxidation characteristics of such lubricating-oil-like hydrocarbons has already been reported by Larsen, Thorpe, and Armfield (*4*), and present work along this line is in complete accord. It suffices to say that alkyl naphthenes, including petroleum white oil, oxidize autocatalytically and are extremely unstable as compared to straight lubricating oils. Alkyl benzenes and alkyl

Table I. Inspections of Oils Studied

Oil Designation	Gravity, ° A.P.I.	Flash Point, ° F.	Viscosity, Saybolt Univ. Sec. 100° F.	Viscosity, Saybolt Univ. Sec. 210° F.	Viscosity Index	Pour Point, ° F.	A.S.T.M. Color	Neutralization No.	Conradson Carbon, %	Sulfur, %
A	21.3	385	627	56.5	8	−20	3	0.04	0.08	0.53
B	30.3	425	183	45.5	100	5	3	0.07	0.03	0.15
C	21.9	410	585	57.5	34	−10	2	0.02	0.03	0.20
D	29.4	480	424	58.1	90	0	1½	0.03	0.02	0.22
E	28.2	445	530	66.4	102	20	6	0.04	0.48	0.10
F	27.0	395	343	51.0	61	−25	Water-white	0.01	0.00	0.03
G	26.8	405	363	51.3	52	−25	1−	0.02	0.01	0.12
H	29.2	435	342	54.2	93	−15	2½	0.10	0.14	0.18
K	20.2	380	455	50.9	0	−10	3−	0.02	0.06	0.82

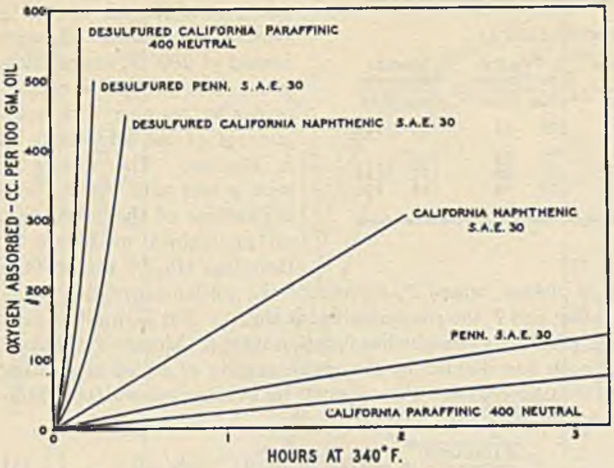

Figure 2. Effect of Desulfurization upon Stability of Lubricating Oils

diphenyls are also extremely unstable. Alkyl naphthalenes, on the other hand, can be extremely stable and even more resistant to oxygen absorption than the best lubricating oils.

In spite of this extreme stability of alkyl naphthalenes, if an attempt is made to blend them with naphthenes in such proportions as to obtain an aromatic content comparable to that of lubricating oils, blends are obtained with stabilities relatively little better than that of medicinal white oil. Therefore, in spite of the temptation to give undue credit to the alkyl naphthalenes, the hydrocarbon fraction of a lubricating oil cannot have much to do with its resistance to oxidation. Larsen *et al.* came to the same conclusion.

Since the hydrocarbon fraction of a lubricating oil does not control its stability, an investigation of the next most abundant fraction was undertaken some years ago. An attempt was made to desulfur lubricating oils completely without appreciably changing the hydrocarbon fraction. At first a simple vacuum distillation from sodium metal was tried. The distillate, however, contained about 90% of its original sulfur and was still stable; in fact, many oils so treated increased in stability. One conclusion to be drawn from this experiment is that natural acidic or phenolic bodies which would be removed by such a treatment play no appreciable part in stabilizing the lubricating oil.

Desulfurization was finally accomplished by contacting the oil for several hours with sodium metal at 500° F. under 200 pounds per square inch hydrogen pressure. After washing and mild clay treatment the oil contained 0.07% sulfur in one run and 0.03% in a check run, a marked reduction from the original 0.53% sulfur. As indicated by bromine number, no olefinization occurred. Since such a treatment might otherwise affect the hydrocarbons, the specific dispersion was measured and a Waterman analysis was made. The results of these analyses after treatment of this moderately refined naphthenic stock (oil A) and of three other lubricating oils from various sources are shown in Table III. Actually, the drop in per cent aromatic rings as indicated by this analysis is known to be excessive since experiments with synthetic sulfur compounds have shown that the addition of 0.1% sulfur as a nonaromatic organic compound gives, in general, an apparent rise of 1% in aromatic rings. Thus any apparent decrease in aromaticity can, within the experimental error of the ring analysis, be attributed to the removal of sulfur compounds. As Figure 2 shows, these desulfured oils exhibited instability of a degree similar to the white oils. Some question might be raised as to whether in this experiment the difference between the original and treated stock was solely due to sulfur compounds. However, since phenolics were eliminated by the results of the sodium distillation and since the Waterman analyses and specific dispersions afforded fair proof of an unvaried hydrocarbon content, natural sulfur compounds seem to be the agents responsible for the stability of straight mineral lubricating oils.

This fact would seem to be the major key to a simplification of the research on lubricating oil oxidation. The problem of oxidation mechanisms can then be best approached by first carefully studying the oxidation mechanism of an idealized sulfur-free oil and then the perturbing effect of sulfur compounds on these reactions.

Table II. Hydrocarbon Analysis of California Naphthenic-Type Lubricating Oil by Solvent Extraction in Fenske Column

Fractions	Yield, %	Sp. Dispersion	C Atoms per Mol.	Aromatic Rings, %	Naphthene Rings, %	Paraffin Side Chains, %
1	3.8	189	20.1	64	18	18
2	3.3	174	21.4	55	15	30
3	2.3	166	22.0	47	18	35
4	2.0	166	22.6	45	20	35
5	1.5	159	22.6	41	23	36
6	2.2	156	23.1	38	23	39
7	3.5	152	23.9	39	23	38
8	3.1	143	24.0	37	24	39
9	3.1	145	24.5	31	28	41
10	2.5	138	24.5	28	30	42
11	2.4	130	26.1	27	30	43
12	2.3	133	25.0	23	35	42
13	2.2	129	23.8	19	39	43
14	2.0	124	25.1	20	37	43
15	1.6	114	27.6	12	41	47
Raffinate	62.1	101	28.7	0.7	44	55
Original oil	..	120	27.0	15	33	52

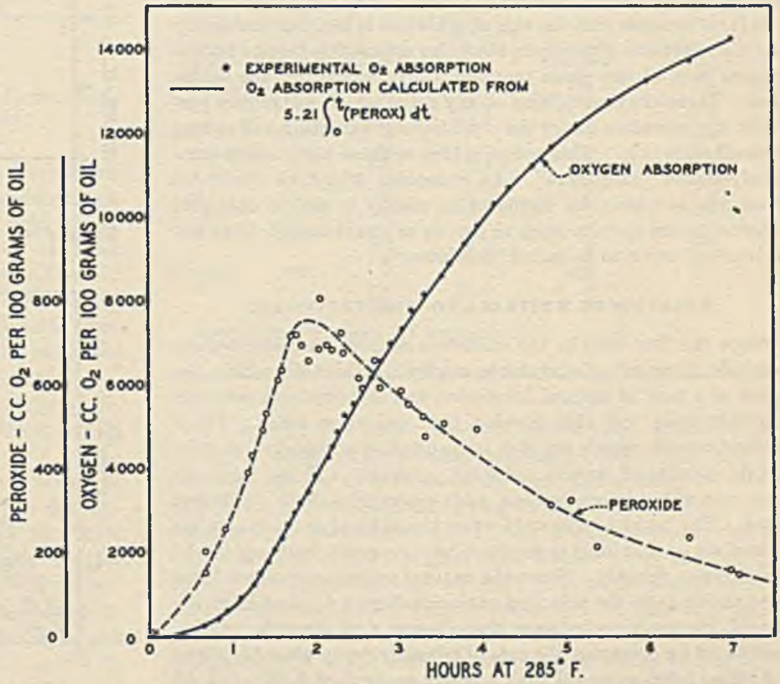

Figure 3. Dependence of Oxygen Absorption on Peroxide Concentration (Oil F)

Table III. Effect of Sodium Treatment on Composition

Oil Investigated	% Sulfur		% Aromatic Rings		% Naphthene Rings		% Paraffin Side Chains		Specific Dispersion	
	Orig.	Final	Orig.	Final	Orig.	Final	Orig.	Final	Orig.	Final
Moderately refined Calif. naphthenic, S.A.E. 30 (A)	0.53	0.07	15	14	33	33	52	53	120	121
Calif. paraffinic 400 neutral (D)	0.22	0.06	1	1	27	27	72	72	106	...
Gulf Coastal lub., S.A.E. 30 (C)	0.20	0.04	10	7	32	35	58	58	117	115
Penn. lub. S.A.E. 30 (E)	0.10	0.01	7	4	16	20	77	76	111	110

DEPENDENCE OF OXIDATION RATE ON PEROXIDE CONCENTRATION

No attempt will be made to consider more than the initial steps of the oxidation reaction since this suffices to depict the role of the sulfur compounds. If the oxidation of a highly refined oil is continued beyond the initial stage and into the region where the oxidation rate degrades to a slower linear reaction, results are obtained as shown in Figure 3 for oil F. The absorption of oxygen, as measured in the Dornte (*2*) type apparatus, proceeds at an ever increasing rate up to a point of inflection, then slows down, and eventually approaches a relatively constant rate. Simultaneously the peroxide concentration as measured by Wheeler's method (*9*) rises to a maximum which is reached as the oxygen absorption curve passes the inflection point. The peroxides then rapidly decrease, eventually tending toward a steady state. Such behavior suggests that the rate of oxygen absorption is possibly proportional to the peroxide concentration. To test this possibility—namely, that

$$\frac{d(O_2)}{dt} = -k\ (\text{peroxide}) \qquad (2)$$

it is mechanically simpler to prove the integrated relation,

$$(O_2) = -k \int (\text{peroxide})\ dt \qquad (3)$$

since a planimeter may then be applied to integrating under the measured peroxide curve. Integrating and evaluating k from one of the known oxygen absorption values, the curve drawn through the oxygen absorption points of Figure 3 was obtained; the validity of Equation 2 is thus established. Moreover, it is known that peroxides catalyze the oxidation of these oils. These two facts indicate that the rate of oxidation is here determined by the concentration of peroxide, the latter apparently being a fundamental part of the chain reaction which constitutes the oxidation. Therefore the addition of any agent which will reduce peroxide concentration under the conditions of oxidation will reduce over-all oxidation. This action is true of those compounds commonly called "inhibitors". An exception might be made for those agents which, by virtue of an ability to poison catalysts external to the system (such as metals or metal soaps), have unfortunately come to be called "inhibitors".

RELATION OF WHITE OIL TO LUBRICATING OIL

Since the first step in the oxidation reaction is controlled by peroxide, those oils (for example, medicinal white oil) which, because of a lack of natural inhibitors, can develop high peroxide concentrations will also develop high oxidation rates. Those lubricating oils which are rich in natural antioxidants—that is, agents capable of rapidly reducing peroxide—will not build up high peroxide concentrations and consequent high oxidation rates. The latter is true only when the natural antioxidants involved are of that ideal type which have no great tendency to absorb oxygen directly. Since the natural sulfur compounds have been shown to be the principal antioxidants in a finished lubricating oil, the reaction between these bodies and peroxide was investigated by observing the rate of peroxide decay when blends of a finished lubricating oil with a sulfur content of 0.53% (oil A) and a peroxide-rich preoxidized white oil are heated in the absence of air. Figure 4 shows the result when a mixture of 88% oxidized white oil and 12% finished lubricating oil were heated at 250° F. under nitrogen. The reduction of peroxides by reaction with components of the lubricating oil is obvious. The results of such a test with various concentrations of the lubricating oil are shown in Figure 5. Here $\log_e (P_o/P)$ rather than P is plotted, where P_o represents the initial peroxide concentration and P the concentration at time t. For each set of data $\log_e (P_o/P)$ is a straight-line function of time. Moreover, the slope of each line divided by the concentration of added lubricating oil is fairly constant throughout; its average value of 0.064 indicates the relation:

$$\frac{d\ (\text{perox.})}{dt} = -0.064\ (\text{perox.})\ (\%\ \text{lub. oil}) \qquad (4)$$

Thus the rate of decomposition is directly proportional to peroxide concentration and to the concentration of the natural inhibitor. Therefore in the oxidation of a typical lubricating oil, peroxides appear to be formed in the same manner as they are in a white oil; but because of a rapid reaction with certain natural sulfur compounds, peroxide concentrations can build up only to that point at which the rate of formation and reduction become equal. This mechanism, then, in addition to the peroxide reduction by highly oxidized products formed in the oxidation, maintains peroxide at an approximately steady value; its concentration depends upon the rapidity with which the oil forms peroxide and the efficiency of its inhibitors in reducing peroxide. In one sense the peroxide concentration, while the natural inhibitors are still present, is determined by a sort of pseudo equilibrium between these two rates. In certain oils this concentration is immeasurably low. Since the over-all oxidation rate is dependent upon

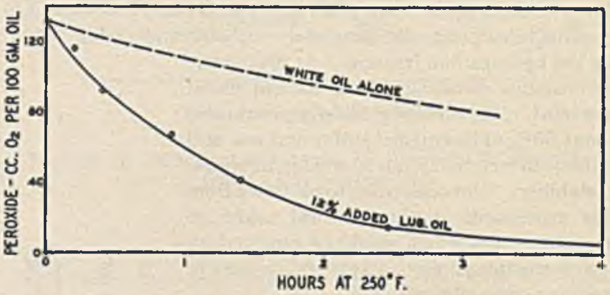

Figure 4. Decomposition of White Oil Peroxide by Added Lubricating Oil

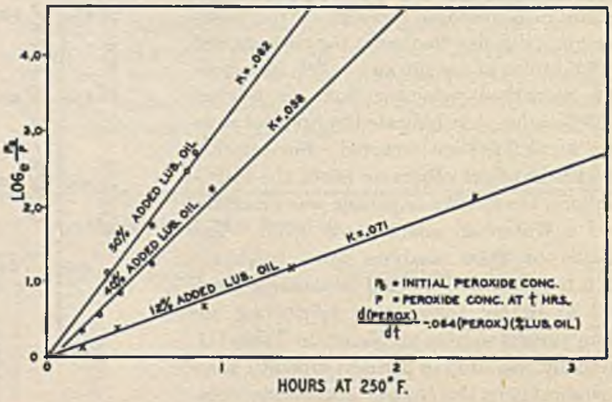

Figure 5. Effect of Concentration of Added Lubricating Oil on Rate of Decomposition of Peroxides in White Oil

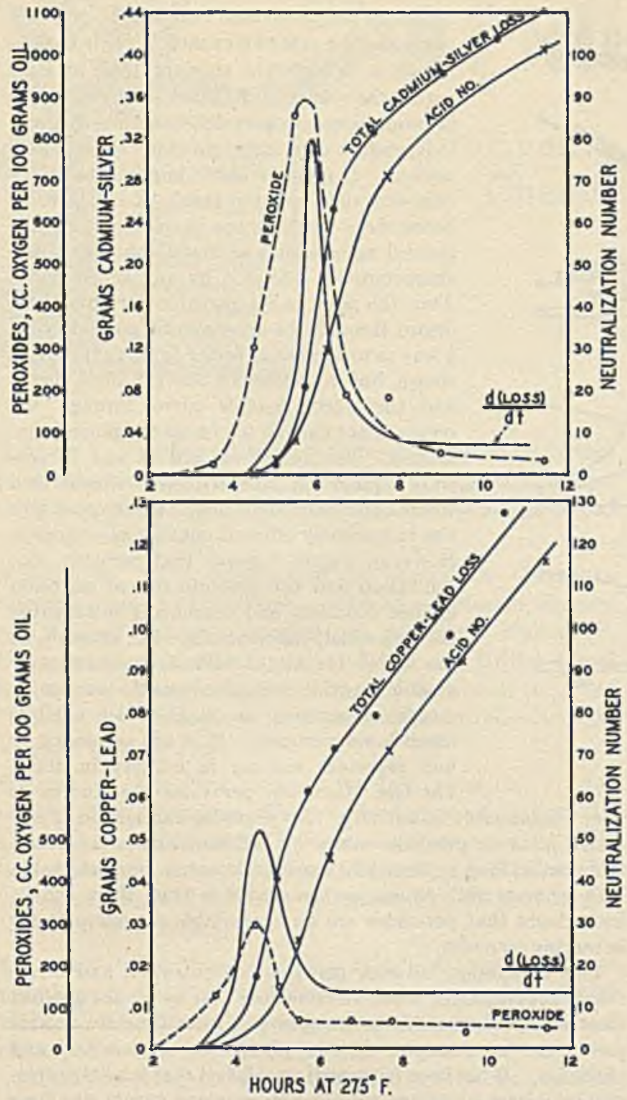

Figure 6. Relation of Peroxide to Corrosion of Cadmium-Silver and Copper-Lead Bearing Metals

peroxide concentration, this results in a low rate of over-all oxidation. In other lubricating oils, the peroxide concentration may be as high as 10 cc. oxygen per 100 grams oil or even higher, with a consequently higher over-all rate of oxidation. It must be borne in mind that the above remarks apply only to oils which have been given a normal amount of refining. In crude distillates, for example, the concentration of peroxide reducing compounds is exceedingly high. In fact, no appreciable peroxides are evident, yet the over-all oxidation rate is exceedingly high. This type of reaction apparently does not involve a chain mechanism but consists chiefly in the direct absorption of oxygen by exceedingly reactive molecules.

The natural sulfur compounds in a refined oil, in the course of their reduction of peroxides, are themselves oxidized to deleterious compounds. For example, peroxide reduction experiments carried out in the presence of lubricating oil show a far greater development of resinous compounds than that in the direct thermal decomposition of petroleum peroxides. What other deleterious agents result from the peroxide oxidation of sulfur bodies can be left to the imagination. However, the refiner is forced to choose the lesser of two evils; he must maintain sufficient natural sulfur compounds to prevent the development of appreciable peroxides and consequent high oxidation rate, yet keep them sufficiently low so that whatever oxidation does occur will not give rise to too many deleterious agents.

CORROSION AND PEROXIDES

Further investigation of the properties of peroxides brings to light the interesting fact that, in addition to controlling the rate of oxidation of refined lubricating oils, they are also the agents responsible for bearing-metal corrosion. No reference has been made in the literature connecting peroxides with the corrosion of bearing metals. Many articles have been written on bearing corrosion, and the statement is generally made that acidic products of oxidation give rise to corrosion; yet in all of this work, attempts to correlate corrosivity with either total acidity or acid strength admittedly failed. Since peroxides were generally known to exist in oxidized oil, it is surprising that their connection with corrosion has not been treated, especially since Engler and Kneis (3) stated in 1887 that certain metals, particularly lead, in contact with oxidizing turpentine are readily oxidized by peroxides and subsequently by reaction with the acids generated, the lead oxide is converted to a soluble soap.

The application of this reaction in present-day bearing corrosion is readily established. Returning to the ideal case of white oil, the following experiment was performed: A sample of oil F oxidized to high acid and peroxide values was freed of peroxide by heating to 250° F. for 2 hours in the presence of 1% moderately refined oil. This sample was called "acid oil". "Peroxide oil", low in acid and high in peroxides, was prepared by washing the oxidized white oil several times with cold aqueous caustic. Table IV shows the action at 275° and 300° F. of these samples on cadmium-silver bearing metal in the absence of oxygen. These data show that the acid oil has a negligible effect upon cadmium-silver, whereas peroxide oil causes appreciable corrosion. The variation between a maximum corrosion of 1.6 mg. at 275° F. and 0.0 mg. at 300° in the case of acid oil is probably indicative of experimental error. It might be remarked that lead is not corroded at 340° F. by naphthenic acids which are free from oxygen and peroxide.

TABLE IV. RELATIVE CORROSIVITY OF ACIDS AND PEROXIDES

Oil	Temp., ° F.	Time, Min.	Total Loss of Metal, Mg.	Peroxide Content[a]	Neutralization No.[b]
Peroxide oil	275	0	..	421	1.0
		85	8.0	54	..
		230	12.0	0	2.1
Acid oil	275	0	..	0	4.4
		85	1.0	0	..
		230	1.6	0	3.5
Peroxide oil	300	0	..	413	0.80
		105	13.0	0	1.61
		165	13.0	0	1.62
Acid oil	300	0	..	0	3.7
		105	0.0	0	2.9
		165	0.0	0	3.0
Oxidized oil	300	0	..	443	2.8
		105	20.0	0	..
		165	20.0	0	..

[a] Expressed as cc. O_2 per 100 grams oil.
[b] Expressed as mg. KOH per gram oil.

Another series of tests consists of determining simultaneously the loss in weight of the bearing metal strips, the acidity, and the peroxide number as a function of time, again using oil F. A single strip of bearing metal having an alloy area of 4.8 sq. cm. in the case of cadmium-silver and 11.6 sq. cm. in the case of copper-lead was suspended by a glass hook in 200 cc. of the test oil. Oxygen was fed in through a fritted glass plate, sealed close to the base of the cell. The rate of oxygen flow was such as to maintain at least two thirds of the bulk volume as foam. Under these conditions, this rate guarantees saturation of the oil with oxygen. Figure 6 shows the results of such tests. The curve for rate of corrosion, plotted as grams per hour, is parallel to the curve for peroxide number and independent of the curve for acidity; this

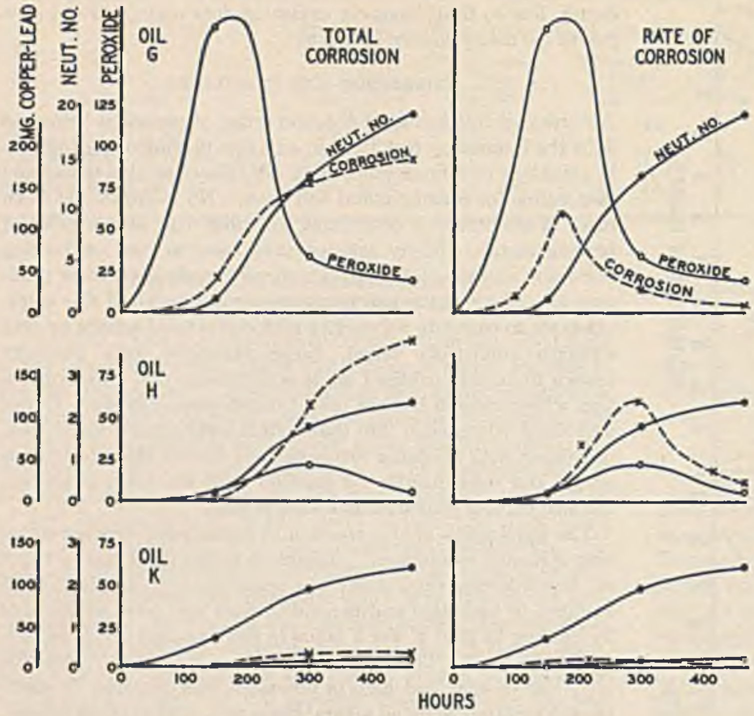

Figure 7. Dependence of Corrosion on Peroxide

supports the argument that peroxides control corrosion. In fact, the data indicate approximately that

$$\frac{d}{dt}(\text{loss}) = -K\ (\text{peroxide}) \qquad (5)$$

The parallelism between curves for acidity and for total corrosion lead to the belief that the rate of acid formation is likewise controlled by peroxide concentration.

A striking example of the over-all mechanism of corrosion is afforded by a test similar to that just described, where at intervals a pure lead strip was removed for observation. It was found that, once appreciable peroxides had formed in the oil but prior to the development of appreciable acidity, the strip was heavily covered with salmon-colored lead oxide. Then as oxidation progressed and appreciable acidity developed, the oxide coat dissolved off and corrosion proceeded. This indicates that at least in highly refined oil, corrosion occurs as a result of the following reactions:

$$M + AO_2 = AO + MO$$

$$MO + 2HA = MA_2 + H_2O$$

where M = metal; AO_2 = peroxide; HA organic acid

Since these reactions were established in white oil rather than in an actual lubricating oil, this proof was extended to commercial lubricants. Figure 7 shows the result of following peroxide number, neutralization number, and rate of corrosion as a function of time in a typical strip corrosion test. For convenience in plotting, rate of corrosion is expressed as milligrams per 100 hours. These experiments were carried out on various commercial samples in a routine strip-corrosion test. The apparatus consisted of glass tubes, 2 inches in diameter and 20 inches long, immersed in an oil bath whose temperature was automatically controlled to 200° ± 1° F. Approximately 300 cc. of the oil under test were placed in each tube, and air was bubbled through at the rate of 10 liters per hour. Strips of bearing metal were suspended in the oil. Before each weighing, the strips were washed in petroleum ether and carefully wiped with a soft cotton cloth. Although the parallelism between the peroxide curve and the rate of corrosion curve is not absolute, it is sufficient to show that, at least within the accuracy of the tests, corrosion rate is proportional to peroxide concentration and independent of acidity, provided some acid is present. It must be borne in mind that these corrosion data are the result of single runs; hence more weight must be placed upon the general agreement and trend than upon the characteristics exhibited by any single curve. Also, the peak on the peroxide curves may be drawn through the experimental points in such a way as to emphasize better agreement than is shown, but the difference between these curves and the worst possible curve through the points is not enough to change the general conclusion. The curves for oils H and K possibly explain the case frequently encountered where two oils develop similar acidity, yet give rise to markedly different degrees of corrosion. However, Figure 7 shows that peroxide concentration and the absolute rate of corrosion are not definitely and universally interrelated between widely different oils. For example, as the curve for oil G indicates, considerably greater peroxide content causes the same magnitude of corrosion as oil H, which exhibits much lower peroxide. It is not surprising to find peroxides varying in activity in different oils. Common peroxides are known to vary considerably in activity. No absolute dependence of corrosion rates on peroxide values for different oils is necessary, however, so long as these two are approximately proportional in each separate oil. As long as the second is true, there can be little doubt that peroxides are an appreciable causative factor in bearing corrosion.

This correlation between peroxide concentration and corrosion is not surprising when we remember that by far the greatest class of corrosion inhibitors are agents which will reduce organic peroxides—for example, organic phosphites, arylamines, and phenolics. It has been fairly well established that the only corrosion inhibitors which are not peroxide-reducing agents owe their effectiveness to the formation of protective coatings on the metals.

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Batch Rectification—Correction

Attention has been called to a misprint in my paper on the above subject, in the April, 1943, issue of Industrial and Engineering Chemistry. In Equation 5, page 408, "q_f" should be "b_f".

R. Edgeworth-Johnstone
Trinidad Leaseholds, Ltd.,
Point-a-Pierre, Trinidad, B.W.I.

APRIL'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ April 1. Winthrop Chemical Company announces further price reductions on Atabrine.~~Finely precipitated calcium carbonate, important to synthetic rubber program, is placed under allocation.

¶ April 3. 107th Meeting of the American Chemical Society opens in Cleveland.~~American Section, Society of Chemical Industry, through its president, Wallace P. Cohoe, presents identical gavels to A.C.S. and British Royal Society.~~Council of A.C.S. adopts definition of the word "chemist".~~Two new local sections approved—Norfolk, Va., and Boulder Dam, Nev.

¶ April 4. Du Pont renames its Deepwater, N. J., dye works, the "Chambers Works", in honor of Arthur D. Chambers, retiring after 47 years of service.~~OPA fixes base minimum price of $3.18 per 100 pounds, f.o.b. plant, for carlots of FF wood rosin.~~Schieffelin & Company marks 150 years in drug field.

¶ April 5. The Wood Chemical Institute, twenty-one corporations, and thirty-two individuals are indicted in alleged violation of antitrust laws in production and sale of natural methanol.~~Robert D. Coghill, government chemist, reveals at Cleveland A.C.S. meeting that twenty-one penicillin plants are now turning out 1.7 pounds per day with goal of 9 pounds.~~Joseph S. Fruton, Rockefeller Institute, receives Eli Lilly & Company Award, and William M. Clark, Johns Hopkins University, receives the Borden Prize.

¶ April 6. WPB extends potash allocation order for 12 months.~~War Food Administration announces portion of soybean meal in 1944–45 will be subject to a set-aside order.~~Board of Trustees, Nutrition Foundation, announces grants of $131,000 for research.~~Plans announced for training 3000–4000 foreign technical students from Europe and Asia in American engineering schools.~~Eugene Hollman, vice president of Standard Oil (N. J.), enters ranks of prognosticators of oil supplies and sees enough for 1000 years.

¶ April 7. Formaldehyde, hexamethylenetetramine, and pentaerythritol are added to schedules of General Chemicals Allocation Order M-300.~~Climax Molybdenum Company's sales in the first quarter of 1944 are 50% below the similar period in 1943.~~PAW bans liquefied petroleum gas as a motor fuel for use in civilian automobiles.

¶ April 10. Supreme Court sustains lower court opinion dismissing Government's antitrust suit against Bausch & Lomb Optical Company.~~Du Pont sales are currently 12–15% ahead of last year.

¶ April 11. WPB indicates that 26 million pounds of casein will be allotted for 1944, 5 million pounds more for paper coating than in 1943.~~Selective Service issues "Critical List of Activities for Occupational Deferment of Men under 26", and chemical leaders see serious danger of decline in production and research. Only those students in chemistry and chemical engineering who will graduate before July 1 will be deferred; medical students, however, will be deferred.

¶ April 12. WPB announces plans to construct 60-mile pipe line to carry natural gas to carbon black plants in Texas Panhandle area.~~Defense Plant Corporation advises Senate committee that its investment in war plants totals 7.5 billion dollars, half of total being in factories making aircraft or airplane parts; 800 million are invested in aluminum plants, and 700 million in synthetic rubber.~~John Fairfield Thompson, vice president of International Nickel Company receives 1944 Egleston Medal of Columbia University's Engineering School Alumni Association.~~Celanese Corporation offers 350,000 shares of $4.75 series no-par preferred stock.

¶ April 13. William L. Batt, chairman of National Planning Association and a high official of War Production Board, advises congressional committee that certain controls over business must remain "for an indefinite period" after the war.~~WPB Requirements Committee refuses to approve plans for production of alcohol from wood; manpower lack and material shortages are listed as principal reasons.

¶ April 14. War Department, in attempt to prevent dumping of surplus drugs, undertakes restudy of recent surplus survey.~~WPB head, Donald Nelson, appoints seven to advise with him on industry shift to civilian economy.~~Ickes, Secretary of the Interior, etc., proposes that war plants be given to veterans as "bonus".

¶ April 15. War Food Administration warns that a deficiency of corn may curtail the production of penicillin and asks farmers to release their stocks.~~Shortening and rationed salad oils are now ration-free.~~Imported menthol is put under ceiling when OPA sets 15 dollars per pound, duty paid, f.o.b. U. S. ports, as curb on competitive bidding.

¶ April 17. Washington officially discloses use of PETN explosive, said to be a third more powerful than TNT.~~The Army and the Petroleum Administrator for War oppose OPA's attempt to ration 73-octane gasoline to civilian flyers.~~Better supply of acetone features April allocations of chemicals by War Production Board.~~Du Pont Company reports, for first quarter, $1.38 per common share as against

$1.16 in the initial 3 months of 1943.∼∼Interstate Commerce Commission orders railroads to show cause May 8 why the Commission should not extend the suspension of freight rate increases now in effect for another 6 months.∼∼WPB announces industry advisory committees for barium chloride and aluminum sulfate.∼∼WPB revokes M-168 under which isopropyl alcohol was allocated, on basis of information available from suppliers' forms, and places product under General Allocation Order M-300.∼∼Du Pont announces use of methylolurea for transmutation of wood, a chemical means of converting ordinary wood into a whole new range of usefulness.

¶ April 18. Benjamin O'Shea, president of Union Carbide & Carbon, tells stockholders that sales are holding at 1943 levels but net profits are slightly lower because of taxes.∼∼U. S. Potash places 20,000 shares of 4% preferred privately.∼∼Attorney General Biddle, before Senate Military Affairs Subcommittee, hits antidumping section of Surplus War Property Bill.∼∼Speakers at National Alcoholic Beverage Control Association criticize WPB for refusal to grant "holiday" to distillers.∼∼WPB clarifies regulations (Limitation Order L-11) covering chlorine as pulp bleaching agent.

¶ April 19. State Department announces three officials of oil companies, John A. Brown of Socony-Vacuum, William S. Rodgers of Texas Company, and A. Jacobson of Amerada Petroleum Corporation, will sit in on discussions underway between British and American oil delegates.∼∼WPB relaxes control on tantalum.∼∼Lend-Lease is renewed for 12 months, with a total to date of 22 billion dollars.∼∼Franklin Institute Medals for 1944 are presented to William D. Coolidge, General Electric Company's vice president and director of research, and to Peter Kapitza, director of Institute for Physical Problems of the U.S.S.R. Academy of Sciences.

¶ April 20. Turkey refuses chrome ore exports to Germany.∼∼Army and Navy heads urge draft law to fill plants.∼∼War Manpower Commission warns of serious impending shortage of workers in mining and smelting.∼∼St. Joseph Lead Company's president sees shortages rather than surpluses for most metals in postwar.∼∼Dipentene goes under allocation as of May 1.∼∼Six oil companies agree on cross licensing and patent royalty rates for use of toluene and aviation gas processes.∼∼Standard Oil Company (Calif.) and Texas Company submit contract covering construction, financing, and operation of Arabian oil pipe line; Gulf Oil Corporation may not participate.

¶ April 21. Shellac allocation revoked, effective April 26.

¶ April 22. State Department is reported to be studying international trade with emphasis on cartels; special section formed in State Department's Office of Economic Affairs to tackle problem.∼∼It is rumored that Department of Justice will release shortly a uniform policy with respect to rights of Government in wartime patents, developed in whole or part by its employees or through contracts with private concerns.∼∼In a move to prevent draft from wrecking naval research projects, Navy announces it will commission or give ratings to men under 26 in three naval establishments in Washington, when drafted, and send them back to old jobs.∼∼Chemicals Bureau of WPB and Manufacturing Chemists' Association ask for continued deferment of 6000 technical indispensables.∼∼Nelson, WPB chairman, asked to review refusal to approve 2.2 million dollar plant in Oregon to produce alcohol from wood waste.∼∼Carbide & Carbon's first-quarter profit is 97 cents per share, compared with $1.01 in 1943.

¶ April 24. War Food Administration freezes corn sales in Midwest to obtain supplies for processing plants making corn products essential in war.∼∼A bill is introduced in Congress to force 4-F's into war work.∼∼Standard Oil Company (N. J.) net climbs to $4.45 a share in 1943, compared with $3 in 1942.∼∼Production goal of 250 million gallons of industrial alcohol is assigned to beverage distilleries in 1944.

¶ April 25. Fred H. Haggerson succeeds Benjamin O'Shea as president of Union Carbide & Carbon; O'Shea is now chairman of the board; James H. Rafferty, vice president, is added to Executive Committee.∼∼Sales by Columbian Carbon Company are up 15% over same period last year.∼∼William S. Rodgers becomes board chairman of Texas Company and is succeeded in presidency by Harry T. Klein.∼∼Mathieson Alkali announces a new synthetic rubber.

¶ April 26. Eberstadt & Company offers 35,000 shares of Westvaco Chlorine $4.25 cumulative preferred stock of no-par value.∼∼Division of Rubber Chemistry, A.C.S., opens 3-day meeting at the Commodore Hotel in New York.

¶ April 27. Attorney General Biddle denies that the Department of Justice has ever taken the position that consultation by any industry committee with the Government violates antitrust laws, or that it has made any effort to prevent industry participation in British-American oil discussions.∼∼Nylon molding powder is cut 50 cents to $1.60 per pound.∼∼Major mercurials are reduced 20 to 30 cents.∼∼Du Pont acquires Tacoma, Wash., plant of Latimer-Goodwin for its Grasselli Chemicals Department.

¶ April 28. United Nations are now producing 400,000 barrels of 100-octane gas daily, according to Petroleum Administration for War.∼∼Defense Plant Corporation undertakes a survey of 1500 government-owned plants to determine postwar possibilities.∼∼New Treasury Department unit is formed to handle disposal of surplus consumer goods with Ernest L. Olrich as head.∼∼War Production Board clarifies filing of WPB Form 541 (formerly PD-1A) for other than controlled materials.∼∼The "Byrnes Special 100-Octane Committee" inspects Marcus Hook refinery of Sun Oil Company, first stop in coast-to-coast inspection trip.

¶ April 29. Establishment of a nation-wide system for a limited civilian distribution of penicillin is announced by War Production Board.∼∼New Chilean nitrates plant costing 12 million dollars, to produce 200,000 tons, will be completed in advance of the 1944–45 season; the fully mechanized new plant is being built by Tarapaca and Antofagasta Nitrate, and output will be stepped up to 300,000 tons.∼∼Department of Commerce predicts a paint business of 740 million dollars a year immediately after the war.∼∼Governor Martin of Pennsylvania warns that Arabian pipe line may bring on World War III.∼∼Corn shortage reaches acute stage as farmers hold stocks for hog feeding.

¶ April 30. Canol, the 130 million dollar American-financed oil project in northern Canada, opens.∼∼Shell Oil Company celebrates tenth anniversary of the first shipment of 100-octane gasoline to United States Army with dedication of twin catalytic cracking units at its Wood River, Ill., works.∼∼War Production Board seeks top-flight executives to guide reconversion of industry.∼∼Secretary Ickes reports that soft coal production is still below maximum capacity.

Last-Minute Flashes

FROM THE EDITOR'S DESK

Fluorspar is one of those unromantic, little-publicized raw materials, yet current demand is unprecedented. It is essential in the manufacture of steel, aluminum, high-octane gasoline, refrigerants, insecticides, etc.—not in all instances as fluorspar, the mineral, but as the raw material for the manufacture of hydrofluoric acid. Consider the quantities of Freon now going into special insecticides for our troups, the role of the hydrogen fluoride alkylation process in the aviation gas program, and the picture becomes clear.

★ April chemical allocations serve to emphasize the tight polystyrene situation. Benzene, one of the important ingredients of high-test aviation fuel, is also an important raw material in the manufacture of polystyrene. Outlook for an increase of polystyrene for civilian purposes will not be bright until Germany is defeated. At that point, or possibly when both Germany and Japan are finished off, tremendous quantities will be available. Production now is astronomical. The rate for the synthetic rubber program is greatly in excess of the quantity that will be consumed in making synthetic rubber in a peacetime economy even though natural rubber fails to make "a return engagement".

★ Milk sugar is scarce (only 80% of the amount requested for less essential uses was granted in April) because it is employed in penicillin manufacture.

★ Inside story of the removal of vegetable shortenings from the ration list is that lard consumption has been increasing heavily at the expense of other shortenings. Hog slaughtering is expected to decline in the immediate months ahead, and the existing large stocks of lard will show sizable declines. Lard may be restored to rationing in an effort to check consumption in the summer months. While stocks of vegetable oils are heavy at the moment, the situation may alter radically later. Much depends upon 1944 crops, and momentarily it looks like a 10% decline from '43 as gaged by farmers' intentions to plant. Do not write the vegetable oils off the ration list for the duration—at least not yet.

★ The Iowa Experiment Station and the Committee for Agricultural Development have earmarked 8000 bushels of Iowax 1, the hybrid corn with waxy characteristics, for use in the manufacture of adhesives and sizing for cloth and paper. This year some 5000 additional acres will be planted in restricted areas of northeastern Iowa.

★ Some of the WPB officials will tell you that DDT, the new delousing agent, is a bigger production headache than penicillin. It is so potent that the Army just cannot resist raising production sights every few days.

★ Tung oil allocations will be more liberal in view of the favorable outlook for domestic-grown supplies.

★ Linseed oil is somewhat easier as evidenced by relaxing of WPB restrictions on the amount that may be used in various protective coatings.

★ One of the most significant bits of news is the decision of Turkey to halt exports of chrome ore to Germany. The United Nations are slowly but surely pulling the noose about Hitler's neck. No nation can wage a modern war without this vital material.