Industrial and Engineering Chemistry
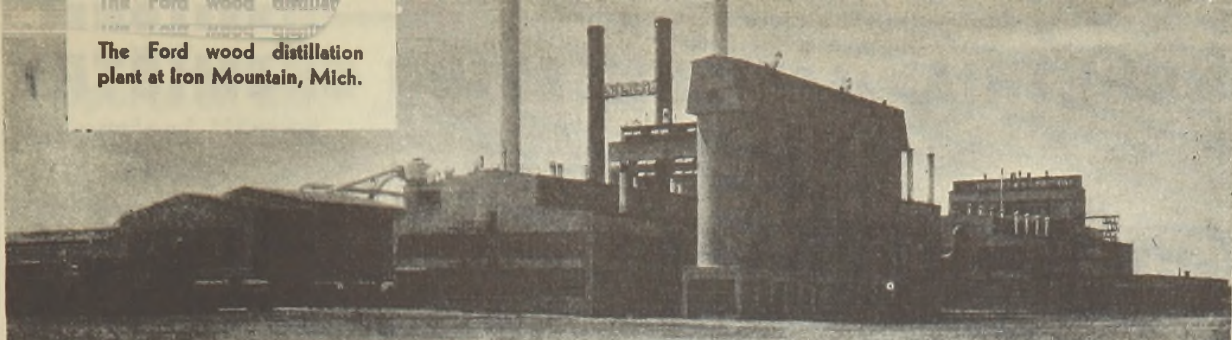
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The Ford wood distillation
plant at Iron Mountain, Mich.

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Technology

Atomic Age. Civilization reached its majority last month. No longer can our world be irresponsible, mischievously play with security and lives, and then, after the damage is totaled, charge it to moral immaturity. Disintegration of atoms changed all that, and the world's twenty-first birthday came generations earlier than expected. The price that will be paid for war in the future will make the holocaust just experienced seem a mere parental slap as compared to execution in the electric chair. Adam's children, answering Cain's question, are indeed their brothers' keepers, forever from this day forward.

For a while it will seem strange in the technical field not to have censorship. For so long we have furtively glanced behind at the mention of Clinton engineer, Oak Ridge, atomic power, and uranium that some time will be required to adjust our lives to the change. We had, along with practically every one else in the scientific and journalistic fields, suspected that the huge mysterious projects in the South and in the state of Washington were concerned with atomic power; but, being on the outside looking in, so to speak, at the field of nuclear physics, we had very little to go on other than pure speculation.

The evidence that the Nation was doing something about the subject came slowly but surely. When we first suspected it, we did what any editor would do—went to the literature and measured the inches of published references on the subject, prewar and at the time. The results made us certain that some sort of a censorship was being exercised, for the references suddenly stopped. The number and the caliber of the men transferring to the cities around the projects gave us another inkling. Naturally there was gossip, gossip, and gossip, but never a direct leak. The secret was well kept, but the very magnitude of the project made complete veiling of activities impossible. One of the real indications was the later censorship code, which specifically enumerated the subjects in this field that could not be mentioned in print. Then this year, while we were in England, we read the *London Express* of May 21, which blazoned on the front page the stories of the atomic bomb race between the Allies and the

> A new columnist has been added to our staff of Contributing Editors. Harold R. Murdock will write a column on the important subject of waste utilization. It will be found each month in the advertising section (see page 97) following "Instrumentation" (Munch) and preceding "Plant Management" (von Pechmann).

Nazis and of the British expedition to Norway to wreck the heavy-water plants at Rjukan. The laboratories at this Norwegian town were brought under the command of the Germans in 1940, but not until Lief Tronstad, Norwegian chemist, had burned all the records and fled to England, where the work of making an atomic bomb was begun. In December, 1942, the British landed, by glider, an expedition of twenty-five men who were assigned to sabotage the plant. Plans went wrong, however, and the men were wiped out. A later expedition, in February, 1943, succeeded in blowing up the laboratory and getting away. The plant was bombed later that year but was recommissioned. By April, 1944, 12 tons of heavy water were ready for transportation to the German laboratories, and were to be taken by ferry across Lake Tinsjoe. Patriots sank the ferry and its load of heavy water by attaching a magnetic mine to the hull. Such leads made the Editors certain that the huge plants had to do with atomic power, and yet, when the news broke, it was in such a way that all were taken by surprise. Technically there is little to discuss except what we have abstracted from the report issued by the War Department. One question that continuously rose to plague us was what the reaction of the press would be to this latest imagination stretcher of science. Science is usually blamed for arousing in man's breast the desire to use the newest plaything of the laboratory. When the end of a war comes in a shorter time than if men were still using clubs, science is blamed for a violation of human ethics which, for some mysterious reason, is kept alive through every war. When science steps in and ends the fight, human ethics collapse.

The *New Yorker* saw in the bomb the end of the quest for a substitute for God, and the urgent need for a universal political structure. One phrase especially sticks: "Nuclear energy and foreign policy cannot coexist on the planet." We should like to see that spread on billboards across the country. The *New Republic* expressed the hope only that the first result would be the end of the Japanese war. The *New York Times* devoted almost three

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

editorial columns to the bomb and its effect; they urged the extension of democracy around the world, with the belief that no people will want war, knowing what the consequences of the atomic bomb will be. Most of the comment we read was along the latter line, except those voicing the opinion that we should dump the bomb and, presumably, those who had invented it, into the nearest ocean. The moralists and philosophers now had more to lecture science about than they had when Darwin's theory of evolution broke upon them, and they were making the most of it.

More energy was expended in rushing to print with explanations of how the bomb works, why it was used, and why it should not be used, than was released in the two explosions over Japan. One thing we hope for—that it does not stop. We hope that man will not become blasé over the bomb, that he will continue to marvel and be frightened. Since the world at large still thinks that the opinion of a movie star or a political boss has more weight than the advice of a scientist, the only hope for man is that scientists keep pulling wonders out of hats to keep the human race thoroughly frightened, duly impressed, and busy explaining atoms, protons, and fissures to one another. Perhaps in that way mankind will be too frightened and/or enlightened to start a third World War.

TECHNICAL DETAILS. Primer for all the present explanations in the press about the new weapon is a report of some 180 pages entitled "General Account of the Development of Methods of Using Atomic Energy for Military Purposes under the Auspices of the United States Government, 1940–1945", written by H. D. Smyth, chairman of the Department of Physics of Princeton University, and consultant to the Manhattan Project. This report was released by the War Department to inform "a substantial group of engineers and scientific men who (can) understand such things and who can explain the potentialities of atomic bombs to their fellow citizens." Most of the following is taken from the Smyth report and represents what we think will be of most interest to our readers.

It all began when G. B. Pegram of Columbia University telephoned the Navy Department in March, 1939, for an appointment for Enrico Fermi, Italian nuclear physicist who was imbued with the idea of harnessing the power of the atom. By the fall of that year matters had progressed until President Roosevelt appointed an Advisory Committee on Uranium. Smyth comments in his chapter on this phase that "at that time (January, 1939) American-born nuclear physicists were so unaccustomed to the idea of using their science for military purposes that they hardly realized what needed to be done. Consequently, the early efforts, both at restricting publication and at getting government support, were stimulated by a small group of foreign-born physicists centering on L. Szilard, and including E. Wigner, E. Teller, V. F. Weisskopf, and E. Fermi." That same spring the physicists imposed a voluntary censorship on the results of their attempts to split uranium. This was many months before Hitler's hordes marched on Poland.

The first government appropriation, 6000 dollars, was transferred from the Army and Navy on February 20, 1940. The following June saw the formation of National Defense Research Committee, and President Roosevelt ordered the Uranium Committee reconstituted under NDRC. The first contract by NDRC for this work was let to run a year from November 1, 1940, and 40,000 dollars were appropriated. By the end of this period, sixteen contracts had been let and 300,000 dollars appropriated. In October, 1940, President Roosevelt wrote to Prime Minister Churchill and arranged for active cooperation between the British and Americans. On November 28, 1941, Vannevar Bush, head of the Office of Scientific Research and Development which included NDRC, had the work transferred to OSRD so that an all-out effort could be made to solve the problem. It remained an OSRD problem until the Army formed the Manhattan Project on August 13, 1942. All work on the project thereafter was labeled "DSM" (development of substitute materials). Over the project was a military policy committee consisting of Vannevar Bush, chairman, James B. Conant, alternate, Major General W. D. Styer, and Rear Admiral W. R. Purnell. These men kept the President informed as to the progress made. Brigadier General L. R. Groves was placed in complete charge of Army activities. Immediately after President Truman's inauguration, Secretary Stimson and General Groves gave the new president up-to-the-minute information about the project, so important had the work become at that time.

PROJECT DEVELOPMENT. Only a brief summary of the processes by which atomic fission is accomplished will be presented here, as explained by Smyth.

Before censorship was imposed, it was known that one of the isotopes of uranium having an atomic mass of 235 disintegrated violently when hit by a neutron. This isotope is present in natural uranium materials in the ratio of 1 part in 140. New knowledge added by the Smyth report is that when ordinary uranium (atomic number 92, atomic mass 238) is hit by a neutron, it changes into another isotope, naturally of the same atomic number; but because the neutron has about the same mass as the protons that make up most of the weight of the nucleus, the mass becomes greater by about 1. Therefore the isotope becomes uranium 239. This is unstable and gives off a beta ray, a negative particle presumably coming from the nucleus, and a new element neptunium is formed. Neptunium has the same mass as the predecessor isotope of uranium 239, but has a different positive charge in the nucleus (a plus charge of one proton) so that the new element is number 93. The same thing happens again—neptunium gives off a beta ray, the mass still is the same, but again an increase in positive charge due to the loss of a negative particle gives element number 94, or plutonium. Plutonium can, over a long period of time, give off a neutron to form uranium 235, but in the natural course of events this happens too slowly to be explosive.

Plutonium is also susceptible if hit by a neutron, and on the basis of early experiments, the

decision was made to investigate the explosive possibilities of this new element. One other concept is necessary, and that is an understanding of the "pile". To change ordinary uranium into the plutonium that is wanted, uranium must be hit with a "slow" or "thermal" neutron. Apparently U-235 must also be hit with the same type of neutron to explode. The fast neutron either bounces off the nucleus or is adsorbed into the nucleus for a nonfission-type strike. Therefore it became necessary to find some way to make the neutrons slow up; this was done by passing them through heavy water or through another moderator, graphite. If a pile of graphite and uranium of the correct shape and size were built, it was conceivable that a chain reaction might be set up. The neutrons generated in the fission of U-235 or plutonium would slow up enough to explode other atoms of these elements, and a point could be reached where the number of explosions and fission captures of the neutrons produced continued to increase. By correctly shaping the pile, the number of neutrons escaping to the atmosphere were minimized and captured in the uranium. Smyth is purposely vague as to the source of the neutrons, but at the University of Chicago the first sustaining pile was built using graphite as a moderator. In the first experiments on measuring the effect of graphite on neutrons (work done at Columbia University) the neutron source was radium-beryllium.

Two methods of attack presented themselves: (1) to separate U-235 from the ordinary uranium, (2) to build a pile and make the new element plutonium. Since the new element was a distinct material, perhaps it could be separated by chemical means. The source of uranium became a problem, and the Mallinckrodt Chemical Works, with experiments carried out at the National Bureau of Standards by J. I. Hoffman as a basis, solved the problem by the ether extraction of huge quantities of oxide. Deliveries started July, 1942, at a rate of 40 tons per month. For a time the metal was made by electrolysis of KUF_5, but this was later changed to uranium tetrafluoride; the latter salt was produced by Harshaw Chemical Company and E. I. du Pont de Nemours & Company, Inc. Smyth becomes vague again, and merely mentions that a new process for making the metal was developed by F. H. Spedding and associates at Iowa State College and by C. J. Rodden at the Bureau of Standards. This apparently was the process mainly used.

Graphite procurement and purity also proved to be a stumbling block. N. Hilberry, the National Carbon Company, and the Speer Carbon Company ultimately provided the answers with a graphite that had 20% less neutron adsorption than the impure material used at the beginning of the experiments. The two main problems of supply were solved, but there were a host of others, and chemists, physicists, and metallurgists worked hard and long at the problems. The size of pile to be constructed, type of coolant for the pile (water or helium), method of protecting uranium from corrosion, means of protecting workers and citizens from harmful radiations, means of recharging the uranium metal, solution of the chemistry problems of plutonium and working out methods for its separation from a

sample of 500 micrograms, methods of separating isotopes—these are only samples of the myriad of difficulties that had to be overcome.

As far as can be gleaned from the report, the method of separating plutonium was chemical. The uranium metal was put up in rods; when the pile had run for a certain length of time, it was stopped and the rods of uranium were pushed out and carried under water (all by remote control) to the beginning of the separation process. Only a few grams of plutonium were obtained from huge quantities of metal. Apparently the metal not changed to the new element was redissolved and made into metal again. We emphasize that the metal bombarded was common uranium 238. The separation processes made use of an alternation between the 4 and 6 oxidation states of plutonium. Such processes involve precipitation of plutonium 4 with a certain compound as carrier, dissolution of the precipitate, oxidation of plutonium to the 6 state, and reprecipitation of the carrier compound while the plutonium remains in solution. The plant at Hanford, Wash., was exclusively devoted to plutonium, but at the Clinton, Tenn., plant not only were methods explored for making this new element, but U-235 came in for much probing.

As finally worked out, the methods of separating this rare isotope were based on the diffusion of a gas through a barrier, and the enriched gas was used in a calutron, an electromagnetic separator of isotopes developed at University of California. This was one of the later developments which produced suitable material for the atomic bomb. The principle of the calutron is the same as that of the mass spectrograph. An ion source provides a beam of uranium ions, an accelerator speeds them to high velocities, and a magnetic field forces them to travel in a semicircle, the lighter ions having the shorter periphery and entering a receiver.

The Hanford plant was run by Du Pont, the calutron unit by Tennessee Eastman, and the gaseous diffusion plant by Carbide and Carbon. That three chemical companies operated the three plants which had such a fateful effect on the course of history is a record to be proud of. Space prevents more from being told, but from time to time we hope to present further data on this subject.

Bombers and Biologists. The dramatic role of the atomic bomb in speeding the end of the war in the Pacific tends to overshadow the part played by the splendid planes that carried the A-bombs, the high-octane fuel that drove them, and the fine human machines that piloted them to their goals. Chemists and engineers are more than familiar with the search and research that has kept a river of high-test gasoline flowing into aircraft, and of the metallurgy and aerodynamics that have increased the speed and efficiency of American planes each month of the war. Some, perhaps, may have lost sight of the superhuman demands made on the human organism to adapt itself to flight in oxygen-deficient atmospheres and at faster-than-sound speeds at which Nature never intended it to function. Problems that confronted biologists who were called in to assist medical officers of the Army

and Navy air forces were discussed recently by D. W. Bronk at the Marine Biological Laboratory, Woods Hole, Mass., where research in biology, biochemistry, and related fields is carried on during the summer by investigators from all over the country. Dr. Bronk, director of the Eldridge R. Johnson Foundation for Medical Physics (part of the University of Pennsylvania Medical School), is Coordinator of Research in the Air Surgeon's Office, A.A.F. His lecture illustrated the efficient way biologists, physiologists, and biochemists have utilized fundamental research to solve wartime problems. The No. 1 physiological difficulty the air surgeon had to combat was the effect of rare atmospheres on man. Basic work done in the biological laboratory on the effect of oxygen deficiency on nerve cells was utilized in tests to determine, among other things, how long man can tolerate the decreased oxygen tension at various altitudes.

Connected with this main problem of adequate oxygen supply were others: How far does breathing pure oxygen raise the altitude "ceiling" which members of a crew can stand? Oxygen masks must fit many types of heads, and anthropologists were finally able to simplify them into four basic designs. If one member of a crew is injured and another has to move about to help him, how long can the latter be separated from his oxygen supply without feeling bad effects or losing consciousness? Where the bomber is equipped with a pressurized cabin, how large a hole can be endured from flak or bullets before the pumping system fails to supply enough oxygen to balance that lost through the gap? What effect does a sudden loss of pressure in a pressurized cabin have on the human organism, and how severe are the results of rapid changes of pressure, which may finally bring about "bends"?

The opposing forces of gravity and centrifugal force at extremely high speeds also put a tremendous strain on the human organism that it was never intended to bear. When a pilot dives on a target at a rate of 500 or 600 miles per hour, and then suddenly ascends, the blood tends to leave the brain, stomach, and upper part of the body and rush into the feet and legs. The result may be loss of vision or even of consciousness. An ingenious G-suit (G for gravity) has been developed which utilizes pressure on the legs and lower parts of the body to counterbalance this rush of blood. Dr. Bronk learned from German air surgeons that this suit impressed them greatly, since they had nothing like it. On the other hand, the Germans were ahead of us in perfecting a seat which utilizes an automatic explosive propellant to force the pilot upward and outward from the plane in case it is damaged at a very high altitude, flying at high speed. In such a case the pilot, unaided, would be unable to overcome gravity and centrifugal force quickly enough to get out of the plane and open his parachute.

An important part of the aviation physiologists' task has been to instruct the flyers themselves in the various ways of protecting their bodies against injury due to the unnatural conditions under which they must operate. A general in the German medical service told Dr. Bronk that the physiological knowledge possessed and utilized by our captured flyers had astounded the enemy air surgeons.

AS WE SEE IT---
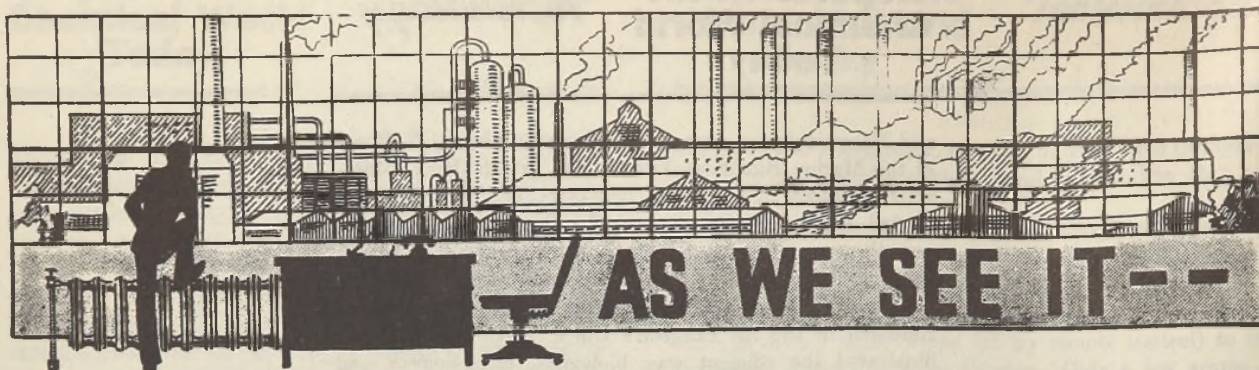
Alumina and the Red Mud. Conservation of bauxite may seem already foreign to our thinking, now that peace is with us once again, but during the dark days of the submarine menace we were really "strapped" for suitable supplies to use in the conventional process for the forerunner of aluminum. The chemists and chemical engineers of the Aluminum Company of America developed a method of making alumina from low-grade ores, the trick being to win the alumina carried away by the silica in the waste red mud. Present in the less concentrated ores are greater quantities of silica, but a successful process for treating the red mud was found. One of the main difficulties was finding a method for eliminating sulfur introduced into the process. This step was performed by crystallizing evaporators, shown in the flow sheet in the article "Alumina from Low-Grade Bauxite," by our Midwest Editor, Robert F. Gould, with the cooperation of the ALCOA technical staff. This article describes another of the new techniques worked out for the war effort, which I.&E.C. will continue to bring to its readers.

Corrosion Sequel. August featured a symposium on corrosion inhibitors; this month we are presenting a paper by Powell, Bacon, and Lill, consulting engineers of Baltimore, who specialize in corrosion and allied problems. The authors prepared this manuscript at the request of the Editor after the symposium had been given at the North Jersey meeting of the A.C.S. last year. The experience they bring to the field is such that all will benefit from their freely given knowledge. War plants, built when copper and brass were scarce, were able to operate without resistant materials because of the methods described here for protecting steel equipment by the deliberate building of a calcium carbonate scale. An excellent history of success has been attached to this process but also a number of failures, which are analyzed by the authors.

C. Madagascariensis and the Emergency. Back when our natural rubber was cut off (remember?) and we were arguing about synthetic *vs.* the domestic natural product, one of the sources that came in for a great deal of investigation and publicity was cryptostegia, a vine bearing a beautiful flower and secreting latex from both stems and leaves. The stem latex has been sold in the past as a rubber source, and now the Department of Agriculture reports on methods of obtaining the latex present in the leaves. There are problems galore attending such an interesting investigation, from the beginning when the cell of the plant containing the rubber is destroyed by fermentation through the solvent extraction and vulcanization of the rubber obtained. See "Cryptostegia Leaf Rubber".

From the Bleachers. Chlorine dioxide is proving itself as quite an agent for the bleaching of many materials, flour being one of the first tried. It is not, then, surprising that a research team of General Mills should publish on research techniques using this gas. Hutchinson and Derby have worked with this bleacher for some time, and give to us the benefit of their experience in making small quantities of ClO_2 for investigational purposes. Depending on what you want, three methods are offered for use.

Bluer and Bluer. Iron blues have long been a staple in the pigment field, but they have an annoying quality of turning brown under the influence of alkalies. Recent progress in the field indicates that, modified with the metal nickel, improved resistance to alkalies is obtained. Holtzman, of Ansbacher-Siegle Corporation, explores this territory thoroughly and advances a theory as to why nickel helps overcome the fault of the iron blues in becoming colorless.

Controlled Combustion. Control of gas combustion is now a fairly common industrial procedure where special atmospheres are needed to accomplish some chemical change in the material being heat-treated. Vandaveer and Segeler, of the American Gas Association, report on their investigations to determine the products formed when a gas is partially burned in a deficiency of air. These data will aid in preventing unwanted side reactions in "heat treat", and will materially extend our knowledge about the mysteries of combustion.

More Phos in Superphos. TVA has been making superphosphate for many years, and we now publish the latest study on making superphos more super. This time the effect of mixing and curing on the conversion of rock phosphate to superphosphate is elaborated on in great detail. Bridger, Burt, and Cerf also indicate that there are important differences in the results obtained in the official A.O.A.C. method of analyzing for P_2O_5 and another analytical method.

Peanut Glues. Burnett, of the Southern Regional Research Laboratory, hopes that glues and adhesives will soon be made from peanuts. The trick is to isolate the protein from the meal without altering the composition too much by heat or alkali. On top of that advice, he proceeds to disect the peanut by chemical means and tells how to accomplish the desired end.

2,3-B.G. Nine papers, five from the Northern Regional Research Laboratory and four from the Polytechnic Institute of Brooklyn, report on the use of 2,3-butylene glycol as an intermediary in the production of butadiene. This work, carried on during the height of the rubber crisis, was of extreme importance, although the critical aspect is past. However, much of a vital nature is contained in the techniques explained in these manuscripts, and they now become part of the record. Future work may uncover many possibilities in this method for the chemical industry.

With the Departments. A new column is introduced in this issue; Harold R. Murdock will comment on waste utilization, and readers will find much of interest there every month. Brown writes about those little appreciated but very vital leak stoppers—gaskets. Von Pechmann explores time study for the chemical industry; strangely enough, up-to-the-minute utilization of a time-study man's ability does not stop at incentive rates, and von Pechmann points out more important uses for this knowledge. Munch shows how data from instrumental analyses can be quickly correlated by electrical computers.

F. J. Van Antwerpen

Peace and a New World

THE cataclysmic explosions in man's thinking and reasoning which followed the indescribable destruction of two Japanese cities by atomic bombs far transcend the physical havoc wrought by the initial application of atomic energy. Never in the long march of history down through the ages has man witnessed and experienced such a bewildering succession of events as those which occurred between August 5 and August 14 and culminated in the total surrender of Japan. One breath-taking climax followed another with such rapidity that man's capacity to comprehend and evaluate was subjected to tremendous stresses and strains.

Our Nation, benign and generous in days of friendship, proved once again that it grasps the sword only to defend the rights of all mankind. The same nation, to which we extended aid and succor when struck by a devastating earthquake, was made to feel the righteous anger and might of an aroused people.

But in fighting and winning the most terrible and horrible of all wars, we did not forget our single objective. To our enemies who would have destroyed and enslaved us if they had prevailed, we now offer help and guidance. We seek not vengeance. Our primer of democracy and freedom is theirs if their peoples will but indicate a sincere and honest interest. Should the same destructive forces of Nature again be turned upon them, our wrath would become charity, the injured cared for, and the homeless provided with shelter. America wants peace, it needs peace, but a sick and troubled world now half destroyed needs peace even more and the whole trembling system needs democracy and America.

Today we are in the long-dreamed-of brave new world. The postwar now is a reality, it is here, and our dreams, ideas, expectations, and desires can and should be satisfied. But it is "we the people" who must cut the pattern. Realization of the goals we seek depends upon expending great effort; otherwise the new world will never come to fruition. The battle-weary veteran may soon be safely home, the hand of Mars stayed once more, but, unless we courageously wage the peace as we did the war, the mute mounds of earth, the final resting places of the mortal remains of our immortal dead, will be but a grim reminder that once more the living have failed in their appointed task and that millions again have but died in vain.

Peace must be nourished with zeal; it must be protected; it must be recognized as one of the most precious blessings we possess; and to continue to possess it we must wholeheartedly dedicate ourselves and our Nation to the task of preserving it in perpetuity. Once the frontiers of this Nation, in a military sense, were the oceans that wash our shores. Today the world, in a military sense, has no frontiers other than those of a scientific character, no natural barriers to guard it against an aggressor nation, large or small.

The frail flower of peace is now susceptible to a neutron. The world of science has brought to the world at large a strange and almost incredible power. It can kill, it can destroy the very civilization that made possible its unleashing, or it can be to that same civilization the gift of the ages, the veritable key to the universe. Utter annihilation or untold benefits can flow from man's unlocking of the force of atomic energy.

The Atomic Bomb

Of all the events of those fateful ten days of August, the one with the greatest effect on the future course of the world was the demonstrated ability of scientists to harness the power of the atom. Unquestionably the defeat of Japan would have been achieved in time and accompanied by great loss of lives of Allied soldiers, but her defeat was assured. Of that there could be no doubt.

Thus we were in a sense expecting the Japanese collapse, but the news of the bombing of Hiroshima with an atomic bomb was numbing, even though we knew that thousands of American, British, and Canadian chemists, physicists, engineers, and other scientists in many varied fields of research and development were straining every ounce of energy, and employing every known scientific means in a desperate race with German scientists. It is well to remember now, and it will be doubly important to recall years hence, that the future of civilization depended upon the outcome of this titanic scientific struggle.

Unreal as it might seem even to those who knew some of the facts and suspected a great many more, the age of atomic power was at long last announced to a startled world, a scientific dream had moved upward through years of experimentation to accomplishment. The stark reality of this achievement when finally assimilated beggars description.

Unfortunately the brave promise of atomic energy, the tool that was expected to relieve man from drudgery, was first

employed in destruction. Like the fixation of nitrogen, success came faster because science was pressed to make weapons of destruction. This is a fact that many recognize, but do not evaluate properly. Science and scientists first thought of the fixation of nitrogen and the harnessing of the latent energy locked in the atom as benefits to humanity. Because the atomic bomb was used in war, because nitrogen was snatched from the air to make deadly explosives, because the airplane had its major advances during war, or because jet propulsion first reacted in the same cauldron, is no reason to castigate the men and women of science. Yet thousands of thoughtless people will condemn scientists, forgetting that it is not science that begets war but the selfishness and willful desires of individuals and even whole nations. In every war in which mankind has engaged, the fruits of scientific minds have been employed as destructive forces. The men and women of science are largely powerless to prevent this prostitution until mankind generally learns to live without resorting to the sword as a means of adjudicating or resolving differences.

Many outcries have been registered against the inhumanity of the new weapon. It is inhumane, but so are all weapons and wars. Winston Churchill provided one of the most striking answers to the critics, at this writing more numerous in Great Britain than in the United States:

There were those who considered that the atomic bomb should never have been used at all. I cannot associate myself with such ideas. Six years of total war have convinced most people that had the Germans or the Japanese discovered this new weapon they would have used it upon us to our complete destruction with the most alacrity.

I am surprised that very worthy people—but people who in most cases had no intention of proceeding to the Japanese front themselves—should adopt the position that rather than throw this bomb we should have sacrificed a million American and a quarter of a million British lives in the desperate battles and massacres of an invasion of Japan. Future generations will judge this dire decision, and I believe if they find themselves in a happier world from which war has been banished and where freedom reigns, they will not condemn those who struggled for the benefits amid the horrors and miseries of this grim and ferocious epoch.

The bomb brought peace, but man alone can keep that peace.

Or perhaps the Irish novelist, St. John Ervine, in replying to those who criticized the use of the atomic bomb, provided the most pertinent remark of all when he stated that he "would rather be killed by an atomic bomb than by a rusty bayonet thrust into my intestines". We would ask those who object on the grounds that the bomb was need-'lessly cruel to pick out a really kind and humane method of eliminating an enemy in war.

History will record the efforts of the United States and Great Britain to prevent the indiscriminate killing of civilians. When the results of the first successful atomic bomb test made in the New Mexico desert were revealed to the Potsdam Conference, the now famous ultimatum was promulgated in order to give Japan a clear and definite understanding of the term "unconditional surrender". She was warned to yield or suffer the dire consequences of continuing a one-sided and entirely hopeless struggle. Citizens of the leading cities were told to evacuate the areas. Such warnings were in sharp contrast to the tactics of the nation guilty of the infamous sneak attack on Pearl Harbor and the sacking and rape of Nanking.

The Future of Atomic Energy

It appears likely that this new tool of man will remain under strict government control. President Truman has announced that he will recommend that the Congress of the United States consider promptly the establishment of an appropriate commission to control the production and use of atomic energy within the United States and will also make further recommendations as to how atomic energy can become a powerful and forceful influence toward the maintenance of world peace.

A stunned and very much bewildered world is now asking, "What is the future of atomic energy?" The brilliant success of a relatively small band of scientists, and in this noted group were many chemists and chemical engineers, demonstrates the definite opportunity now before us of gradually developing a nuclear industry with many and varied ramifications. When the age of atoms in every home will come, no one can foresee. Research will go forward at an ever-increasing pace, and practical results, we are confident from the record of scientists and science in the past, will inevitably follow. As scientists, however, let us eschew the role of the prophet. Soberly reflecting what has been achieved so far, we must honestly inform an expectant and impatient public that we have but crossed the threshold of an entirely new and revolutionary storehouse of energy. Let us not in our boundless confidence and enthusiasm over the future permit the lay public to assume that any radical decline in the importance of present energy sources, such as coal and oil, will occur for some time, perhaps even for several generations. Scientists at the moment simply are accepting still another opportunity to serve mankind.

With respect to the future of atomic energy, the viewpoint of the Army on secrecy is interesting. The release which accompanied the H. D. Smyth report of the record of the development of the atomic bomb stated that, "the best interests of the United States require the utmost cooperation by all concerned in keeping secret now and for all time in the future all scientific and technical information not given in this report or other official releases of information by the War Department".

If we read and interpret this statement correctly, it is the intention of the Army to become the sole censoring authority of all research information and data on nuclear physics. We earnestly hope that no such authority is vested permanently in our Army officials, and that future research is not directed and controlled by the Army. Certainly a High Command which forced thousands and thousands of scientists into the Armed Forces instead of retaining them in research and production, a High Command that has denuded our colleges and universities of teachers and bona fide students in scientific courses, a High Command that has robbed America of a whole generation of future scientists, and one that has steadily refused support of the aims and purposes of the McDonough Bill, has demonstrated that it should not be entrusted with any such authority or power over postwar developments in atomic energy.

In view of the widespread knowledge of nuclear physics, we cannot expect that scientists of other nations will not ultimately discover the processes by which the atomic bomb was produced and detonated. Indeed, we should expect that they not only will make such discoveries independently, but will improve upon them. Thus we must not depend alone upon secrecy enforced by the military. We must make certain that our research in the field of atomic energy will surpass that of any other nation on earth. Direction and control of this program should rest with a body of highly qualified individuals, independent of Army domination and responsible to the people as a whole. Otherwise Army influence will inevitably throttle research, and release of research accomplishments of use to industry and mankind will be withheld or delayed on the plea of an Army officialdom which thinks largely, if not entirely, of research as a military weapon and therefore necessarily secret information.

The effects of the development of atomic energy on a huge scale upon industry, economic laws, and the social structure of the entire world are unfathomable. The forces of the atom in the hands of a government can become the greatest monopoly ever to spawn upon this earth. A State may easily become a very sinister force for evil. Incorrect use of such power will lead to the same end in the age of atomic energy as it did in the age of coal and oil. Only an alert, enlightened attitude of all the peoples of the earth determined that there shall be no more wars will save mankind from destruction.

Future of Research

One of the most profound repercussions of the solution of man's greatest riddle, the unlocking of the energy contained in the atom, will be in the future pattern of research organization in this country. Even before the sensational news of August 5 was released, several bills were before Congress designed to provide government with varying degrees of control and supervision over future research activities in the United States. The atomic bombs dropped over Japan have made it clear beyond all doubt, even to the layman, that scientific research is absolutely essential to national security. We who are directly engaged in research should be doubly concerned with the form in which government participates.

To inform the members of the AMERICAN CHEMICAL SOCIETY and chemists and chemical engineers generally of the proposals now before Congress, *Chemical and Engineering News* published in the August 25 issue the essential portions of the report of Vannevar Bush to the President, "Science— The Endless Frontier", and is summarizing in the September 10 issue various bills affecting research and industrial development which Congress will consider in the near future. Every scientist should study with care the Bush Report and the proposed measures. Three of these bills are identical and embody the basic proposals of the Bush Report. Others go much further in the degree of control, direction, and supervision of research given to government and contain a very different type of philosophy on the relationship of government, research, industry, science, and scientists. It is the duty of chemists and chemical engineers to express to their Senators and Congressmen their considered opinions on a program that represents in many ways a decided departure from the past and that will have a profound effect on the whole future

of research. Can we afford to remain silent when not only the future of our country is at stake but the future of every scientist is involved? Now is the time and the opportunity of demonstrating to Congress and to America that scientists can be a potent constructive force to be considered seriously when legislation affecting the future welfare of our country hangs in the balance.

Scientists and the Future

In all of the millions and millions of printed and spoken words employed by the press and radio in acquainting America with the discovery of the ways and means of utilizing atomic energy, we believe none were employed to suggest that scientists be given a direct role in the shaping of the world that is to be. Praise, to be sure, was heaped upon those who pioneered in their roles as scientists, yet few venture the opinion that scientists be invited to participate in the control of the use of atomic energy. Why?

Some will say that this refusal comes from a lack of sufficient publicity for the men and women of science. But is this really so? Scientists receive tremendous amounts of publicity, but almost universally that publicity is solely based on outstanding scientific achievements. When the men and women of science come out of their laboratories and in large numbers actively participate in the affairs of the world, when they contribute to the shaping of social, cultural, governmental, and international policies in common with other professions and groups and with the same force and conviction, then they will be publicized, not only for their scientific achievements, but also for their roles as molders of public opinion. Until we as individuals and in large numbers are willing to divide our time and energy between scientific pursuits and the affairs of government and of the world, we will continue to be largely ignored. We have a moral responsibility to mankind to assist it in so governing itself that the forces we release are reserved for good, not for evil. No one man, no small group can perform this service. It is the responsibility of every individual who rightfully calls himself a scientist and he cannot delegate that personal responsibility to others.

There is a pressing need in our new world for still closer cooperation between scientists of all nations. Science recognizes no geographical boundaries, and those who unlock the wonders of the universe should and must assume leadership in the creation of a new spirit of cooperation and understanding at an international level.

The Hope of the World

The need of the hour, the year, the generation, and the century is intelligent understanding of the forces that have been unleashed, an unflagging determination on the part of every man, woman, and child to share the moral responsibility of seeing that the new power which man has at long last achieved is used solely for the advancement of mankind—not its annihilation.

Now, if ever, the principles and philosophy of the Golden Rule must be accepted, must triumph in man's mind, and must govern his actions. It is civilization's last chance.

ALUMINA FROM LOW-GRADE

Robert F. Gould
310 SOUTH MICHIGAN AVENUE, CHICAGO 4, ILL.
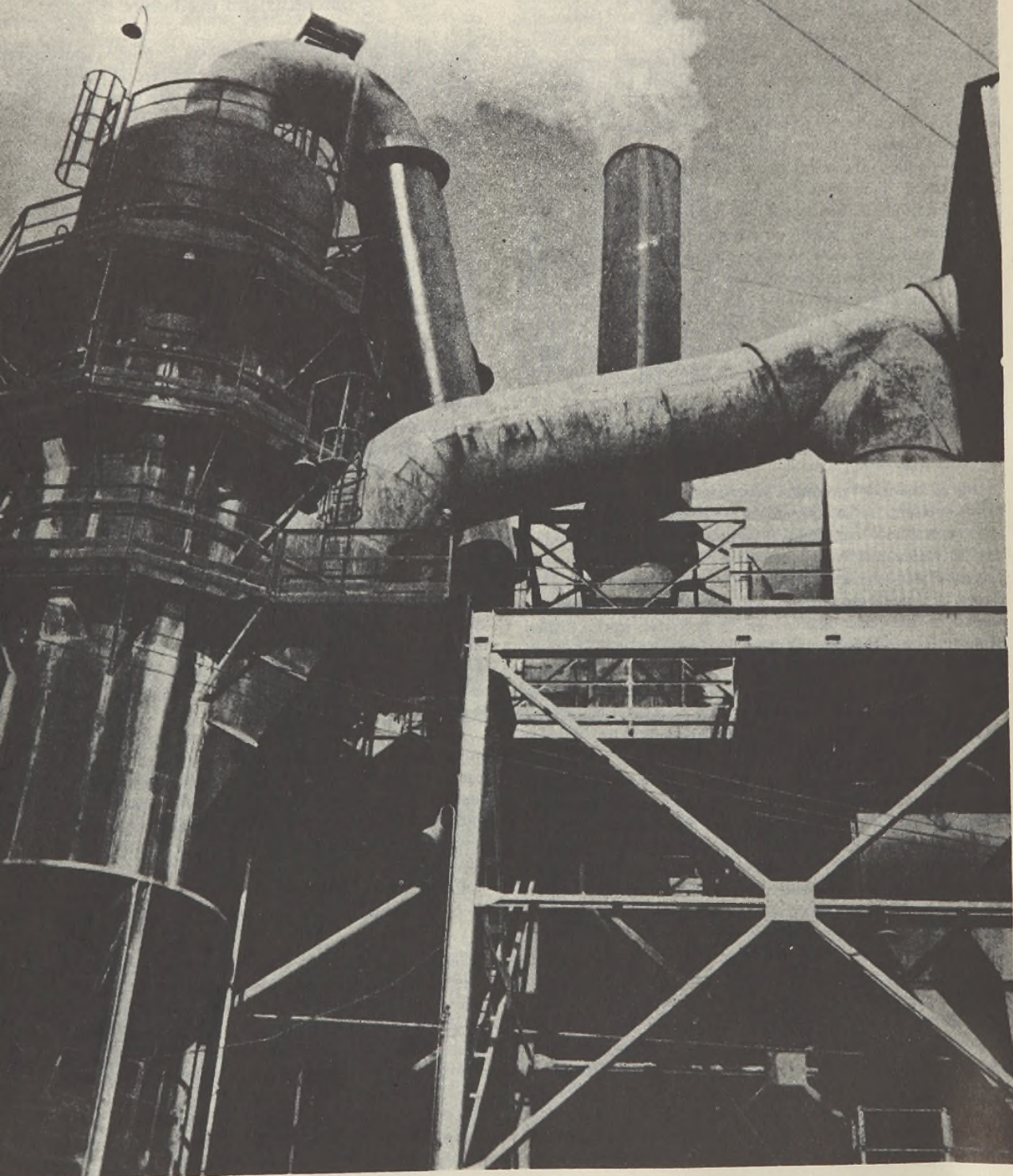
BAUXITE

THE necessity to use domestic low-grade bauxite when high-grade ores from South America were cut off early in the war resulted in bringing to completion a combination process for the recovery of alumina values in the red mud waste from the Bayer process. The red mud slurry is ground with limestone and soda ash and kilned at high temperature; the sinter is leached with water, and the filtrate is passed into the process liquors of the Bayer process where alumina and soda ash are recovered. The sinter operation is an adjunct to the Bayer process, and together they constitute a more economical treatment than a direct sinter on the original bauxite. Four plants utilizing the combination process have been erected, but only two are now in operation because of the present availability of South American ores. Various economic factors and future possibilities of the process are considered in this article.

ONE of the indirect outcomes of the war has been the establishment on a commercial basis of a so-called combination process for the treatment of low-grade aluminum ores. Possibilities of such a process had long held the interest of the aluminum industry, but as long as high-grade ores were available, economic considerations prevented their full development. With the increasing activity of enemy submarines in the Caribbean Sea in 1942, however, supplies of South American bauxite which constituted the main source for the domestic aluminum industry at that time were virtually cut off, and other sources of alumina had to be found. Attention was once again turned to the utilization of low-grade ores. Chemists of the Aluminum Company of America quickly brought to the commercial stage a new process, invented by Ralph W. Brown, for treating low-grade bauxites containing between 10 and 18% silica. There is a substantial reserve of this type of ore in the United States. So great was the need for production capacity of alumina that the new plants were started before the pilot plant investigations had been completed. First construction was in December, 1942, at the Hurricane Creek plant, Bauxite, Ark.; work on a plant at East St. Louis, Ill., began a month later. Both plants commenced operation in December, 1943. Until December, 1944, because of a government secrecy order, details of the combination process were released only to certain operating groups.

Unlike smelting operations, such as those for iron in which impurities are removed in the slag or in subsequent treatments, the electrolytic production of aluminum by the Hall process requires an ore of high purity, since impurities are reduced and then can alloy with the metal. The ore must be in the form of an oxide of the metal and must also be anhydrous. In the early

days of the industry, alumina to meet those exacting specifications was available from a manufacturer of chemicals. By the latter part of 1900 this source was able to provide little more than half the amount of aluminum hydrate needed, and attention was directed to other sources of supply.

Hydrated oxides which occur as bauxites are best suited for production of aluminum metal. Other minerals that contain aluminum, such as clay, shale, feldspar, and granite, are not commercial sources of alumina because in them aluminum is combined principally in the form of silicates; the latter are not economical to process by present methods. Most American bauxites are obtained from Arkansas, but lesser deposits also occur in Georgia, Tennessee, Virginia, and Alabama. The higher grades of Arkansas bauxites contain about 56-59% alumina, 27-30% combined water, 5-12% silica, 1-3% ferric oxide, and small amounts of titania.

BAYER PROCESS

There are two general methods for purifying aluminum ores. In the acid processes, silica causes no trouble but more or less iron is dissolved; in the alkaline processes the reverse is true. Among the alkaline processes, which utilize fusion with soda ash, alkaline earth carbonates, sulfides, or sulfates, and digestion with alkalies or alkaline earth chlorides, the Bayer method has been most generally used. In the latter, bauxite is digested with caustic soda to dissolve alumina, and the silica, iron oxide, and titania impurities are left behind as an insoluble residue, or "red mud", which is separated from the solution. The dissolved alumina is then precipitated from the liquor as aluminum trihydrate, washed, and calcined to produce anhydrous aluminum oxide.

Raw materials for the Bayer process are bauxite, soda ash, and lime. During digestion most of the alumina goes into solution as sodium aluminate. The iron, silicon, and titanium remain in the insoluble residue, the silica forming an insoluble sodium aluminum silicate which carries both soda and alumina into the red mud. Thus, the silica content of the bauxite is important since it causes losses of both soda and alumina. This makes it desirable to use bauxite with as low a silica content as possible. Bauxites for the Bayer process are valued according to their silica and alumina contents.

When the digestion is completed, the sodium aluminate liquor is separated from the suspended mud by settling and filtration. Complete removal of the mud is required because any suspended mud remaining in the liquor will pass on through the process and come out as an impurity in the aluminum oxide. The mud is thoroughly washed, and the wash liquor is clarified along with the sodium aluminate liquor and is then ready for the recovery of alumina. The sodium aluminate solution is pumped to precipitating tanks where it is mixed with a seed charge of aluminum hydrate obtained from a previous cycle and circulated for many hours. During this operation approximately half of the alumina content of the liquor precipitates as aluminum trihydrate; the quantity of alumina cycled is about the same as that produced.

When the precipitation cycle is completed, the liquor with the suspended hydrate is pumped through a classification system which separates the coarser particles for washing and calcination. The finer fraction is returned to the precipitators as seed charge for the next cycle. The coarse fraction of the hydrate is thoroughly washed to reduce the soda content to a low value. The

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One of Seven Scrubbers Which Clean Gases Leaving the 250-Foot Rotating Kilns at the East St. Louis Combination Process Works

washed hydrate is then calcined in rotary kilns to a temperature of more than 1800° F. which converts it into anhydrous and non-hygroscopic alumina suitable for electrolytic reduction to aluminum. The hot alumina discharged from the kilns is passed through a cooler so that it can be handled for shipping.

The chief advantages of this process are low cost and high quality of product; its disadvantage is that a bauxite of low silica content is required. Silica causes loss of both alumina and soda in the Bayer process. For this reason it has been customary in the past to class as high-grade bauxites only those containing less than about 7% silica. In general, the low-grade domestic bauxites available during the war contained approximately 13% silica. Most of the silica is present as one of the clay minerals, usually kaolin; quartz sand can be largely avoided by careful stripping. Kaolin consists of one molecule of alumina, two of silica, and two of water; as such it has the following composition: Al_2O_3, 39.5%, SiO_2 46.5%, H_2O 14.0%. Therefore, each pound of silica present in the bauxite represents 2.15 pounds of kaolin.

When kaolin is digested in a solution of caustic soda and sodium aluminate, a new combination of soda, alumina, silica, and water is formed. This insoluble complex is known as the desilication product; its composition is variable, but it may sometimes be represented by the formula $3Na_2O.3Al_2O_3.5SiO_2.5H_2O$. Assuming the formation of this compound, there would be a loss of 1.05 pounds of sodium carbonate; and whereas 1 pound of silica was combined with 0.85 pound of alumina before digestion, it is combined with 1.01 pounds of alumina after digestion. One pound of silica present in the ore as clay, therefore, causes the loss of about 1 pound of soda ash and 1 pound of alumina. This soda ash must be replaced, and with it must go enough lime to convert the soda ash to caustic soda.
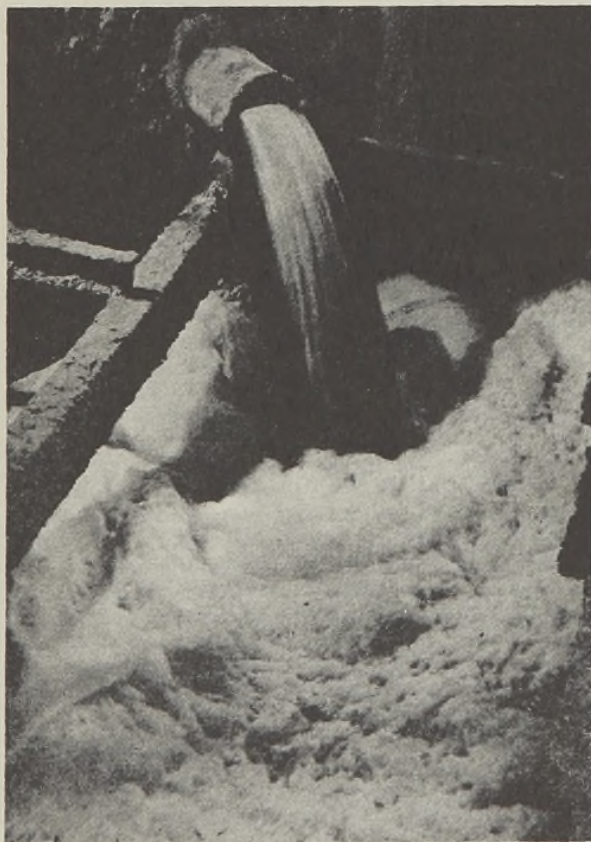
Green Liquor Entering Precipitator

Let us consider gibbsite, a pure bauxite. It consists of 65.4% alumina and 34 6% water. It is completely soluble in the Bayer digest, and no desilication product is formed. Now consider the effect of adding 1% silica in the form of clay. The ore then consists of 2 15% clay and 97.85% gibbsite, and contains 1% silica, 64.84% alumina, and 34.16% water. When this ore is digested, 1.0% alumina is lost, and the alumina is reduced from 64.84 to 63.84%. Thus a silica increase of 1% decreases the recoverable alumina by 1.56%.

Likewise, in digesting a mixture of gibbsite with clay containing 10% silica, 10.1% alumina is lost, and the recoverable alumina is reduced by 15 66% from 59.84 to 49.74%. In the extreme case if pure kaolin is digested, no alumina is dissolved, but the liquor is robbed of alumina equivalent to 7.74% of the kaolin charged to the process.

It is evident, then, that an increase of 1% in silica not only takes out 1% alumina as an inert diluent would do, but also causes the loss of additional alumina due to the formation of desilication product. These four examples are hypothetical ores consisting of two minerals only. Naturally occurring bauxite consists of a variety of minerals with gibbsite and clay predominating. Oxides of iron and titanium function as inert diluents and are always present. Quartz is encountered only rarely in Arkansas bauxite. Some monohydrated oxides of alumina are always present, the amount varying from a trace to several per cent of the total. As a result of these factors a natural bauxite contains alumina in the form of trihydrate, alumina in the form of monohydrate, and alumina as aluminum silicate or clay. If the trihydrate is overheated during drying, it will lose water and become relatively insoluble in the Bayer process digest.

COMBINATION PROCESS

The new method is called "combination process" because a sintering operation is combined in a novel manner with the Bayer process. The efficiency of the combination process is such that the proportion of alumina recovered from high-silica bauxite is higher and the soda loss is lower than in the old Bayer process operating on high-grade bauxite.

In the Bayer process the principal losses of alumina and soda are in the red mud residue which remains after the bauxite has been digested with caustic soda, and the sodium aluminate solution containing the major part of the alumina values has been separated. The red mud contains about one pound of alumina and one pound of soda ash for each pound of silica. In the combination process this red mud is sintered with limestone and soda ash; then it is leached, and the leach liquors are put back into the digester at the start of the Bayer process.

Heretofore the application of the Bayer process has been economically limited to ores with silica contents below about 7%, and yields of approximately 80 to 85% are obtained. With the combination process, however, it becomes feasible to treat ores with as much as 13% or more of silica, which includes much of our domestic bauxites. Even though the yield from the Bayer process is reduced to 70%, as much as 80% of that remaining in the red mud is recovered by the sintering operation. Thus when the 30% alumina remaining in the red mud from a 13% silica bauxite is sintered, up to 24% can be expected to be returned to the process liquors to give an over-all recovery as high as 94% by the combination process. This figure is more than was often obtained by the Bayer process from high-grade bauxites. Yields of 85 to 90% of the total alumina in low-grade ores have been obtained in the commercial operation of the combination process.

The red mud from the Bayer process is mixed with ground limestone and soda ash and sintered in the kiln. The amounts of limestone and soda ash are adjusted so that there is a slight excess of lime over that necessary to combine with silica and a slight excess of soda over that necessary to combine with alumina. The sinter is then ground and leached with water to produce a solution of sodium aluminate and caustic soda which contains the

major part of the alumina and soda which were in the red mud. After filtering and washing, the residue (largely calcium silicate, now known as sinter mud) is run to waste. The filtered solution, which contains sodium aluminate and caustic soda formed during the sintering operation, is then returned to the digester in the Bayer process. The sintering and leaching operation does not separate silica completely, but a small part of it passes back to the digesters with the sodium aluminate solution. Here, however, the silica is completely insolubilized and passes again into the red mud, together with silica and alumina from the bauxite charge.

In comparing performance, the Bayer process requires 2.01 pounds of a 6% silica bauxite per pound of alumina produced as against 1.80 pounds for the combination. At the same time 0.442 pound of lime-free mud is formed with the Bayer process compared to 0.396 pound with the combination. For a 13% silica bauxite the corresponding figures are 2.86 and 2.20 pounds of bauxite and 1.373 and 1.057 pounds of mud, respectively. The advantage of the combination process thus increases at higher silica contents, but the use of clays which are still higher in silica present a greater problem than low-grade bauxite.

In addition to the improved recovery of alumina by the combination process, losses in soda have been reduced. The amount of soda recovered from the red mud in the sintering operations is greatly in excess of the soda ash added in that part of the process, recoveries of 60 to 70% being obtained. In consequence, the amounts of soda ash added at the beginning of the Bayer phase have been materially reduced. Also, the additions of lime to causticize the soda ash in the Bayer phase have been greatly reduced since its function is now largely performed by the limestone which is added and calcined in the sinter process.

INITIAL BAYER OPERATIONS

Bauxite from plant stock piles is moved by clamshell crane, hopper car, and pan conveyors into the grinding building where it is passed through ring roll crushers and 10-mesh scalping screens. It is then ground fine in hammer mills and passed through vibrating screens to bins for analysis. Lime is ground to the same size in hammer mills. All solids are measured into the process by manually operated weigh hoppers.

Medium for the digestion of bauxite is the spent liquor returned from the precipitation of alumina in a previous cycle. After analysis its soda values are brought up by addition of soda ash and lime, and to it is added sufficient bauxite to bring the alumina content up to a par value in the digester. This par value is varied according to the quality of bauxite and the rate of production to obtain the maximum extraction of alumina.

The sinter operation in the combination process has reduced the amounts of soda ash and lime to be added at the beginning of the Bayer phase, both depending on the amount of sinter liquor being used. When this is large, only small quantities of soda ash and lime are needed to bring up the strength of the spent liquor for digestion.

The soda ash is put into solution by mixing it with a portion of the spent liquor. After this fortified portion is sent back to the main body of the solution, it is again divided; part of it goes to continuous slurry mixers to pick up the bauxite and lime, and the remainder passes to the digesters through exchangers, where it is preheated by exhaust steam from the blowoff tanks. The slurry mixers are horizontal cylindrical vessels equipped with paddle agitators.

The digesters are horizontal cylindrical steel tanks equipped with agitating mechanisms. A steam pressure of 50 pounds per square inch or more is maintained in the digesters until the extraction of the alumina is complete. From the digesters the slurry passes to blowoff tanks and then through classifiers where sand is trapped out. The slurry is concentrated in mud thicken-
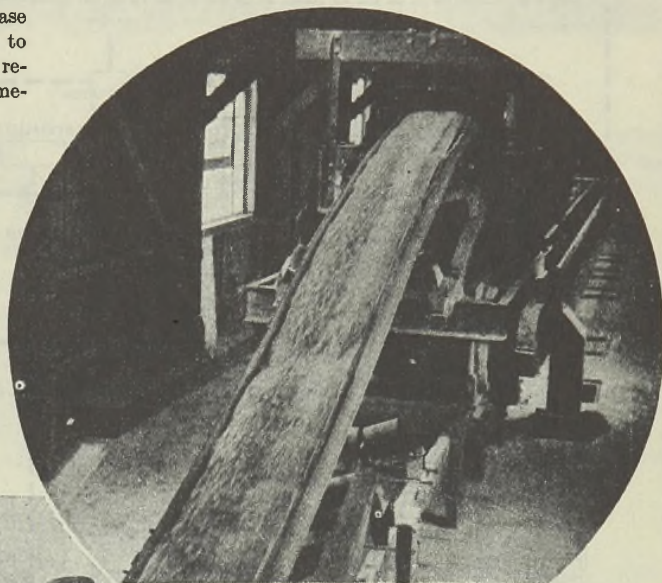
Limestone Feed to Tripper

General View of Kiln Building, Showing a Kiln Feed Slurry Tank, Sinter Kiln, and Scrubber
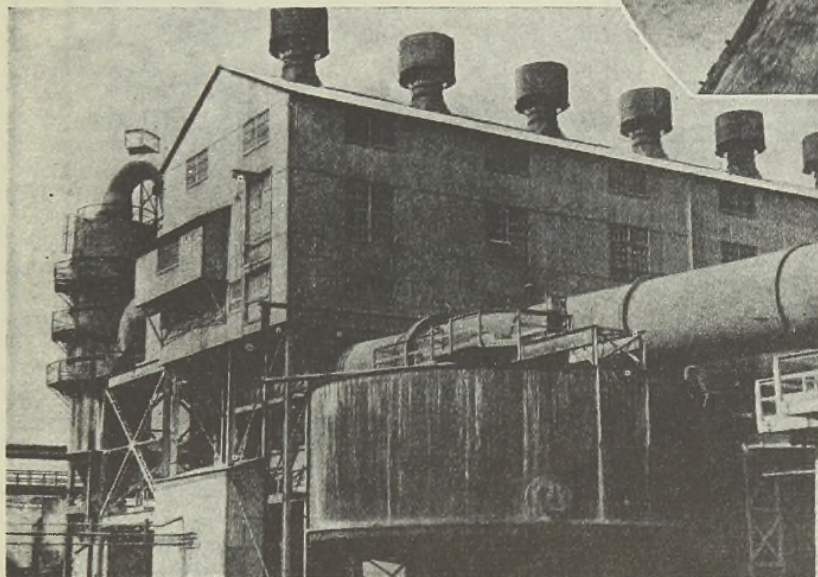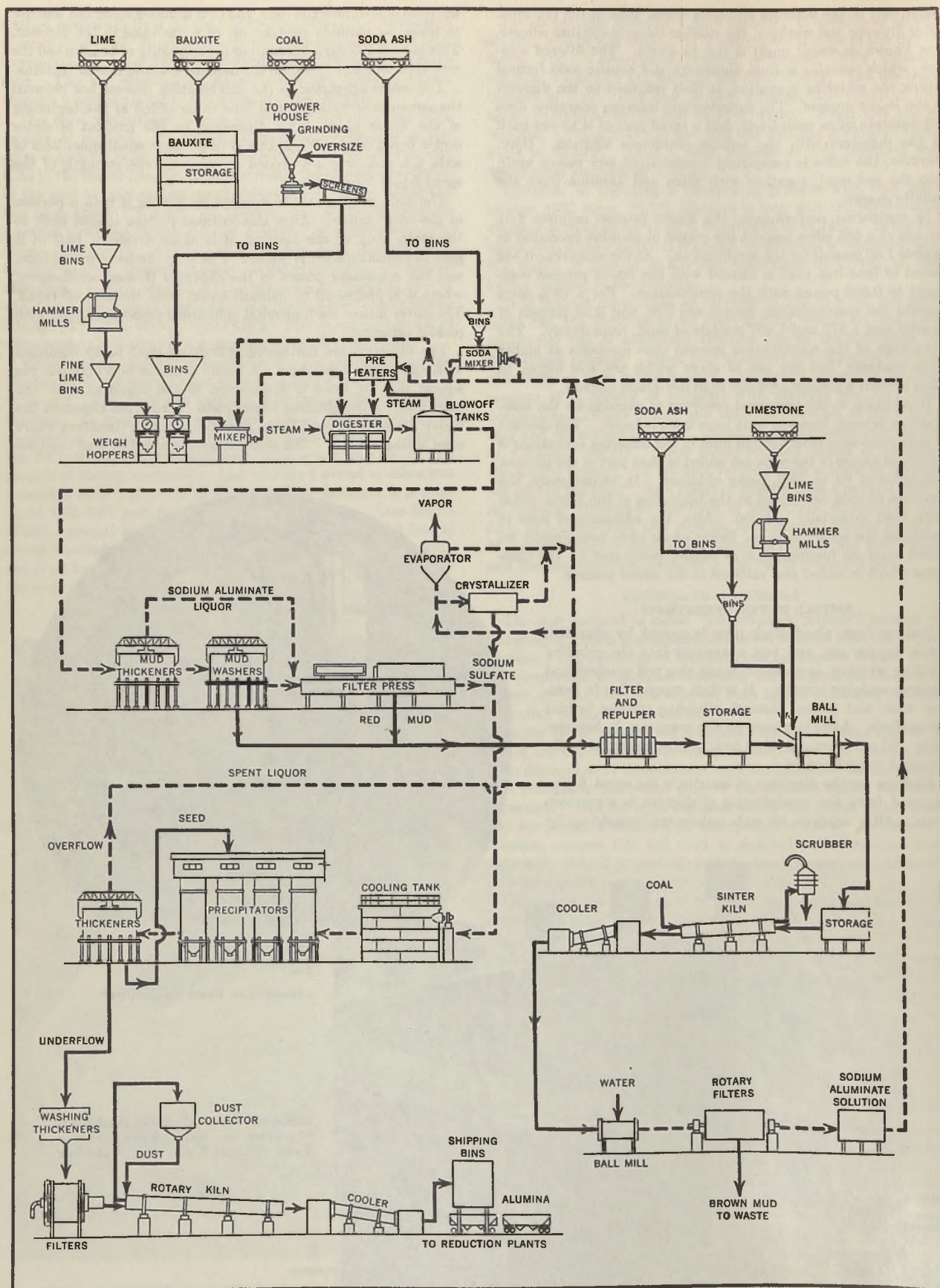
ers, 35 feet in diameter. The overflow goes to Kelly filter presses for clarification, and the underflow goes to mud washers. Before the use of mud thickeners was introduced at the East St. Louis works, the red mud was entirely separated by filtration, but the Kelly presses are now used only to remove the last traces of solids from the green liquor.

The mud washers are 55 feet in diameter. The time of mud passage through the mud thickeners and mud washers may be as long as 24 hours. The overflow from the washers is combined with that from the thickeners and clarified in the Kelly presses. Cake from the Kelly presses is washed from the leaves and may be combined with the red mud for treatment in the sinter process; but the amount is so small that unless the sinter plant is operating at full capacity, it is usually run to storage in the red mud lake.

SINTERING OPERATION

At this point the red mud is diverted to the sintering operation while the green liquor continues in the Bayer process through precipitation to give aluminum trihydrate. In the sintering operation red mud slurry comes from the washers and filter presses at a consistency of about 25% solids, is thickened by filtration, and is then repulped to about 50% solids. It is next pumped to tanks for analysis and storage.

From the results of analysis are determined the amounts of soda ash and limestone to be added to the contents of each tank. An excess of lime is added to combine with the silica present in the red mud, and an excess of soda ash is added to combine with the alumina. The limestone is ground in a primary crusher to less than 0.75 inch and stored in bins, one for each ball·mill. It is discharged into the bins from a belt conveyor equipped with a tripper. From the bins limestone is fed directly into the ball mills through a poidometer.

From the storage tanks, the red mud is pumped through volumetric feeders to be measured. Soda ash is added continuously to the slurry through a poidometer. The slurry is fed to the ball mills through wiers and then flows into the mills along with the limestone. Mixing and grinding take place in ball mills driven by 750-horsepower synchronous motors. Consistency of the slurry discharged from the mills is about 60% solids.

Slurry from the ball mills is stored under the kilns in tanks equipped with agitators and centrifugal pumps for mixing. From the tanks the slurry is pumped into rotary kilns, 9.5 feet in diameter and 250 feet in length, with a capacity of 10 tons per hour. Chain festoons, similar to those in cement manufacture, are used in the kilns to dry the slurry, to improve heat transfer, to cool the gases, and to reduce dust losses. The kilns are operated at 1800° to 2000° F. Scrubbers to recover the dust from the kilns are not standard, having been designed by company engineers. The underflow from the scrubbers is added to the kiln feed slurry.

The sinter is discharged from the kilns into coolers which also serve as preheaters for air to the coal burners. The cool sinter is
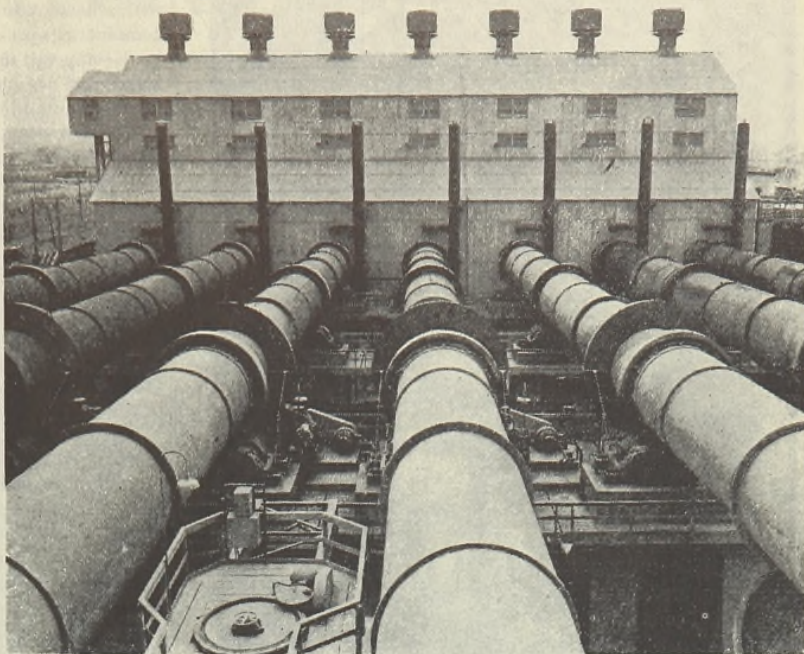
Seven 250-Foot Sinter Kilns

dropped onto a carrier which, in turn, discharges onto a belt conveyor that carries the sinter to storage bins. From storage the sinter is weighed into ball mills where it is mixed with water to be ground and leached.

On leaving the ball mills, the leached sinter slurry is pumped to filters. After passing through a repulper, the sinter mud is pumped to waste in the mud lake behind the plant, and the filtrate goes into the spent liquor cycle in the Bayer process. Some of the spent liquor is passed through evaporators to keep the volume constant, but the amount of spent liquor in the Bayer plant is large enough so that no undue day-to-day fluctuations are experienced through the addition of sinter or other liquors. Part of the liquors are, at the same time, passed through quadruple-effect crystallizing evaporators to remove sodium sulfate which collects in the liquors as a result of the sintering operation.

FINAL STEPS OF BAYER PROCESS

Returning to the Bayer process, the green liquor is a supersaturated solution of alumina in caustic soda. A typical composition in grams per liter is: Al_2O_3, 80–90; $NaOH$, 100–110; Na_2CO_3, 60–90. With an average temperature after filtration around 40° C., depending on the season and the time required for clarification, the green liquor should be cooled before precipitation, the actual temperature being varied to control particle size, impurities, etc. Cooling is accomplished in two ways: The green liquor serves to heat the spent liquor going to the digesters in heat exchangers, and final cooling is done with air in a spray tower, which may be by-passed by part of the liquor in cold weather.

The precipitators are vertical tanks as high as a five- or six-story building. An air lift provides for circulation of the liquors. The cooled green liquor is pumped into the precipitators along with a seed charge of aluminum trihydrate crystals, and the batch is agitated for a day or more. During this period, about half of the aluminum content of the green liquor separates out as aluminum trihydrate.

The precipitate is separated from the liquor by thickeners which collect the coarsest precipitates. The overflow goes to

Flow Sheet for Refining
Bauxite to Produce Alumina   ←
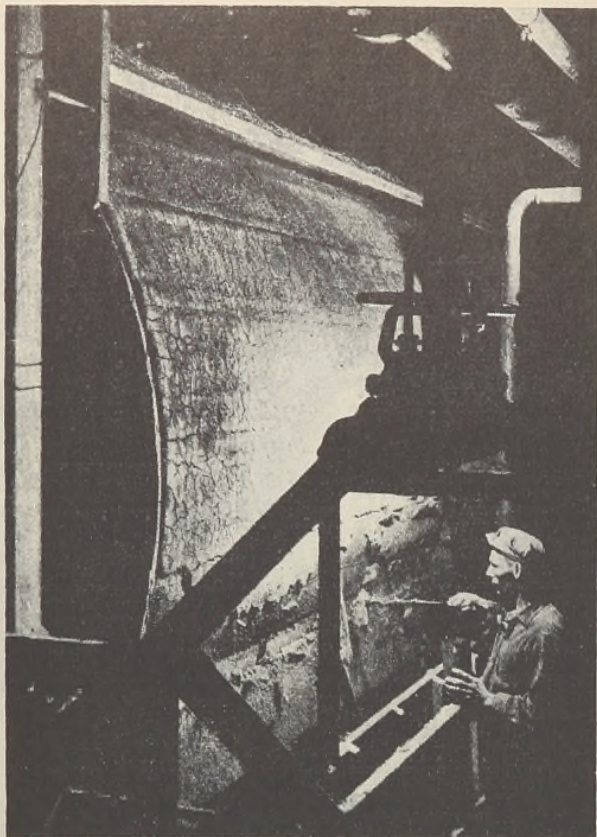
Drum Filter for Separating Sinter Mud from Leach Liquor

tray thickeners for complete clarification. The coarse aluminum trihydrate is washed countercurrently; the final wash passes into the spent liquor cycle through evaporators, since it contains caustic soda, and the aluminum trihydrate goes to the kilns. The thickened slurry is fed to the kilns directly from filters by means of screw conveyors. At this point the moist aluminum trihydrate is a light buff color and has the texture of fine sand.

During calcination the aluminum trihydrate is converted to anhydrous gamma alumina at about 450° C. Finally at about 1000° C. the gamma alumina is converted to the nonhygroscopic alpha form. This is preferred for the production of alumina, in order to avoid carrying water into the electrolytic cell and to avoid water pickup during shipping. It is desirable to have the alumina fairly coarse with a minimum of −400 mesh to avoid dusting losses both during manufacture and at the reduction plant. Some dust is entrained in the kiln gases, however, and it is recovered both by electrical precipitators and by wet scrubbers. The slurry from the wet scrubbers is thickened in settling tanks, further thickened to 90% solids by the addition of precipitator dust, and fed directly into a kiln. Time in the kiln varies from 1.5 to 2 hours.

ECONOMIC CONSIDERATIONS

Although alumina could be produced by a direct sinter process on the original bauxite, the preliminary digestion is an economical treatment. It removes much of the alumina from the ore by a cheaper operation, and by reducing the amount of sinter to be produced, less soda, lime, and coal or gas are required. In general, the amount of sinter to be treated by furnacing a 13% silica bauxite would be twice as much as that required in sintering its red mud.

Some additional considerations that would be introduced by

sintering the original bauxite might be mentioned. Starting with a low-grade bauxite, soda ash would have to be added to combine with all of the alumina, and the sodium carbonate would be decomposed in the furnace to form sodium aluminate. After solution of the sodium aluminate, only half the alumina would be precipitated in the Bayer process. The other half, remaining soluble as sodium aluminate, would have to be precipitated with carbon dioxide, and the regenerated soda crystallized from solution in order to return soda to the next cycle of sintering. These additional operations would make the direct sintering of ores more complicated than sintering of muds obtained after extraction of a large part of the alumina by the Bayer digest.

If, on the other hand, the Bayer spent liquor were returned to the initial sinter step in order to supply caustic soda, then all of the soluble alumina in the spent liquor would have to be refurnaced. More sinter would then be produced than would be obtained from bauxite alone, and the cost of the process would increase.

The combination process, therefore, removes as much alumina as possible by utilizing the less costly Bayer process before the furnacing treatment is applied. About 70% of the alumina in the red mud is being recovered at the East St. Louis sinter plant at the present time, but recovery is expected to be raised to 80% in the near future. One factor that may materially increase operating efficiencies is the removal of several hundred thousand pounds of sulfates per day from the process liquors through the use of crystallizing evaporators, recently installed at the East St. Louis plant. Although the sulfur content of the coal used in firing the sinter kilns is a significant source of these sulfates, they are normally present in all ores but have not heretofore appeared in the process liquors. Formerly passing out of the process with the red mud wastes, the sulfates are now dissolved in the sintering operation and must be removed to permit normal operation of the Bayer cycle. The substitution of gas or oil for coal would diminish but not eliminate this problem. Natural gas from near-by fields is used in firing the kilns at Hurricane Creek, and the sulfur problem is less acute at that plant.

The economic picture in the production of alumina has changed. In 1902, when the original plant was built at East St. Louis, high-grade ores were available in this country, and it was economical to ship them some distance for processing in order to locate near sources of the other heavy raw materials—coal, limestone, and soda ash. This is no longer true. Natural gas and oil are replacing coal in the alumina plants, soda ash is manufactured in many parts of the country, and limestone can be obtained almost anywhere; all of these factors minimize the influence of secondary raw materials on the location of a plant. If domestic ores are used, they are such low grade that it is uneconomical to ship them over long distances; in fact, it is no longer feasible to ship bauxite to any distant plant if it can be refined at the source. Furthermore, since there is no relation between the refining and reduction of alumina, it is not necessary that these operations be located together.

A sinter plant was built at Mobile, Ala., in 1943 on the expectation that South American ores could not be obtained. By the time it was finished the submarine menace had been dispelled, and the ship building program had increased imports to a point where the sinter plant was not needed. A plant was completed at Baton Rouge, La., about the same time; it was operated for several months and then shut down completely since other sources proved sufficient without it.

As to the future of the combination process, it should be remembered that the sinter plants were a war measure, erected solely to permit scheduled production of existing Bayer plants with low-grade domestic ores as the entire source of alumina. They served to carry the aluminum industry through a critical period. How long they will be continued after the war depends on economics, future developments, and the desirability of maintaining them as stand-by plants.

CRYPTOSTEGIA LEAF RUBBER

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CRYPTOSTEGIA, a leafy tropical vine native to Madagascar, produces a latex which contains rubber. This rubber has been marketed from time to time; its properties are generally similar to those of hevea rubber (*1*). The leaves of the plant contain benzene-soluble material considered to be rubber (*4*). Two species, *Cryptostegia grandiflora* and *C. madagascariensis*, were introduced into this hemisphere, and the former has become widely dispersed throughout the West Indies, Central America, Mexico, and the extreme southern portions of the United States. For a number of years the United States Department of Agriculture has conducted botanical investigations upon *Cryptostegia* as a possible source of rubber (*13*). This work confirmed the existence of rubber in the leaves. Jenkins reviewed the information available in January, 1943, on *Cryptostegia* as an emergency source of rubber (*5*).

Properties of the leaf rubber became of interest when plantations were established with the primary aim of producing latex rubber from cryptostegia stems, since large quantities of leaves would thus be made available from normal pruning operations. Moreover, it was possible that the plant would be grown for the production of leaf rubber alone, provided its quality was high and satisfactory means of recovery could be worked out. In fact, the labor required to tap the vines for latex practically precluded the employment of this process in the United States and Mexico.

The characterization and isolation of the leaf rubber have been of primary interest. Whittenberger, Brice, and Copley (*19*) demonstrated that only 10 to 15% of the rubber in the mature leaf occurs in the latex ducts; 85 to 90% is embedded in the individual chlorenchyma cells as discrete globules. This "cell rubber" is, of course, not directly available by tapping the latex system of the leaf and has not been satisfactorily recovered by pebble-milling procedures of the type used in the production of guayule rubber. The latex duct rubber of the leaves is essentially the same as the rubber obtained by tapping the latex system in other portions of the plant. In the dried leaves it is coagulated and therefore contains the nonrubber constituents of the latex, which are largely removed during coagulation of latex obtained by tapping procedures. Extensive studies were carried

The leaves of *Cryptostegia grandiflora* have been investigated as a possible emergency source of rubber, supplementing the latex rubber from the stems. The leaf rubber consists of two distinct portions; 85 to 90% is a relatively low-polymer rubber which occurs in the chlorenchyma cells, and 10 to 15% is a latex rubber of better quality which occurs in the latex ducts. Isolation of the leaf rubber by a combination of fermentation and chemical extraction, and the characterization of vulcanizates are described.

out on fermentation as a step in the recovery of the leaf rubber. An anaerobic fermentation by *Clostridium roseum* was worked out in which more than 60% (dry weight) of the leaves is digested. After two days' incubation the leaves are well digested and disintegrated. This slurry is passed over a vibrating screen (80 × 80 meshes to the inch). The liquid and protoplasts pass through, and the bagasse (cuticle, veins, and small stems) remain on top. The latex ducts in cryptostegia leaves are closely associated with the veins and, owing to their length, are trapped in the bagasse. The bagasse is suspended in one half the original volume with water and again screened to recover an additional quantity of protoplasts that are trapped mechanically. The bagasse is freed of excess water by pressing and then dried. The protoplasts (specific gravity 1.17–1.27) are recovered from the liquor in which they are suspended by gravity settling and decantation; they yield a slurry containing about 4–7% solids. The slurry is further freed of soluble materials by rediluting with water, settling, and decanting. Figure 1 shows the fermentation equipment. The bacteriological aspects of this fermentation have been described elsewhere (*12*).

This paper presents two procedures for the recovery of the cell rubber from the fermentation products. The first consists in isolation of the protoplasts followed by a "caustic cook" to liberate the rubber. The photomicrographs of Figure 2 illustrate the successive stages in this process. By the second procedure all the leaf rubber is extracted by benzene. Chemical and physical data on the raw rubber obtained by these processes are given, and certain properties of the vulcanizates are evaluated.

CAUSTIC-CREAMING PROCESS

Previous work demonstrated that the protoplasts obtained by fermentation could be digested by dilute alkali and thus release the rubber globules (*12*). Boiling a 10% suspension of the protoplasts for 20 minutes in water containing 2% sodium hydroxide was the standard procedure in the work described here. One per cent powdered JZF (4,4'-diphenylphenylenediamine), based on the amount of rubber, was added as antioxidant. The suspension containing the liberated rubber globules formed a "cream" when it stood without stirring. The cream was siphoned off the surface, dis-

TOP VIEW

RUBBER GASKET
GAUGE GLASS
MOTOR
CO₂
WATER LEVEL
STIRRER
STEAM
4'-0"
2'-6"
QUICK OPENING VALVE
DRAIN
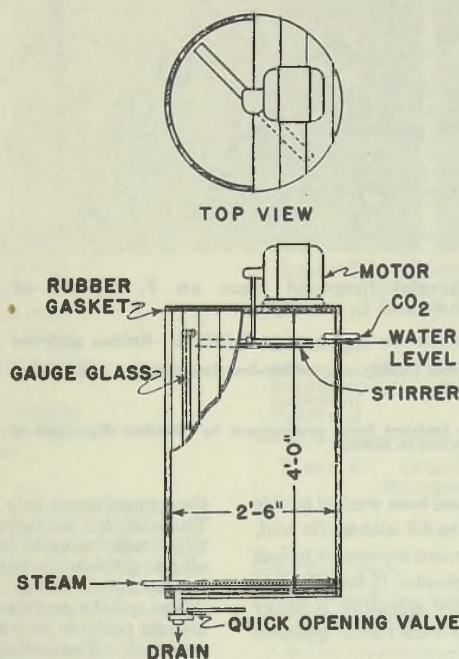
Figure 1. Anaerobic Fermentation Tank
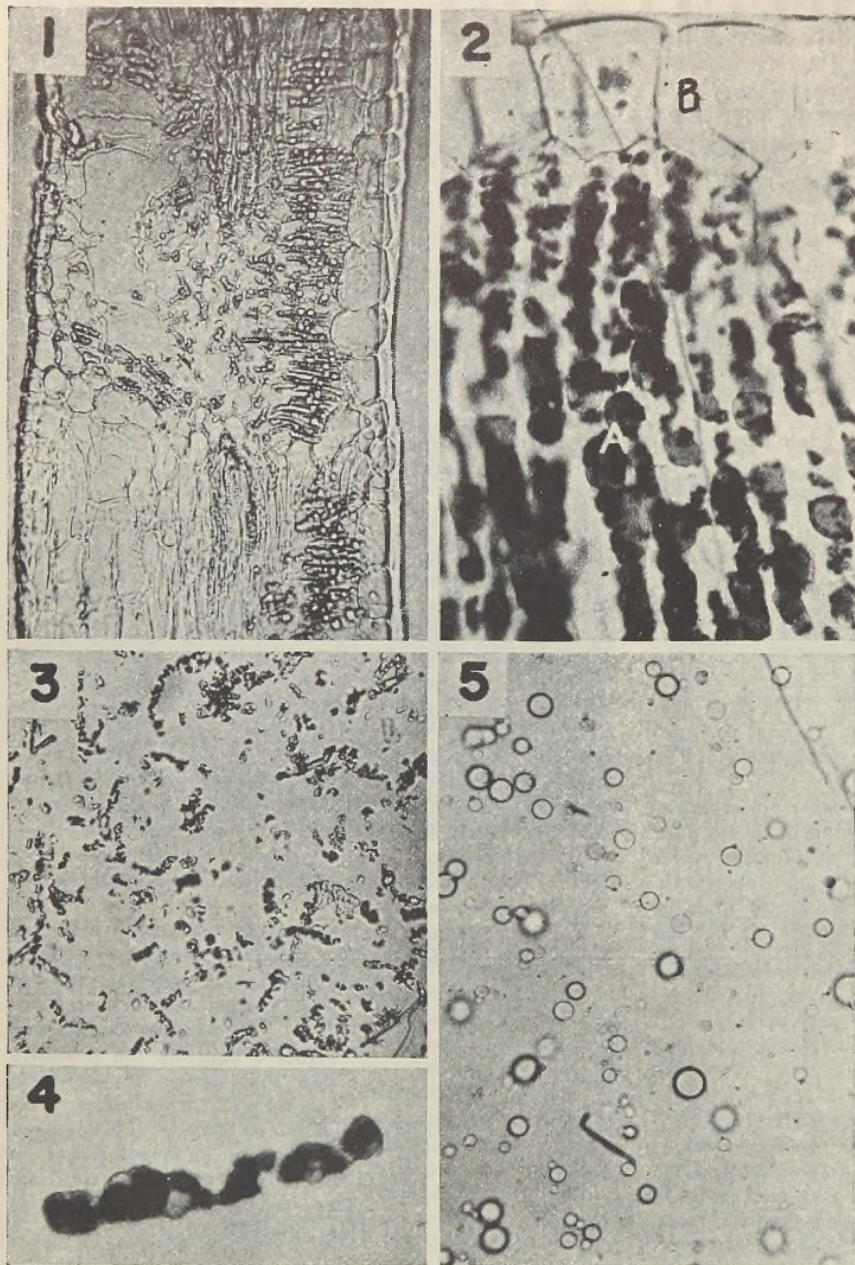
Figure 2. Photomicrographs of Material Prepared from an F₁ Hybrid of *C. madagascariensis* and *C. grandiflora*

1. Cross section of preserved specimen of mature leaf, unstained (×130). Rubber globules visible in chlorenchyma.
2. Cross section of fresh, living, senescent leaf (×460). *A*, rubber-bearing globules and chloroplasts within palisade cells; *B*, upper epidermis.
3. Protoplasts from retted leaves (×130).
4. Protoplast from retted leaf (×1000).
5. Suspension of rubber-bearing globules isolated from protoplasts by alkaline digestion of protoplasts (×460). Many of the globules are not in focus.

of methods for their recovery. About 4 liters of the liquor produced by boiling the protoplasts in alkaline solution was allowed to cream overnight in a depth of approximately 25 cm. A small sample (0.1 ml.) of the cream was taken off and diluted for microscopic observation (sample A), after which the dispersion was stirred thoroughly with a mechanical stirrer, sampled (B), and subjected to centrifugation at 2000 r.p.m. (925 × gravity) for different periods. After centrifugation the rubber was completely removed from the surface and the liquor underneath analyzed for rubber (Table I). Microscopic observations were carried out upon the liquor of the 20-minute sample (C).

The analytical results reported in this paper were obtained by Willits and co-workers (20). The samples were extracted with benzene, benzene insolubles were determined by filtration of the benzene solution, and rubber hydrocarbon was then determined gravimetrically by precipitation as the tetrabromide. Resins were calculated by difference. Rubber could not be quantitatively extracted from the raw leaves unless a preliminary treatment with oxalic acid was applied. Resins and rubber were determined by a modified Spence-Caldwell procedure.

The samples were prepared for microscopic examination by mixing 0.01 ml. of each with 0.01 ml. glycerol on a slide, carefully evaporating the water, and covering with a cover slip. Brownian motion of the particles was thereby suppressed, and the globules could be accurately measured and counted. The number of globules in each size group was determined in a large number of fields selected at random; a calibrated eyepiece micrometer was used. (The count of the smallest globules in whole liquor B is an estimate obtained by calculation from the count of the centrifuged sample C. This was necessitated by the denseness of the slide of the whole liquor and the number of bacterial cells present, which caused difficulty in counting the smaller particles. An appreciable error in this estimate would not affect the weight distribution markedly, for the total weight of this fraction was only 4% of the whole.) The data are presented in Table II and Figure 3. Data for hevea latex taken from Lucas (8) are included in Figure 3 for comparison.

To calculate the results, the globules were assumed to be homogeneous and identical in composition, independently of size. This assumption is justified within the limits of accuracy desired here. Analysis of the data shows that 91% of the total number of globules in the whole liquor were present in the two smallest size classifications (1 and 2μ diameter), yet they constituted only 16% of the weight of the rubber present. These smaller particles were almost entirely absent in cream A which rose during 16 hours' standing. Moreover, they constituted all the globules in liquor C after a centrifugation equivalent to 300 hours' standing.

The specific gravity of the globules was determined by the equilibrium position they assumed when centrifuged in water-alcohol mixtures. The average specific gravity of the globules recovered by creaming was 0.92, although for some it was as high as 0.96. The specific gravity of the alkaline cook liquor was 1.02. Substitution of these values and the microscopically determined

persed in water, and recreamed. After it had been washed in this manner several times, the pH was adjusted to 4.6 with acetic acid, whereupon the globules "clumped", the cream separated in less than half an hour, and clear serum remained. If the alkaline liquor was adjusted to pH 4.6 without prior creaming, a heavy precipitate of proteinaceous material trapped the rubber globules and carried them down with it.

CREAMING STUDIES. The distribution of particle size and density of the globules were determined to facilitate development

TABLE I. REMOVAL OF CELL RUBBER BY CENTRIFUGATION
(AT 925 × GRAVITY) OF ALKALINE DISPERSION

Centrifugation Time, Min.	Rubber Content of Liquor, Mg./100 Ml.	Proportion of Total Rubber, %
0	198	(100)
5	49	25
10	50	25
20	45	23
40	34	17

TABLE II. NUMBER AND WEIGHT DISTRIBUTION OF GLOBULES OF CRYPTOSTEGIA LEAF CELL RUBBER

Av. Diam. of Globules, μ	% in Whole Liquor B		% in Gravity Cream A		% in Centrifuged Liquor C	
	No.	Wt.	No.	Wt.	No.	Wt.
1	67	4.2	0	0	72	24
2	24	12	10	0.3	28	76
3.6	3.5	9	23	4	0	0
5	2.2	17	25	13		
6.5	1.4	25	24	26		
8	0.8	27	12	26		
9.5	0.1	6.4	1.1	4.2		
11	0	0	2.4	18		
12.5			1.1	8.9		

radii in Stokes equation gave satisfactory agreement with the observed rate of creaming.

Microscopic and chemical data indicate that a maximum of about 80% of the rubber in this sample could be recovered by direct creaming of the suspension. Attempts to find creaming agents or conditions which would facilitate the separation of the smaller particles were not successful.

These data were obtained on globules prepared from a typical sample of Cuban leaves having a rubber content of 3.2%. A sample of mature selected leaves later obtained from the U. S. Rubber Company plantation at Yuma, Ariz., had a rubber content of 6.9%, and a large proportion of the rubber globules were 30 to 40μ in diameter. It is obvious that the rate of creaming depends upon the size of the globules. It has been well established that the rubber content (13) and the size of the globules vary with the age of the leaves (9, 19), and therefore the rate of creaming varies with the maturity of the leaves.
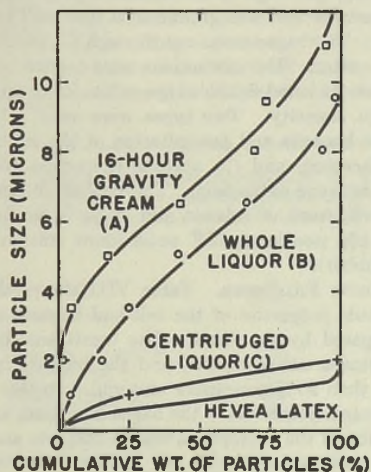
Figure 3. Cumulative Weight Distribution of Cryptostegia Cell Rubber Globules

COMPOSITION OF LEAF CELL RUBBER. Samples of globule rubber were prepared by gravity creaming and centrifuging. The first sample was allowed to cream for 14 days. The cream was then drawn off, diluted with water, and recreamed three times at 48-hour intervals to remove the alkali and other contaminants. The final cream, containing about 50% solids, was dried in vacuo at 50° C. Other samples were creamed for 2 to 4 days, and an antioxidant (JZF) was introduced into the alkaline liquor. The recovery of rubber hydrocarbon by this method ranged from 70 to 75%, which agrees well with the data obtained in the creaming studies. Samples were also prepared by centrifugation to elimi-

nate the effect of long exposure to the air during creaming. The cell rubber was recovered in a total time of less than 3 hours by centrifuging the alkaline cook liquor, adjusting the pH to 4.6, and washing the cream twice. Table III gives analytical data on typical preparations. The crude rubbers obtained both by gravity creaming and by centrifuging were soft and tacky, and contained a large proportion of acetone-soluble material (resins).

Rubber deresinated by precipitation from benzene solutions with acetone was prepared for further studies of its properties. It was firmer than the resiniferous material but still relatively soft and tacky. Inasmuch as the physical properties indicated that it was a relatively low polymer rubber, it was extracted with methyl ethyl ketone (MEK), which is considered to be a solvent for the lower-molecular-weight fraction of hevea and for depolymerized rubber (3). The leaf cell rubber was almost completely soluble in MEK (Table IV). Comparative data were obtained upon a sample of smoked sheet of cryptostegia latex rubber which had been exposed to the air for several months. The MEK solubility indicates that the latex rubber is comparable to hevea latex rubber in this respect. Cheyney found that 5 to 8% of crepe and vulcanized rubber and 25% of reclaim were extracted by MEK (3).

Further evidence concerning the molecular weight of the cell rubber was obtained by measuring the viscosity of dilute benzene solutions of the rubber. These experiments were based on the methods of Kemp and Peters (6). Several samples gave molecular weight values in the range 10,000 to 16,000. These results are consistent with the physical properties and solubility relations, all of which indicate that the leaf cell rubber is of relatively low molecular weight.

The possibility that there had been oxidative breakdown of the rubber during drying, storage, and shipment of the leaves from Cuba was investigated. Several samples of mature leaves were prepared at Yuma by (a) air drying and (b) sterilizing by canning the fresh leaves in water. It was assumed that oxidative breakdown would be minimized in the sterilized samples. These leaves were shipped to Philadelphia, and globule rubber was prepared from each by the anaerobic fermentation process. There was no significant difference in the acetone-soluble contents (resins) of these two preparations, nor did they differ from results previously obtained upon Cuban leaves (Table IV). It was therefore concluded that no appreciable oxidative breakdown was caused by drying and storing the leaves.

COMPOUNDING AND PHYSICAL PROPERTIES. Samples of crude cell rubber prepared by the caustic-creaming process were compounded by a modified A.S.T.M. evaluation procedure. The recipes (Table V) were similar to those employed by McKennon and Lindquist compounding rubber obtained from goldenrod by extraction methods (10). Considerable difficulty was encountered in securing satisfactory dispersion of the compounding ingredients in the soft crude stock.

Because of the limited quantities of rubbers available, a test slab 0.030 inch thick was substituted for the usual 0.075- or 0.100-inch slabs. Also, sandwich-type, stainless steel molds having exceptionally broad bands were used because of the excessive plasticity of the compounded stocks. A curing temperature of 260° F. was used for the gum stock recipes, except for certain slow-curing samples which were cured at 274°. The thin test specimens probably had slightly greater tensile strengths than specimens of standard thickness, but the increase would probably

TABLE III. COMPOSITION OF CRYPTOSTEGIA LEAF CELL GLOBULES OBTAINED BY CAUSTIC CREAMING PROCESS

Sample	% Rubber Hydrocarbons	% Resins	% Benzene-Insoluble Material
Gravity-creamed	68.3	30.9	0.8
Gravity-creamed	57.5	38.2	4.3
Centrifuged	52.7	45.5	1.8
Centrifuged	62.3	36.2	1.5

TABLE IV. COMPOSITION OF CRYPTOSTEGIA LEAF CELL RUBBER[a] AND SOLUBILITY IN MEK

Source of Rubber	Rubber, %	Resins, %	Benzene Insol., %	Sol. in MEK, %
Typical Cuban leaves	57	39	4	93
Dried Yuma leaves	64	33	3	91
Canned Yuma leaves	60	37	3	94
Typical Cuban leaves, pptd. from benzene soln. by 2 vol. acetone	91	9	0	100
Latex, smoked sheet (Haiti)		9	..	17

[a] Rubber was determined as tetrabromide, insolubles by direct extraction, and resins by difference (20). Solubility in MEK was determined by direct extraction.

TABLE V. RECIPES USED IN EVALUATING CRYPTOSTEGIA LEAF RUBBER STOCKS

	Recipe, Parts		
	A	B	C
Crude cryptostegia rubber	100	100	100
Zinc oxide	6	6	6
Mercaptobenzothiazole (Captax)	1	1	1
Stearic acid	4	4	4
Diphenylguanidine (DPG)	0.5	0.5	0.5
Sulfur	3.5	3.5	2.5
Reinforcing black (Standard Micronex)	...	30	30

TABLE VI. COMPOSITION AND PHYSICAL PROPERTIES OF CRYPTOSTEGIA LEAF CELL RUBBER RECOVERED BY CAUSTIC CREAMING

	Recipe A			Recipe B	
	Resiniferous		Deresinated, creamed	Resiniferous, centrifuged	Deresinated, creamed
	Creamed	Centrifuged			
Composition, %					
Rubber hydrocarbon	68.3	52.7	85.0	52.7	85.0
Resins[a]	30.9	45.5	14.3	45.5	14.3
Benzene-insol. material	0.8	1.8	0.7	1.8	0.7
Physical properties					
Optimum cure, min.	25	20	20	35	20
Cure temp., ° F.	260	274	260	274	274
Optimum tensile, lb./sq. in.	400	1000	1500	650	1950
Ultimate elongation, %	720	630	680	350	550
Modulus at 500%, lb./sq. in.	...	....	600	...	1750
Hardness (Durometer)	25	28	37	57	60

[a] Includes 1% of JZF antioxidant.

not be greater than 200 pounds per square inch. Table VI shows tensile properties of the cryptostegia leaf cell rubber as recovered by caustic creaming.

To determine the effect of resins on the properties of cell rubber, the resiniferous stock was dissolved in benzene and precipitated by acetone. Table VI also shows the composition and physical properties of the deresinated rubber. It is evident that the deresinated cryptostegia leaf cell rubber recovered by the caustic-creaming process was superior in tensile properties to the resiniferous creamed product. Improvement in tensile strength resulting from deresination is probably due in part to improved dispersion of the ingredients as well as to reduction of nonrubber constituents in the specimen.

SOLVENT-EXTRACTION PROCESS

The possibility of direct solvent extraction of the fermentation products appeared worthy of investigation. This method would have the advantage of recovering the latex duct rubber in the leaves as well as the cell rubber not recovered by creaming.

Fermentation as an aid to solvent extraction of rubber was patented in 1873 (7). That rubber can be more easily extracted from fermented plant materials has been repeatedly demonstrated (15, 17). Moreover, the removal of nonrubber constituents and the consequent increase in rubber content of the extractor charge decreases the cost of extraction greatly. Improvement in aging properties caused by leaching of metal salts, etc., during fermentation might be an additional advantage. This factor was not investigated, however, as it was impossible to prepare the leaf rubber satisfactorily by any method which did not involve fermentation or leaching.

Table VII gives typical data on the rubber content and bulk of the raw leaves and fermentation products. The increase in rubber content of the extractor charge averaged 2.9 fold on a weight basis and 3.3 fold on a volume basis. Recovery of rubber was essentially quantitative in all four experiments. These fermentations were run for two days, as in the previous work. Unpublished work has shown that greater decomposition can be obtained in additional time; the gain, however, is not great, and the products become progressively more slimy and difficult to filter.

RATE OF EXTRACTION. Ease of extraction of both resins and rubber from the fermented leaves was markedly increased. Data to illustrate this effect were obtained by periodically weighing the extract of small samples extracted by hot percolation of solvent in the regular analytical equipment (Figure 4). The resin extractions were run for 24 hours; the residues were dried in a current of air until free of acetone, and then extracted with benzene. Both extractions proceeded more rapidly in the fermented materials. The difference in the rate of extraction of rubber was especially great. In fact, the rubber could not be completely recovered from untreated leaves even with prolonged extraction[1], whereas extraction of rubber from the fermented leaves was essentially complete in 2 hours under the conditions employed. Lack of pilot-plant equipment made it impossible to obtain data under conditions comparable to those used in large-scale solvent extractors.

METHODS OF EXTRACTION. Solvent extraction can be applied to both protoplasts and bagasse when the two fractions are separated by screening. The bagasse contains the latex duct rubber of the leaves, which presumably is of better quality than the cell rubber. Any protoplast rubber not released by fermentation would also be in this fraction.

Although in practice the fermentation products would probably be recovered and dried without fractionation, for purposes of evaluation the two fractions were prepared by screening the fermented slurry (through 80 mesh) and drying in air at 70° C. The protoplast fraction was ground in a disk mill to pass a 20-mesh screen. The bagasse was cut through a 1/8-inch screen in a rotary knife cutter. The extractions were carried out in an improvised steam-jacketed Soxhlet-type extractor of approximately 0.8 cubic foot capacity. Two types were used: (1) direct extraction with benzene and precipitation of the rubber with 2.5 volumes of acetone, and (2) acetone extraction (deresination) followed by benzene extraction. The rubber obtained by both procedures was freed of solvent and dried in vacuo, after the addition of 1% powdered JZF antioxidant (estimated on the amount of rubber).

LEAF RUBBER FRACTIONS. Table VIII shows the composition and tensile properties of the cell and bagasse rubber fractions as prepared by process 1. The treatment did not completely deresinate either sample, and the bagasse fraction contained more than 20% nonrubber material. In this experiment 35% of the total rubber was in the bagasse portion, an indication that separation of the protoplasts was incomplete and that latex rubber was contaminated with cell rubber. Nevertheless, the crude bagasse rubber was considerably firmer and less tacky than the cell rubber. The tensile properties of the bagasse fraction were definitely better and probably reflected the better quality of the latex duct rubber it contained.

The protoplasts were then extracted by procedure 2, first with acetone and then with benzene. The benzene solution was divided into two portions; one was precipitated with acetone, and the second was evaporated dry in vacuo. Both prepara-

[1] Willits and co-workers (20) had previously found it necessary to use special chemical treatments prior to extraction to obtain complete extraction of rubber from untreated leaves.

TABLE VII. ENRICHMENT IN CRYPTOSTEGIA LEAF RUBBER BY FERMENTATION BY *Clostridium roseum* AT 40° C. FOR TWO DAYS

	Original Leaves				Fermentation Products				Enrichment Factor for Rubber	
			Rubber Content				Rubber Content			
Expt. No.	Dry wt., lb.	Vol., cu. ft.	%	Lb.	Dry wt., lb.	Vol., cu. ft.	%	Lb.	By wt.	By vol.
S25N30	16.44	0.85	4.2	0.684	6.02	0.27	11.0	0.662	2.6	3.2
S24N3	52.9	2.7	2.8	1.455	18.06	0.82	8.0	1.434	3.1	3.3
S24N4	51.8	2.7	2.5	1.257	17.82	0.81	6.7	1.190	2.7	3.3
S24N5	52.2	2.7	2.2	1.170	17.74	0.84	6.6	1.170	3.0	3.2

tions of the cell rubber were almost free of resins. Table IX presents the composition and tensile properties of the two preparations compounded by the gum recipe A. The difference between the two samples is slight, and the results agree well with those obtained with the deresinated cell rubber prepared by the creaming method (Table VI). The tensile properties of both samples were superior to those shown by the less completely deresinated sample of cell rubber in Table VIII.

WHOLE LEAF RUBBER. Properties of the mixture of duct and cell rubber which would be obtained if the fermented residues were extracted without fractionation were determined. The small amount of higher-grade duct rubber would certainly not justify extraction for this fraction alone, but there would be no point in discarding it if solvent extraction were to be utilized for recovery of the leaf rubber. For this experiment and the following one on blending with GR-S, several fermentations were carried out (Table VII). The leaf fractions were separated, dried, ground, and extracted with acetone and benzene. [The acetone extract, "resin", investigated by White and Senti (18) as a by-product of possible value, contained ursolic acid and higher paraffins typical of leaf and fruit cuticle waxes.] The benzene extracts were freed of solvent in vacuo. Yields ranged from 95 to 105%, on the basis of the rubber content of the leaves fermented. The rubber from the two fractions was combined on a cold mill in the same proportions as the fractions bore to the original amount in the leaves (27% bagasse rubber to 73% cell rubber).

The mixture was so tacky that it was unsuitable for processing according to standard rubber mill techniques. It should be noted here that the solution method of compounding developed by McKennon and Lindquist (10) for solvent-extracted goldenrod rubber would be directly applicable to cryptostegia leaf rubber and would make it suitable for processing on conventional rubber mill equipment. However, this type of compounding and precuring was not investigated in this experiment. When this stock was compounded on a roll mill by recipe A and cured in a standard 6 × 6 inch A.S.T.M. test slab mold, it was too soft to be retained in the mold, and the resulting vulcanizate was porous. Presumably it could have been compounded and cured in the smaller quantity and special mold used in the previous work.

TABLE VIII. COMPOSITION AND PROPERTIES OF RUBBER RECOVERED FROM CELL AND BAGASSE FRACTIONS OF CRYPTOSTEGIA LEAF BY SOLVENT EXTRACTION AND ACETONE PRECIPITATION

	Cell Rubber	Bagasse Rubber
Composition, %		
Rubber hydrocarbon	86.4	77.1
Resins[a]	10.7	22.0
Benzene-insol. material	2.9	0.9
Physical properties[b]		
Optimum cure, min. at 260° F.	20	20
Tensile strength, lb./sq. in.	1050	2050
Ultimate elongation, %	730	720
Modulus (600%), lb./sq. in.	150	1000
Hardness (Durometer)	31	40

[a] All resin values include 1% JZF.
[b] Compounded by gum recipe A.

TABLE IX. EFFECT OF RECOVERY BY PRECIPITATION OR EVAPORATION ON COMPOSITION AND PROPERTIES OF SOLVENT-EXTRACTED CELL RUBBER

	Pptn. from Benzene by Acetone	Evapn. of Benzene
Composition, %		
Rubber hydrocarbon	95.3	94.0
Resins	3.8	5.9
Benzene-insol. material	0.9	0.0
Physical properties[a]		
Optimum cure, min. at 260° F.	25	20
Tensile strength, lb./sq. in.	1700	1600
Ultimate elongation, %	660	590
Modulus at 400%, lb./sq. in.	<100	<100
Hardness (Durometer)	43	43

[a] Compounded by gum recipe A.

TABLE X. COMPOSITION AND PROPERTIES OF WHOLE CRYPTOSTEGIA LEAF RUBBER (CONTAINING 27% BAGASSE RUBBER AND 73% CELL RUBBER)

	Bagasse Fraction	Cell Fraction		
Composition, %				
Rubber hydrocarbon	84.8	89.6		
Resins	14.8	10.1		
Benzene-insol. material	0.4	0.3		
Physical properties of blend[a]		Cures		
Curing time, min. at 287° F.	20	35	65	90
Tensile strength, lb./sq. in.	2350	2400	2300[b]	1650
Ultimate elongation, %	560	500	500	400
Modulus, lb./sq. in.				
At 200%	460	480	480	490
At 300%	810	840	900	1000
At 400%	1350	1380	1480	1650
At 500%	1930	2090	2280	...

[a] Compounded by recipe C.
[b] One dumbbell only.
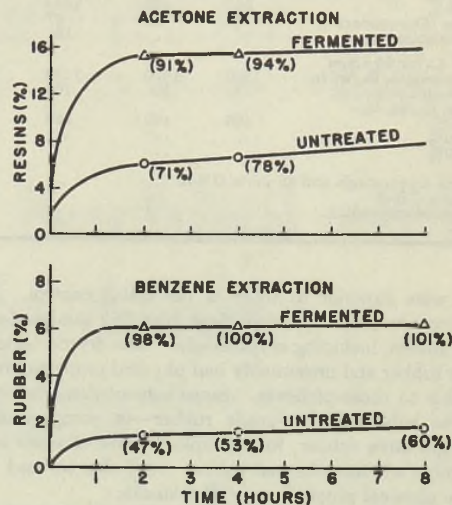
Figure 4. Rate of Extraction of Resins and Rubber from Fermented Cryptostegia

Figures in parentheses show percentage of total amount of constituent extracted.

The stock was therefore compounded by recipe C and cured at 287° F. under standard A.S.T.M. conditions. Table X shows curing characteristics and tensile properties together with the composition.

The curing characteristics and tensile properties of the whole leaf rubber recovered by solvent extraction were, in general, inferior to those of latex rubbers (Hevea, cryptostegia, or kok-saghyz). An accelerator-activator (0.5 part diphenylguanidine) was necessary to obtain a satisfactory cure. Although the tensile strength was not high, 2400 pounds per square inch with 500% elongation, the modulus compared favorably with those obtained on latex rubbers with equivalent loading. The cure was reasonably flat, with little or no evidence of reversion caused by overcure.

BLEND OF CRYPTOSTEGIA LEAF RUBBER AND GR-S

The possibility of using these stocks as modifiers for synthetic rubber was also considered. Carlton and Reinbold (2) observed that when hevea rubber was combined with GR-S in a ratio of approximately 25 hevea to 75 GR-S, the mixture could be compounded by a GR-S formula without the addition of softeners. This blend had improved processing characteristics, and the tensile properties, resilience, and tear resistance of the vul-

TABLE XI. RECIPES USED IN EVALUATING A BLEND OF CRYPTO-
STEGIA LEAF RUBBER AND GR-S

	Blend, Parts	Control, Parts
GR-S	80	100
Cryptostegia	20	...
Zinc oxide	5	5
Softener (Bardol)	5	5
Cyclohexyl benzothiazyl sulfonamide (Santocure)	1	1
Semireinforcing black (Pelletex)	50	50
Sulfur	3	3

TABLE XII. PHYSICAL PROPERTIES OF GR-S BLENDED WITH
CRYPTOSTEGIA LEAF RUBBER

Physical Properties	Optimum Cure (20 Min. at 287° F.)		Overcure (35 Min. at 287° F.)	
	Blend[a]	Control[b]	Blend[a]	Control[b]
Green				
Tensile strength, lb./sq. in.	1590	1480	1710	1630
Ultimate elongation, %	450	540	360	330
Modulus, lb./sq. in.				
At 100%	210	120	260	240
At 200%	310	320	790	840
At 300%	990	670	1430	1490
Hardness (Durometer)[c]	52	47	57	60
Tear resistance	..	..	123	101
Aged 100° C. for 96 hours				
Tensile strength, lb./sq. in.	1300	1620	1130	1290
Ultimate elongation, %	170	190	160	150
Modulus, lb./sq. in.				
At 100%	500	460	540	600
At 200%	..	..	..	..
At 300%	..	..	..	..

[a] 20 parts cryptostegia and 80 parts GR-S.
[b] 100 parts GR-S.
[c] Instantaneous reading.

canizate were superior to those of the GR-S control. Morris and co-workers (11) expanded these blending studies to other natural rubbers, including cryptostegia. The cryptostegia stock was latex rubber and presumably had physical properties roughly comparable to those of hevea. Since solvent-extracted cryptostegia leaf rubber is low-grade rubber—in comparison with cryptostegia latex rubber, for example—it was of some interest to determine whether the leaf rubber could also be used to improve the physical properties of GR-S stocks.

A compounding recipe (Table XI) similar to the high sulfur recipe of Morris et al. was used. The GR-S was given a preliminary breakdown on a cold 6- by 12-inch standard rubber mill, and all the chemicals were added according to the A.S.T.M. procedure, a master batch technique being used. The master batch was divided into two equal parts, and to one the cryptostegia stock (Table X) was added on the basis of 80 parts GR-S to 20 parts cryptostegia; a warm mill (160° F.) was used for blending. A control was provided by adding unmilled GR-S to the remainder of the master batch stock in the same ratio. The plasticity (Williams at 70° C. for 5 minutes) of the blended stock was 0.097 inch; that of the control was 0.110 inch.

The blend of cryptostegia and GR-S stock and the GR-S control were cured at 287° F. in standard A.S.T.M. molds. Limited tensile properties of the vulcanizates are shown in Table XII. The blending of 20 parts of cryptostegia leaf rubber with 80 parts of GR-S yielded a vulcanizate whose physical properties differed only slightly from those of the control stock. The differences observed could be ascribed to variations in rate of cure. In general, the physical properties of the blend of cryptostegia leaf rubber and GR-S stock paralleled those of a similar stock tested by Morris et al.—namely, a blend of goldenrod and GR-S. [Like cryptostegia cell rubber, goldenrod rubber also occurs in the chlorenchyma cells as discrete globules (14); chemical data (16) indicate that it is similar to the cryptostegia cell rubber.]

Morris and co-workers demonstrated substantial improvement in elongation of GR-S carcass stock by the addition of 20% natural rubber. However, this improvement was not retained after the blended stock had been aged for 96 hours at 100° C.

Their data also showed that the tear resistance of the natural rubber and GR-S blends was greater than that of the GR-S control.

ECONOMIC CONSIDERATIONS

The primary purpose of the work was accomplished. The two fractions of the leaf rubber were isolated, and their character and properties were fairly well established. The cell rubber was given the major emphasis, for previously little was known about it. A method involving preliminary fermentation was worked out for recovery of the leaf rubber, which should be feasible if rubber of this type is ever required. Economic aspects of the recovery process have not been evaluated because the cost depends primarily upon the rubber content and yield per acre of leaves. Such information should be available upon the completion of agronomic studies now being carried out by the U. S. Department of Agriculture. The fermentation process, which is relatively simple, produces a three-fold increase in the rubber content, regardless of the actual initial rubber content of the leaves. The cost of the solvent-extraction step likewise would depend upon the rubber content of the material. If leaves of high rubber content could be produced cheaply, the over-all cost of the recovery process probably would not be unreasonable in an emergency.

Solvent extraction of the fermentation products recovers all the rubber of the leaf. The properties of this rubber differ little from those of the cell rubber, which makes up the major portion of the total. Although the duct rubber is of higher quality than the cell rubber, preparing it separately does not appear feasible, since it constitutes only 10 to 15% of the total.

SUMMARY

Leaves of Cryptostegia grandiflora contain 2 to 7% rubber. The greater part of this rubber (85 to 90%) occurs in discrete globules within the individual chlorenchyma cells; the remainder (10 to 15%) is in the latex vessels of the leaf.

An anaerobic fermentation of the leaves by Clostridium roseum for two days at 35° to 40° C. decomposed the cell walls so that the cell content (protoplasts), bearing the globules, was readily separated from the latex vessels in the veins, the cuticle, etc., by screening the fermentation products. The rubber was then recovered from the two fractions by solvent extraction. An alternative procedure for recovery of the cell rubber consisted in alkaline digestion of the protoplasts followed by creaming the rubber globules.

Removal of nonrubber constituents by fermentation effected a 2.9 fold enrichment in rubber content calculated on a weight basis and a 3.2 fold enrichment on a volume basis. In addition, the rate of solvent extraction of both resins by acetone and rubber by benzene was markedly increased.

The cell rubber was a relatively soft, low-polymer rubber, soluble in methyl ethyl ketone, which could be compounded to produce a gum tensile strength of 1500–1700 pounds per square inch, with an ultimate elongation of 600–700%.

The duct rubber of the leaves, which comprised about 15% of the total, was latex rubber of relatively higher quality than the cell rubber but contained all the water-insoluble constituents of the latex.

The rubber of the whole leaf, consisting of the cell rubber and the duct rubber, was prepared by fermentation followed by solvent extraction of the fermentation products. Although the mixture was of slightly better quality than the cell rubber, it was relatively soft and tacky. When compounded in a carbon black recipe, it had a tensile strength of 2400 pounds per square inch with an ultimate elongation of 500%. The compounded stock cured to optimum tensile strength in 35 minutes at 274° F.; the curing curve was flat and exhibited no evidence of reversion when the rubber was overcured.

The leaf rubber, when blended with GR-S in the proportions 20 to 80 and compounded by a soft-carcass stock recipe, produced a vulcanizate having substantially the same properties as the GR-S control.

ACKNOWLEDGMENT

LITERATURE CITED[*]

(1) Anonymous, *Bull. Imp. Inst.*, 10, 210–12 (1912).
(2) Carlton, C. A., and Reinbold, E. B., *Rubber Age*, 52, 29 (1942).
(3) Cheyney, L. E., IND. ENG. CHEM., 34, 1426–8 (1942).
(4) Dolley, C. S., *India-Rubber J.*, 41, 1155–8 (1912).
(5) Jenkins, D. W., Board of Economic Warfare, *Tech. Bull.* 3 (1943).
(6) Kemp, A. R., and Peters, H., IND. ENG. CHEM., 33, 1263–9 (1941).
(7) Lamb, D. N., U. S. Patent 144,623 (Nov. 18, 1873).
(8) Lucas, F. F., IND. ENG. CHEM., 30, 146 (1938).
(9) McGavack, J., and Hoover, S. R., "Brief Study of Cryptostegia Problem in Haiti", unpub. rept. to Rubber Development Corp., June 15, 1943.
(10) McKennon, F. L., and Lindquist, J. R., *Rubber Age*, 56, 289–92 (1944).
(11) Morris, R. E., Barret, A. E., Harmon, R. E., and Werkenthin, T. A., IND. ENG. CHEM., 36, 60 (1944).
(12) Naghski, J., White, J. W., Jr., Hoover, S. R., and Willaman, J. J., *J. Bact.*, in press.
(13) Polhamus, L. G., Hill, H. H., and Elder, J. A., U. S. Dept. Agr., *Tech. Bull.* 457 (1934).
(14) Rollins, M. E., Bailey, T. L. W., Jr., and deGruy, I. V., *India Rubber World*, in press.
(15) Saunders, W., *Proc. Am. Pharm. Assoc.*, 23, 655–8 (1875).
(16) Skau, E. L., Runckel, W. J., Kreeger, F. B., and Sullivan, M. A., *J. Phys. Chem.*, in press.
(17) Spadaro, J. J., Pollard, E. F., and Porges, N., *Rubber Age*, 56, 53 (1944).
(18) White, J. W., Jr., and Senti, F. R., *J. Am. Chem. Soc.*, 67, 881 (1945).
(19) Whittenberger, R. T., Brice, B. A., and Copley, M. J., *India Rubber World*, 112, 319–23 (1945).
(20) Willits, C. O., *et al.*, in preparation.

Drying Oils from Sorbitol and Linseed Fatty Acids

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USEFUL drying oils can be prepared by the esterification of drying oil acids with polyhydric alcohols containing more than three hydroxyl groups. Pentaerythritol esters of drying oil acids have been available commercially for several years. Drinberg and Blagonravova (1) described mannitol esters of linseed acids. Results of their tests indicated only partial esterification under the reaction conditions. Sorbitol esters of monobasic aliphatic carboxylic acids have been disclosed in patents issued to I. G. Farbenindustrie (3). Goepp and Brown (2) made a comparative study of hexitols and glycerol in linseed oil modified alkyds. However, so far as is known, no systematic study of conditions for the preparation of drying oils from sorbitol or mannitol has previously been published.

The first part of this investigation was concerned with the effect of acid ratio and other variables on the preparation and properties of drying oils from linseed fatty acids and sorbitol. This was considered important because the nature of esters obtained from sorbitol and mannitol is influenced to a greater extent by the reaction conditions than in the case of either a glycerol or pentaerythritol ester. The reason for the difference in behavior is the well-known tendency of the hexitols to anhydrize, so that it was necessary to find conditions which would promote esterification and at the same time cause minimum anhydrization of the hexitol. The optimum conditions were established for the preparation of a commercial product. After selecting the product which was most desirable commercially, certain comparisons were made between the sorbitol drying oil and corresponding products from mannitol, pentaerythritol, and glycerol, as well as natural

A systematic study was made of conditions for the esterification of sorbitol with linseed fatty acids, and the effect on the resulting drying oil of varying the reaction conditions was determined. The rate of esterification was increased not only by raising the temperature but also by using an excess of linseed fatty acids or by adding certain basic compounds. The degree of esterification of the sorbitol was increased greatly by raising the mole ratio of linseed acids to sorbitol, and increased slightly by esterifying at a lower temperature. Evaluation of varnishes showed that the higher the degree of esterification of the sorbitol drying oil, the faster drying was the varnish, and the harder and more alkali resistant was the film. From a practical standpoint, the optimum ratio was found to be 4.5 moles of linseed acid per mole of sorbitol. A sorbitol drying oil with this ratio of reactants was compared with pentaerythritol, mannitol, and glycerol drying oils, as well as with natural linseed oil. Tests made on the oils and on varnishes therefrom showed that the sorbitol ester is superior to the others with respect to drying time, and about equal to the best of the other oils in hardness and alkali resistance.

linseed oil. Both oils and varnishes made therefrom were studied.

The sorbitol used in this investigation contained 1 to 3% water, 0.1 to 0.2% ash, and about 0.1% reducing sugar, and was made by catalytic pressure hydrogenation of glucose. The mannitol and pentaerythritol were the regular commercial grades of these materials. A synthetic linseed oil was prepared with C.P. glycerol.

Several preparations were carried to a high body by heating to 300° C. immediately after the esterification.

The rate of reaction was followed by withdrawing small samples from the reaction mixture periodically to determine the acid number. For the greater portion of the reaction the data could best be represented by plotting the logarithm of 100 minus the percentage of the total acid consumed, $100 (x - z)/(y - z)$, against time, where y is the initial acid number of the reaction mixture,

TABLE I. DATA ON PREPARATION AND PROPERTIES OF DRYING OILS FROM SORBITOL AND LINSEED FATTY ACIDS

1 Preparation No.	2 Mole Ratio, L.O.F.A.[a] to Sorbitol	3 Esterification Catalyst, %	4 Esterification Temp., °C.	5 1st-Order Rate Constant × 100, Min.[-1]	6 Yield in Lb./100 Lb. of Reactants	7 Moles H$_2$O Evolved per Mole Sorbitol	8 Moles L.O.F.A.[a] Consumed per Mole Sorbitol[b]	9 Properties of Product Viscosity, Gardner-Holt	Acid No.	Saponification No.	I$_2$ No.[c]
1	4.44	None	200	0.55	91.7	5.05	3.94	E	18.9	186	168
2	4.50	None	250[d]	1.84	89.8	4.61	3.83	Z-3	19.3	180	148
3	5.19	None	200[d]	0.57	87.7	4.86	3.93	Z-2	31.8	181	129
6	4.33	None	200[d]	0.57	87.5	4.94	3.71	Z-4	18.5	186	130
7	3.87	None	200[d]	0.41	87.8	4.62	3.37	Z-1	17.1	185	127
8	4.45	None	200	0.55	89.8	....	3.95	K	14.5	187	154
9	4.74	None	200	0.47	91.2	....	4.13	G	18.3	190	159
15	5.77	None	180	0.30	85.8	....	4.53	M	25.1	194	148
16	5.46	0.12 Ba Ac + 0.41 Ca Ac	180	0.44	92.2	....	4.66	G	25.0	198	162
18	4.39	None	180	0.21	91.4	....	3.91	F	15.3	185	159
19	5.75	None	200	0.64	92.5	....	4.37	D	42.0	192	161
20	4.73	None	180	0.25	92.4	5.17	4.03	J	24:5	186	148
21	4.70	0.12 Ba Ac + 0.35 Ca Ac	180	0.50	91.8	4.74	4.14	I	18.8	190	148
22	5.27	None	180	0.30	92.8	....	4.02	G	38.8	199	150
23	10.45	Same as 21	180	0.60	92.8	5.50	5.23	F	88	194	153
24	4.50	0.13 Ba Ac + 0.38 Ca Ac	180	0.53	92.7	4.63	3.96	J	18.9	191	150
25	5.05	Same as 24	180	0.55	92.6	....	4.31	K	23.7	196	150
26	5.56	Same as 24	180	0.57	93.3	....	4.40	F	36.5	192	158
27A	6.13	Same as 24	180	0.60	93.2	....	4.79	G	42.5	188	156
27B[e]	...	....	....	....	....	....	....	O	16.2	192	149
28	7.10	Same as 24	180	0.58	93.6	....	4.87	G	55.7	199	162
29	8.94	Same as 24	180	0.60	94.4	....	5.01	F	81.5	197	161
30	4.43	Same as 24	180	0.46	92.8	....	3.94	F	19.9	191	157
31	4.97	Same as 24	180	0.59	93.0	4.56	4.04	G	33.5	190	151
32A	5.50	Same as 24	180	0.42	93.7	4.63	4.48	E	31.6	191	158
32B[e]	...	....	....	....	....	....	....	I	16.1	191	155
33A	5.94	Same as 24	180	0.44	91.9	4.98	4.64	F	39.4	197	158
33B[e]	...	....	....	....	....	....	....	J	19.3	193	152
34A	6.06	Same as 24	180	0.44	92.8	....	4.81	E	36.0	186	163
34B[e]	...	....	....	....	....	....	....	I	18.4	189	158

[a] Linseed oil fatty acids.
[b] Column 8 values represent the degree of esterification.
[c] The iodine number was determined by the Wijs method.
[d] After esterification these oils were bodied at 300° C.
[e] A portion of preparation A was vacuum-distilled to reduce the acid number.

The linseed oil used in the tests was a refined grade (Superb grade, Archer Daniels Midland Company). The fatty acids were a commercial grade of distilled linseed acids (Linseedine Supra fatty acids, Woburn Chemical Company).

ESTERIFICATION OF SORBITOL

The esterification of sorbitol with linseed fatty acids was carried out in three-necked glass flasks with interchangeable ground joints. The contents were stirred mechanically with an oil-sealed stirrer, and a slow stream of carbon dioxide was passed over the surface of the reaction mixture. Volatiles (water and some fatty acids) from the reaction were collected in a dry ice trap. The fatty acids were brought to reaction temperature, and molten sorbitol at the same temperature was then introduced. The esterifications were conducted at 180° or 200° C. until the reaction rate diminished to approximately 10% of its maximum value, and then the temperature was raised to 250° C. and held there to the completion of the reaction except for a few runs bodied at 300° C. Table I presents data on esterification conditions and properties of the oils.

An accurate material balance was obtained by weighing the reaction flask before and after reaction and determining the water and fatty acid collected in the trap. More than 99% of the material was accounted for. In a number of cases the excess fatty acid was subsequently distilled from the reaction product under an absolute pressure of 5–10 mm. of mercury at about 250° C.

x is the acid number at any intermediate time, and z is the final acid number. The typical runs presented in Figure 1 show that a line through the points is straight for most of its length but has a curvature at the beginning; this indicates an induction period during which the reaction proceeds slowly. This induction period may be accounted for by the immiscibility of sorbitol and linseed fatty acids. Toward the end of the reaction the rate again deviates from linear, presumably because of the steric effect of several adjacent fatty acid groups which hinder the esterification of the last hydroxyl group. A first-order rate constant—that is, the slope of the linear portion of the reaction curve—was determined for each run from curves similar to those in Figure 1.

The rate of reaction as measured by first-order rate constant was determined at several temperatures, and it was found that the rate approximately doubled when the temperature was raised from 180° to 200° C. The rate of reaction also increased with an increase in the ratio of linseed fatty acid to sorbitol, as the curves in Figure 2 show. Several materials accelerated the rate of reaction of sorbitol and linseed fatty acids. The most effective catalysts were the acetates, carbonates, oxides, and hydroxides of calcium and barium. The addition of about 0.5% of a mixture of three parts calcium acetate and one part barium acetate approximately doubled the rate of esterification at all ratios of linseed fatty acid to sorbitol.

The degree of esterification—that is, the number of moles of fatty acid which reacted with a mole of sorbitol—was calcu-
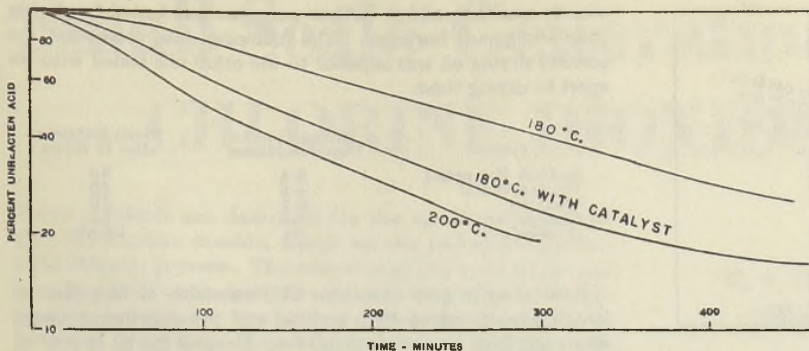
Figure 1.   Rate of Esterification with Ratio of Linseed Oil Fatty Acid to Sorbitol of 4.7

lated from the consumption of fatty acid during the reaction. The degree of esterification of the sorbitol was directly related to the mole ratio of linseed fatty acid to sorbitol, and in general it was possible to vary the degree of esterification over a wide range by varying the ratio of reactants. These data are presented in Figure 3. Thus, when 4 moles of fatty acid were heated with 1 mole of sorbitol without catalyst at 200° C., the product contained 3.5 moles of linseed fatty acid combined per mole of sorbitol, and when 6 moles of fatty acid were employed, the product contained 4.3 moles of linseed fatty acid combined with each mole of sorbitol.

The degree of esterification was found to be somewhat dependent on the temperature of reaction. Usually, the lower the reaction temperature, the higher was the degree of esterification with a given mole ratio of reactants (Figure 3). When the reaction was carried out at a lower temperature, the reaction time was greatly increased. The effect of the catalyst was to overcome the slow reaction rate at a low temperature and thereby obtain a higher degree of esterification in a reasonable period of time.

TABLE II.   COMPARISON OF 50-GALLON-OIL-LENGTH PHENOLIC RESIN VARNISHES CONTAINING SORBITOL OF VARIOUS DEGREES OF ESTERIFICATION

Preparation No.	Degree of Esterification of Sorbitol	Acid No.	Viscosity	Drying Time, Hr. Dust-free	Drying Time, Hr. Tack-free	Pencil Hardness after 72 Hr.	2% Alkali Resistance, Hours
24A	3.96	8.8	H	$10^1/_4$	$23^3/_4$	4B	$1^3/_4$
24B	3.96	9.1	J	$9^1/_4$	$22^3/_4$	4B	$1^1/_2$
25A	4.31	8.9	I	$10^1/_4$	$18^1/_4$	4B	$4^1/_2$
25B	4.31	8.8	H	$9^1/_4$	$16^3/_4$	4B	$3^1/_2$
26A	4.40	9.9	H	$9^1/_4$	16	4B	$3^1/_2$
26B	4.40	9.3	J	9	16	4B	$2^3/_4$
27A	4.79	10.1	H	8	$16^1/_2$	3B	$3^1/_2$
27B	4.79	7.9	H	8	$16^1/_2$	3B	$3^1/_2$
23B	5.23	11.2	J	10	$15^1/_2$	3B	...

It is evident from the data in columns 7 and 8 of Table I that more water was evolved in each run than the amount which would be expected from the consumption of linseed fatty acids. The excess water was produced by ether formation between the hydroxyls of the sorbitol. Figure 4 shows the relation between acid number of the product and mole ratio of the reactants. The acid number varied from about 15 when the mole ratio was 4, to 90 when the mole ratio was 10. In order to compare sorbitol drying oils on the same basis, the excess acid in the products with a high acid ratio was removed by vacuum distillation at 250–260° C. to give oils with acid numbers below 20. By retaining the oil under high vacuum for a more prolonged period the acid number could be reduced below 5.

The yield of drying oil before removal of excess fatty acid was approximately 90%. This yield was practically independent of the ratio of reactants and was only slightly affected by the temperature and the rate of flow of carbon dioxide.

For comparative purposes the sorbitol drying oils were cooked into varnishes. One-gallon batches were prepared in gas-fired stainless-steel open kettles. This small-scale equipment is known to give results which are in good agreement with full-size varnish kettles. The varnish formula used in evaluating these drying oils was 10% phenolic resin (Krumbhaar K-1010), 40% drying oil, 25% mineral spirits, and 25% V. M. & P. naphtha.

The schedule by which the varnishes were cooked follows: Heat the resin and one sixth of the oil to 300° C. in 30 minutes. Add one third of the oil and regain 300° C. Add the remainder of the oil and regain 300° C. Hold at 300° C. until a slight string forms. Cool and thin with solvents to 50% solids.
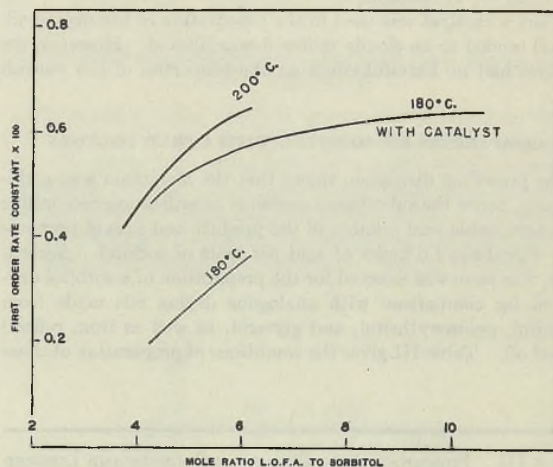
Figure 2.   Rate of Esterification of Sorbitol

(L.O.F.A. = linseed oil fatty acid)

A drier combination consisting of 0.75% lead, 0.20% manganese, and 0.075% cobalt, as naphthenates (based on the oil content of the varnish) was added at least 24 hours before films were formed. Varnish films were cast on glass panels with a Bird applicator; the resulting wet film thickness was 0.003 inch, and the films were tested for drying time and pencil hardness. Alkali resistance was run on films formed by dipping test tubes into the varnish and air drying in an inverted position for 72 hours at room temperature before testing.

Varnishes made from sorbitol drying oils of various degrees of esterification were compared for film properties (Table II), and the properties of the varnish improved somewhat as the degree of esterification of the sorbitol was increased. The higher the degree of esterification, the faster drying was the varnish and the harder the film. The alkali resistance was also improved slightly with a high degree of esterification of the sorbitol. However, the improvement in alkali resistance was not so marked as was the improvement in the other properties. Varnishes prepared from drying oils having a high acid number were similar in
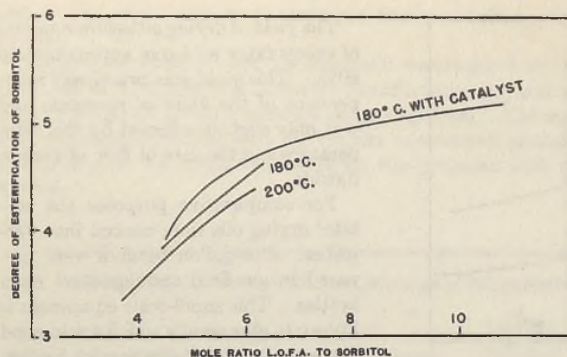
Figure 3. Degree of Esterification of Sorbitol

properties to varnishes prepared from the same oils from which the excess fatty acid had been vacuum-distilled. The yield of varnish was lower for the oils of high acid number, presumably because of distillation of excess acid during varnish preparation. The slight improvement of film properties resulting from an increase in ratio of reactants over 4.5 (corresponding to a degree of esterification of about 4 moles of fatty acid per mole of sorbitol) is not believed to justify the additional expense involved in removing the excess acid.

When a catalyst was used in the preparation of the drying oil, the oil tended to be cloudy unless it was filtered. However, the catalyst had no harmful effect on the properties of the varnish film.

COMPARISON OF SORBITOL WITH OTHER POLYOLS

The preceding discussion shows that the maximum acid-sorbitol ratio, hence the subsequent degree of esterification compatible with acceptable acid number of the product and ease of preparation, was about 4.5 moles of acid per mole of sorbitol. Accordingly, this ratio was selected for the preparation of a sorbitol drying oil for comparison with analogous drying oils made from mannitol, pentaerythritol, and glycerol, as well as from refined linseed oil. Table III gives the conditions of preparation of these oils.

TABLE III. PREPARATION OF OILS FROM POLYOLS AND LINSEED FATTY ACIDS

Polyol	Mole Ratio, Acids to Polyol	Cooking Schedule ° C.	Hours	Acid No. of Oil	Color of Oil (Gardner)
Glycerol	2.74	225	22	1.5	9
Mannitol	4.0	{225 {250	8³/₄} 9}	13.8	5–6
Pentaerythritol	4.02	225	9¹/₄	18.0	5–6
Sorbitol					
1st preparation	4.6	{220 {250	2} 8}	18.3	...
2nd preparation[a]	4.5	{200 {250	2} 12}	16.5	11

[a] Prepared in 40-gallon kettle.

The data in Table III show that sorbitol yielded darker colored drying oils than did glycerol and pentaerythritol. However, since this work was done, an improved technique has been devised which makes it possible to obtain drying oils from sorbitol with colors as light as 6–7 on the Gardner scale.

The oils described in Table III were bodied by heating in an open kettle at 300° C. to a viscosity of Z4 to Z5 on the Gardner-Holt scale, and prepared for testing by thinning to 50% solids with mineral spirits. The drier combination mentioned pre-

viously was then added. Films were cast and tested for drying time and pencil hardness. The following data show that the sorbitol drying oil was superior to the other oils tested with respect to drying time:

Polyol	Drying Time to Dust-Free, Hours	Pencil Hardness after 72 Hours
Sorbitol (1st prep.)	3–4	3B
Pentaerythritol	4–5	3B
Mannitol	6–7	3B
Glycerol	20	5B
(Linseed oil)	20	5B–6B

Neutral ester gum (Arochem 345) varnishes of 50-gallon oil lentgh were prepared from sorbitol and pentaerythritol linseed esters and from linseed oil as follows: Heat all the oil to 300° C. and hold until a slight string forms. Add all the resin and regain 300° C. Hold for 10 minutes, cool, and thin to 50% solids with a 50-50 mixture of mineral spirits and V.M. & P. naphtha.
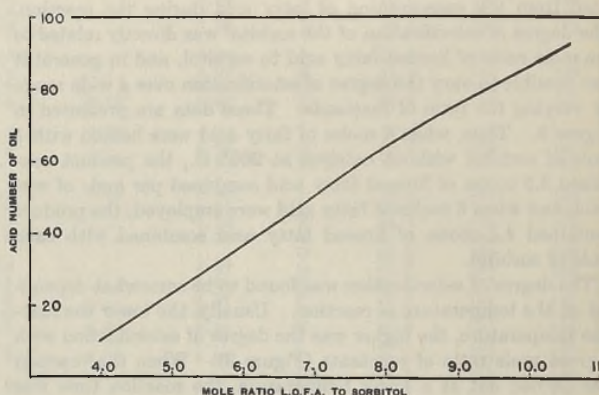
Figure 4. Acid Numbers of Sorbitol Drying Oils

Drier was added and films were cast as described previously. Results of the evaluation tests follow:

Drying Oil	Color of Varnish	Drying Time, Hr. Dust-free	Tack-free	Pencil Hardness after 72 Hr.	1% Alkali Resistance, Hr.
Sorbitol (2nd prep.)	11	3¹/₂	21	3B	3
Pentaerythritol	6–7	6	49	2B	3
Linseed oil	7–8	8	72	4B	¹/₄

In these tests the sorbitol product led the others in drying time, was equal to pentaerythritol in alkali resistance, and was superior to linseed oil in hardness and alkali resistance.

The results on the preparation in glass and the properties of sorbitol drying oils together with experimental runs in small laboratory kettles led to the establishment of 4.5 as the optimum mole ratio of acid to sorbitol, with a heating schedule of 200° C. to an acid number of 100, followed by heating at 250° C. to an acid number of about 20. The suitability of these conditions has been confirmed by many runs in industrial equipment of 100-gallon and 500-gallon capacity.

LITERATURE CITED

(1) Drinberg and Blagonravova, Natl. Paint, Varnish, Lacquer Assoc., Circ. 501, 21 (1936).
(2) Goepp and Brown, IND. ENG. CHEM., 30, 1222 (1938).
(3) I. G. Farbenindustrie A.-G., Brit. Patent 350,992 (1929).

Small-Scale Generation of CHLORINE DIOXIDE

Three methods are described for the small-scale generation of chlorine dioxide, based on the gaseous chlorine-solid chlorite process. The selection of the method for any specific application depends on the purity of the chlorine dioxide desired, the amounts needed, the feasibility of batch or continuous production, the accuracy of control required, and the partial pressure of chlorine dioxide needed in the ClO₂–air mixture generated. All three methods produce chlorine dioxide at low partial pressures at substantially atmospheric pressures and temperatures.

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CHLORINE dioxide is rapidly finding a place among the more important oxidizing and bleaching agents. Its widespread use in the past was retarded by the lack of economical and convenient sources of the gas. Availability of chlorites in commercial quantities has made possible the plant-scale generation of chlorine dioxide in several ways, as recently described by Woodward, Petroe, and Vincent (4).

Since chlorine dioxide and equipment for its generation and distribution are now available at reasonable prices, numerous plants and laboratories are interested in trying the reagent in their processes or for bleaching their products. Because no suitable method is available in the literature for the small-scale production and handling of this highly reactive oxidizing gas, the purpose of this article is to describe small-scale methods for the production of chlorine dioxide that have proved useful in experimental work on the bleaching of flour in small quantities.

The number of available methods for producing the gas under accurately controlled conditions was found to be extremely limited. The electrolytic process described by Logan (3) was given extensive trial, in which chlorine dioxide is produced from a sodium chloride and sodium chlorite solution. The chlorinated brine method of Cunningham and Losch (1) was also tried; it consists of introducing chlorine diluted with air into a solution of sodium chlorite. The difficulty inherent in these continuous processes is mainly a control problem when small quantities of the gas are generated. The time for an output equilibrium to be established for any given level of chlorine dioxide concentration in the effluent gas was lengthy and uncertain.

The chief difficulties with the wet processes are corrosion of the equipment and the solubility of chlorine dioxide in aqueous solutions which makes necessary the achievement of an equilibrium between the chlorine dioxide generated, that in solution, and that stripped from the solution by air or other inert gases. Such an equilibrium is difficult to achieve and maintain, either on starting the generator or in changing the output of chlorine dioxide from one level to another. Another drawback is the necessity for the complete stripping of the chlorine dioxide from the chlorite solution to prevent undue corrosion of the equipment when it is not in use. This is a slow and wasteful process.

Early in the experimental work on flour bleaching, a need became evident for a simple method of generating small amounts of chlorine dioxide which could be precisely controlled. A successful method was found which depended on the reaction of accurately metered dry chlorine obtained from a cylinder, with substantially dry, powdered sodium chlorite according to the equation:

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$
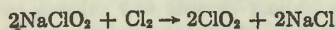
This process was described by Hutchinson and Mecham (2).

Three methods were developed for the utilization of this process in the laboratory. The selection of the method to be used for any specific application depended on the purity of chlorine dioxide desired, the amounts needed, the feasibility of batch-scale or continuous production, the accuracy of control needed, and the partial pressure of chlorine dioxide in the ClO₂–air mixture produced. These methods will be given in detail to facilitate the small-scale production of the gas for use in any reactions involving chlorine dioxide diluted with air or other inert gas at substantially atmospheric pressures and temperatures.

NONCONTINUOUS PRODUCTION ADMIXED WITH INERT GASES AND CHLORINE

This method yields chlorine dioxide and chlorine in the effluent gases. For flour bleaching, and probably for many other uses, the action of the excess chlorine to ensure completion of the reaction is of slight or no consequence when compared to the oxidizing power of the chlorine dioxide produced. For example, in flour bleaching the amount of chlorine dioxide generally used on a patent flour is about 1.5 grams per 196-pound barrel. The
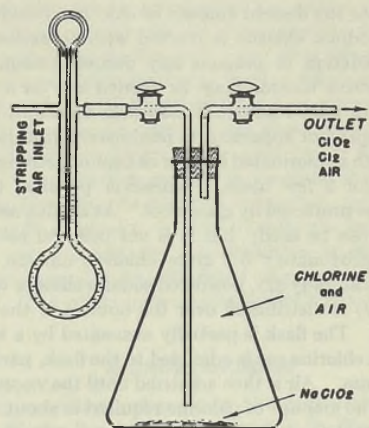
Figure 1. Apparatus for Small-Scale Production of Chlorine Dioxide Gas

chlorine required to produce 1.5 grams of chlorine dioxide, calculated from the reaction equation, is 0.79 gram. Since 100% excess of chlorine gas is used for the reaction, the amount of chlorine introduced to the flour along with 1.5 grams per barrel of chlorine dioxide would be 0.79 gram per barrel (0.028 ounce). The color removal effect of this amount of chlorine would be too slight to be determined by the usual methods of flour color analysis. To
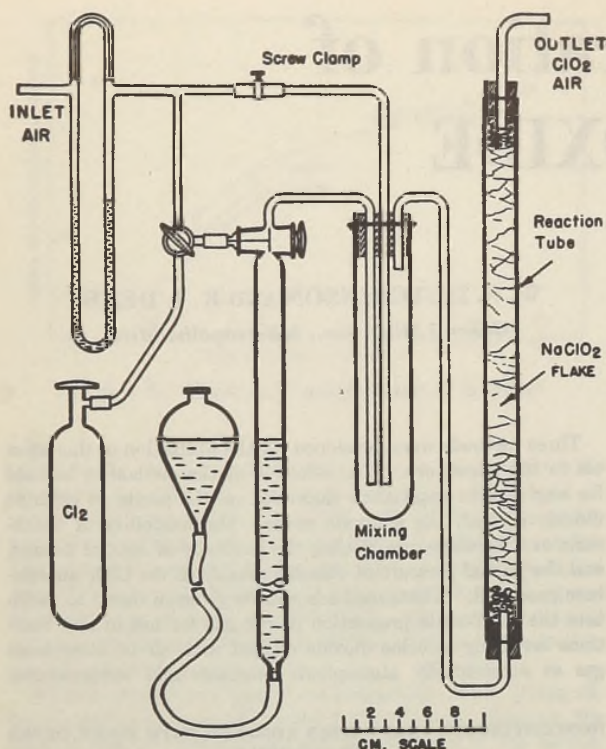
Figure 2. Apparatus for Production of Pure Chlorine Dioxide Gas in Admixture with Inert Gases

equal the color removal effect of 1.5 grams chlorine dioxide per barrel, the chlorine would have to be used at a rate of about 43 grams (1.5 ounces) per barrel. Thus on a weight basis chlorine dioxide is about thirty times as effective as chlorine for flour color removal.

To generate the desired amount of chlorine dioxide, a weighed amount of sodium chlorite is reacted with an excess of chlorine gas. The reaction to produce any desired amount up to 0.1 gram of chlorine dioxide may be carried out in a 1-liter flask equipped with inlet and outlet stopcocks as shown in Figure 1. Rubber stoppers for apparatus to produce chlorine dioxide should be coated with a chlorinated lacquer or kept in a strong atmosphere of chlorine for a few hours. Whenever possible, the stoppers should also be protected by glass wool. As an alternative, ground glass joints can be used; but it is not believed necessary. To generate approximately 0.1 gram chlorine dioxide, about 0.13 gram of substantially dry, powdered sodium chlorite (approaching 100% purity) is distributed over the bottom of the liter Erlenmeyer flask. The flask is partially evacuated by a water pump, and metered chlorine gas is admitted to the flask, partially releasing the vacuum. Air is then admitted until the vacuum is wholly released. The amount of chlorine required is about 100% in excess of the theoretical amount indicated by the reaction equation. The excess is used to ensure that all the sodium chlorite is reacted in a reasonable time. It also eliminates the need for controlling the quantity of chlorine dioxide produced by the metering of such minute quantities of chlorine gas, and throws the burden of control on weighing the chlorite on an analytical balance. The amount of chlorite needed is calculated on a moisture-free basis and corrected for the purity of the chlorite salt with respect to the percentage of sodium chlorite present. The reaction goes to completion in about 3 hours; during this time the flask must be kept in the dark, since chlorine dioxide is photochemically active. After reaction, the resulting gaseous mixture is stripped from the flask and conducted to the point of

application by a stream of air at a velocity of about 300 cc. per minute.

The reaction is about 94% efficient at a chlorine dioxide partial pressure of 30 mm. mercury, since a small amount of the sodium chlorite is converted to sodium chlorate. Chlorate formation becomes less as the partial pressure of chlorine dioxide is decreased. The greatest efficiency for the process is therefore found for the lower partial pressures of chlorine dioxide. The exact efficiencies for any given set of conditions may be checked by titrating for the purity of the sodium chlorite and by analyzing the effluent gases.

The purity of sodium chlorite is determined by the following procedure: An accurately weighed sample of about 2 grams is dissolved in a liter of water, and an aliquot of 25 ml. is taken for titration. To this aliquot are added 2 ml. of 50% potassium iodide solution and 10 ml. of glacial acetic acid. The reaction is allowed to proceed in the dark for 5 minutes; the liberated iodine is then titrated with 0.1 N standard sodium thiosulfate solution using starch as indicator. The reaction equation is:

$$NaClO_2 + 4HC_2H_3O_2 + 4KI \rightarrow \\ NaCl + 2I_2 + 4KC_2H_3O_2 + 2H_2O \quad (1)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \quad (2)$$
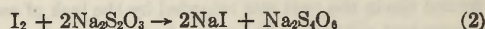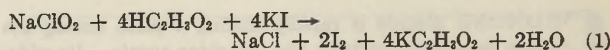
Thus 1 mole of sodium thiosulfate is equivalent to 0.25 mole of sodium chlorite, the milliequivalent weight of the sodium chlorite being 0.0226. The equation for the percentage of sodium chlorite in the original sample follows:

% $NaClO_2$ = (ml. standard thiosulfate $\times$ normality $\times$ milliequivalent wt. of $NaClO_2 \times 100$)/(wt. of sample in aliquot soln.)

The mixed gas may be analyzed according to the procedure of Woodward, Petroe, and Vincent (4).

No more than 0.135 gram of 95–97% sodium chlorite should be reacted in a liter flask since the partial pressure of the resulting chlorine dioxide will be approximately 26 mm. mercury at usual room conditions of temperature and pressure. This is about the highest concentration recommended by the authors for this type of apparatus, since at a partial pressure of 36 mm. of mercury (20° C.) Woodward, Petroe, and Vincent (4) indicated that chlorine dioxide can be exploded by an electric spark. However, chlorine dioxide does not appear to decompose spontaneously at room temperature but only when it comes in contact with easily oxidized material. Thus the recommended maximum concentration is given as a precaution. The gas may be produced at somewhat higher concentrations if the apparatus is kept free of all oxidizable materials and protected against damage due to questionable conditions. It must be remembered that these reagents are moderately strong oxidizing agents and should be handled as such. For generating greater amounts of the gas, a number of flasks may be used or the gas may be produced in a larger chamber. In the latter case, more time should be allowed to ensure diffusion of the chlorine to the chlorite for the reaction.

In many applications other than flour bleaching, the presence of chlorine would probably not interfere; but in numerous cases chlorine admixed with the resulting chlorine dioxide would preclude the use of this method.

NONCONTINUOUS PRODUCTION ADMIXED WITH INERT GASES

If larger amounts of chlorine dioxide free from chlorine as a contaminant are desired, a method in which output of the dioxide is controlled by chlorine input may be utilized. The required amount of chlorine is metered in a buret, using a salt solution saturated with sodium chloride and chlorine as the metering fluid. This chlorine is slowly introduced into a mixing chamber; from there it is swept by a continuous stream of air (about 200 to

300 cc. per minute) through a column, as shown in Figure 2; the column is approximately 0.75 inch in diameter and 8 to 16 inches long, and is filled with substantially dry, flaked chlorite. As the chlorine is metered into the mixing chamber, the dilution air flow is through the central tube leading into the mixing chamber (Figure 2). However, after all chlorine has been displaced from the buret, the air flow is directed through the three-way stopcock and the buret stopcock, the screw clamp being closed. This procedure ensures that all metered chlorine is flushed into the reaction tube. The effluent gases are then conducted to the point of application. No chlorine is present in the effluent gases, which are composed of chlorine dioxide in admixture with air. The dioxide is preferably kept at a partial pressure of 30 mm. mercury or less, depending upon the usage to which the gases are to be put.

The reaction is practically instantaneous, and the output gas is chlorine dioxide and air, with no chlorine present until about two thirds or more of the sodium chlorite is reacted and the chlorine channels through the salt. The absence of chlorine in the effluent gases can be assured by testing the output stream with ammonium hydroxide fumes, since chlorine, but not chlorine dioxide, produces the typical white cloud of ammonium chloride.

The input chlorine and air flow is so adjusted that the partial pressure of chlorine dioxide in the effluent gas-air mixture is held at or below 30 mm. mercury. Thus, according to the reaction equation, if 5 cc. of chlorine are used per minute, chlorine dioxide will be produced at a rate of 10 cc. per minute. The amount of air which must be used for diluting the chlorine at 740 mm. mercury barometer pressure to obtain chlorine dioxide at 30 mm. mercury partial pressure will be:

$$\text{Air/minute} = \frac{10 \text{ cc. } ClO_2/\text{min.} \times 740 \text{ mm. Hg bar. press.}}{30 \text{ mm. Hg partial press. } ClO_2} - 10 \text{ cc. } ClO_2/\text{min.} = 237 \text{ cc./min.}$$

The air should be flushed through the chlorite column for several minutes after all chlorine has been swept through it to ensure complete stripping of all chlorine dioxide from the chlorite column.

CONTINUOUS PRODUCTION ADMIXED WITH INERT GASES AT CONTROLLED PARTIAL PRESSURES

This method is preferred to those cited above in cases where large amounts of chlorine dioxide are desired, where it is necessary to have chlorine dioxide at a carefully controlled partial pressure, or where a continuous stream of the dioxide diluted with inert gases is desirable. In this case the amount of chlorine dioxide applied to a process or product may be controlled; or the product may be immersed in or treated with an atmosphere of chlorine dioxide at a controlled partial pressure for a given time by running the dioxide stream through a chamber from which partially spent gas is constantly withdrawn. The partial pressure of chlorine dioxide in the effluent gases from the chamber is less than in the input gaseous mixture.

A suitable generator for carrying out this process will be described. Quantities, dimensions, and flows may be altered to suit the equipment or the usage under consideration. The generator will serve for many uses requiring less chlorine dioxide than its minimum output by carefully proportioning the effluent gases at a given dioxide production rate. The waste gas may be exhausted to the air or absorbed in caustic solution.

Control in this process depends upon the chlorine input; the chlorite is in excess and sufficient is used to allow operation over a relatively long period of time.

Two or more glass tubes, about 2.5 inches in diameter and 4 to 5 feet long, are filled with technical grade sodium chlorite flakes and connected in series with glass tubing. Chlorine and air or other inert gases to generate a considerable quantity of chlorine dioxide at 30 mm. mercury partial pressure are introduced at the
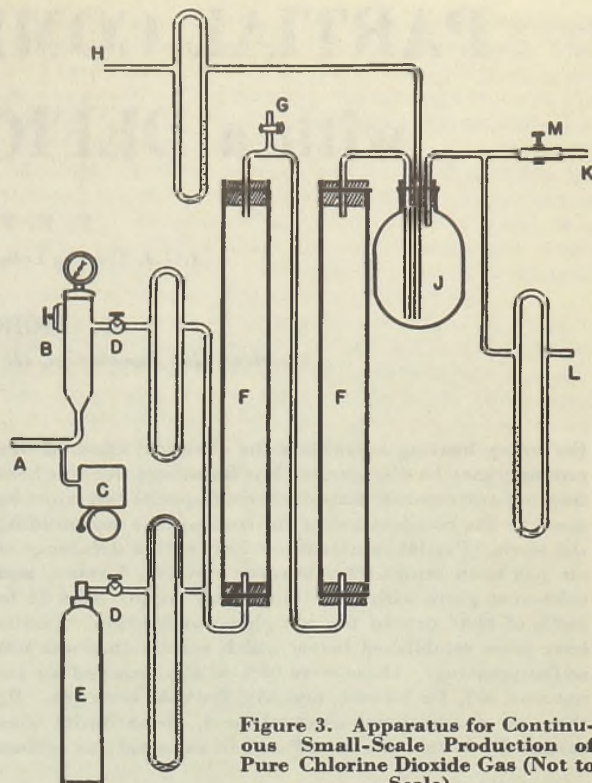
Figure 3. Apparatus for Continuous Small-Scale Production of Pure Chlorine Dioxide Gas (Not to Scale)

A. Compressed air inlet	G. NH₄OH test point for Cl₂
B. Pressure-reducing valve	H. Dilution air
C. Pressure-operated signal	J. Mixing bulb
D. Needle valves	K. Main flow outlet
E. Chlorine cylinder	L. Effluent gas proportioning meter
F. Reaction tubes	M. Screw clamp or valve

bottom of the first tube and pass through the two tubes in series. The effluent gases are then conducted to a mixing chamber where they are diluted to any desired concentration with air. The generator is sketched in Figure 3. For flour bleaching, the apparatus was designed to deliver as high as 1.3 grams chlorine dioxide per barrel to a 16-barrel-an-hour flour stream at a partial pressure of about 2 mm. mercury for about 20 hours per tube. This is equivalent to 20 grams per hour for 20 hours or about 400 grams chlorine dioxide per charge of sodium chlorite per tube.

As the sodium chlorite becomes exhausted, tubes with fresh charges may be inserted in the line to make the process continuous. The chlorine flow for this apparatus is controlled by a needle valve and a U-tube differential manometer containing sulfuric acid. The other manometers contain water as the fluid medium.

LITERATURE CITED

(1) Cunningham, G. L., and Losch, B. J., U. S. Patent 2,043,284 (1936).
(2) Hutchinson, W. S., and Mecham, D. K., Ibid., 2,309,457 (1943)
(3) Logan, J. O., Ibid., 2,163,793 (1939).
(4) Woodward, E. R., Petroe, G. A., and Vincent, G. P., Trans. Am. Inst. Chem. Engrs., 40, 271–90 (1944).

PARTIAL COMBUSTION of GAS
with a DEFICIENCY of AIR

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For many heating operations the chemical effect of flue products may be disregarded, but for others, such as heat treating and ceramic manufacturing, special care must be given to the composition of the atmosphere surrounding the work. Partial combustion of gas with a deficiency of air has been studied for burning natural, butane, and coke-oven gases with variations of air supply from 10 to 100% of that needed for complete combustion. Limits have been established below which combustion was not self-supporting. These were 65% of the required air for natural, 60% for butane, and 53% for coke oven gas. By the use of additional external heat, these limits were materially lower. Ratios of carbon monoxide to carbon dioxide and of carbon monoxide to hydrogen have been determined for these gases. The sharp odor which usually accompanies and identifies partially burned fuel gases is generally attributed to aldehydes and other hydroxylated hydrocarbon compounds. Quantitative tests were made for aldehydes, ketones, organic acids, alcohols, and combined nitrogen. Analytical methods for these compounds in the products of incomplete combustion of gas were not located in the literature. However, the most applicable of the numerous methods for analyses of these compounds were selected and tried. Formaldehyde present up to 0.0842% was the principal constituent. The amounts of other compounds are reported.

THE use of fuel gases for industrial heating and processing is far greater than is commonly believed. In the case of natural gas, for example, the total volume sold to industry is almost six times as great as the amount used for domestic heating, cooking, and refrigeration; in the manufactured gas field, fuel gas use, including coke-oven gas, is almost four times as great as domestic consumption. Statistics show that the astronomical figure of 2762 billion cubic feet of natural gas were used for industrial purposes during 1942, while 776 billion of gases were made from coal and other raw materials for commercial and industrial establishments. Although accelerated by war needs, the growth in this use of gas by industry has continued to expand at a rate of about 15% per year for more than a decade. In addition to its utilization as an efficient and easily applied form of energy for heating and power purposes, gas and its products of combustion are widely applied in a manner to utilize the chemical properties of various constituents. While it is still true that many installations of gas as a fuel do not make use of its chemical aspects, there are an increasing number of applications in which the chemical nature of the flue products and their effect on materials being processed are of the greatest importance.

The best known example of this point is in the steel treating field. Formerly gas was applied primarily as a heating fuel to take advantage of its speed and flexible control of temperature. Factories had to put up with more or less destruction of the surface of the metal due to the presence of oxidizing flue products. For a number of years now, the use of special atmospheres made from gas has changed this picture. It is now possible to maintain any desired surface condition without injury by the proper selection and application of prepared atmospheres making use of the chemical properties of various gaseous constituents. The simplest atmospheres of this type are produced by partial combustion of gases with less than the amount of air required for complete combustion followed, when necessary, by further treatment to remove any flue gas constituent considered objectionable in the untreated atmosphere. In general, this class of prepared atmosphere finds its principal application in the field of annealing and other relatively low-temperature operations.

For high-temperature operations and, in general, for the treatment of steels of medium or high carbon range, the partial-combustion atmosphere does not produce optimum composition. Therefore, the air supply furnished to the special atmosphere machines is further restricted and external heating is applied. The rich gases produced in this manner are high in hydrogen and in carbon monoxide but have little or no carbon dioxide and water.

Although the use of special atmospheres with steel has been mentioned as an illustration, it should be borne in mind that present-day applications of partially burned gases, with and without cracking and further purification, cover a wide range of industrial processes. The literature in this field is already voluminous, particularly in connection with the protection of metals, steel, copper, silver, vitreous enameling, ceramics, and many other products.

Although there are many instances in industry where furnace atmospheres prepared by careful control of combustion with limited air supply are being successfully employed to produce a desired chemical effect on a certain product, basic principles of the combustion process under such conditions are less completely known than for combustion under oxidizing conditions. In many cases a heating practice producing a desired result for a given application was developed only after considerable experimenting by the method of trial and error. Thus, empirical heating processes which produced desired chemical results on the materials involved were often developed without a knowledge of the effect of various factors influencing the composition of the atmospheres produced. As a result, many of the data published on this subject are incomplete or seemingly contradictory. In an attempt to control the chemical effect of a furnace atmosphere on the material heated, it is often endeavored to duplicate a procedure which has been successfully used previously for a similar heating process. The fact that so many of these attempts result

in failure to achieve the desired objective may generally be attributed to lack of essential data, inaccuracies in reported data, or improper evaluation of different variables affecting the results.

Because of the confusion existing on this subject, the American Gas Association has been carrying on an investigation of the underlying principles of gas combustion with limited air supply (1). The purpose of this paper is to summarize the research conducted to date on the general subject of burning gas with a deficiency of air. A previous article (6) gave initial results on special atmospheres.

TABLE I. TYPICAL ANALYSES OF NATURAL, MANUFACTURED, AND BUTANE GASES

Constituent	Natural Gas	Mftd. Gas	Butane
CO_2	0.2	0.8	...
O_2	0.2	...	...
H_2	...	53.5	...
CO	...	17.7	...
CH_4	83	22.7	...
C_2H_6	16	4.1	...
C_3H_8	...	...	22.15
C_4H_{10}	...	...	77.85
N_2	0.6	1.2	...
Total	100	100	100
B.t.u./cu. ft.^{a}	1108	534	3207
Sp. gr.	0.63	0.404	2

^{a} Gross heating value.

PRINCIPAL CONSTITUENTS OF PARTIAL COMBUSTION

The investigation carried out by the American Gas Association quantitatively determined the various aspects of partial combustion under controlled conditions. A number of different burner and furnace assemblies were set up as shown in Figures 1, 2, and 3, and were supplied with air and gas, controlled and metered to each particular burner.

Three test gases were employed: 1100 B.t.u. natural gas, 534 B.t.u. coke-oven gas, and 3207 B.t.u. butane gas (Table I). Gas samples were obtained in a water-cooled quartz tube, collected over mercury in a glass container. Gas analyses were made with a modified Orsat gas analysis apparatus; analyses for oxygen when less than 0.2% were made by the manganese hydroxide method (2). Gas and air volumes were corrected to standard conditions of 60° F. and 30 inches of mercury.
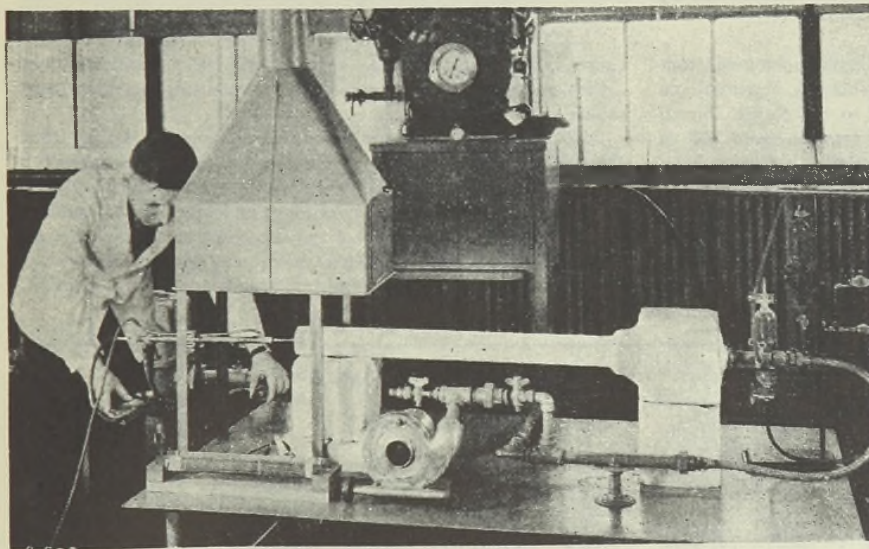
In this paper all compositions of various flue gas constituents are expressed as percentages of the total dry flue products. This is the basis obtained when analyses are made by Orsat-type gas analysis apparatus. Percentages of nitrogen are not shown but may be determined, if desired, by subtracting the sum of all other constituents except water vapor from 100%. The amount of water vapor (3) produced can be calculated, if such data are needed at any time, from the fuel gas composition and the flue gas analysis. To reduce all gases, including water vapor, to a common basis totaling 100%, the various percentages would have to be multiplied by a factor $100/X$, where X is the total percentage of nitrogen, water, and other constituents.

When natural gas was burned with a deficiency of air, Figure 4 shows the composition of principal constituents obtained. As the percentage of air was decreased from 100%[1] required for complete combustion, a flame could be maintained continuously down to 65% of the air needed for complete combustion. From 65 down to 25% air, external heating to 1800° F. was applied and the gas-air mixture was passed through a nickel-impregnated ceramic catalyst. Carbon deposition prevented further decrease of air. With decreasing percentage of air, the carbon dioxide content of the products of incomplete combustion decreased in practically a straight line from 12.2% with all air needed for combustion to 0.2% with 25% air. Under the same conditions the carbon monoxide content increased from 0 to 22%, the hydrogen content increased gradually from 0 to 21.2% except for a change in direction of the curve at aerations between 70 and 50%, and methane appeared in traces at 90% air and gradually increased to 4% at 20% aeration. From the curves of Figure 4, the composition of resultant products of partial combustion from natural gases with any limitation of air from 100 to 25% can readily be obtained. At 70% aeration, for example, the flue products would consist of 7.4% carbon dioxide, 7.4% carbon monoxide, 8.1% hydrogen, and 0.4% methane. If it is desired to produce a gas mixture free from carbon dioxide and to obtain carbon monoxide and hydrogen with some methane, the percentage of air supplied for the combustion reaction should be dropped to slightly below 25%.

Water vapor content of flue gases produced from burning natural gas and maintained at temperatures considerably above the dew point will decrease with decrease in air supplied for combustion. At 100% aeration the flue gases will contain about 22.2% water vapor, at 65% aeration about 18%, at 30% aeration 1.5%, and below 22% aeration less than 0.5% water vapor. Because of the small amount of water vapor found in the combustion products at low aerations, it was not possible to calculate percentages of moisture, since small errors in analysis as well as small changes in carbon-hydrogen ratio of the fuel gas would result in appreciable errors in water vapor calculations. Moisture content of aerations below

[1] For some purposes a composition of air-gas mixture is expressed in terms of an "air-gas ratio"; a ratio of 1.1, for example, denotes a mixture of one part air to one part gas. To avoid complications caused by different gas compositions and air requirements, the data here presented are based on percentage aeration. It is simply the percentage of air required for theoretical stoichiometric combustion.

Figure 1. Test Furnace A, 2-Inch Vitreosil Tube; Sample of Flue Gas Is Being Taken at Left
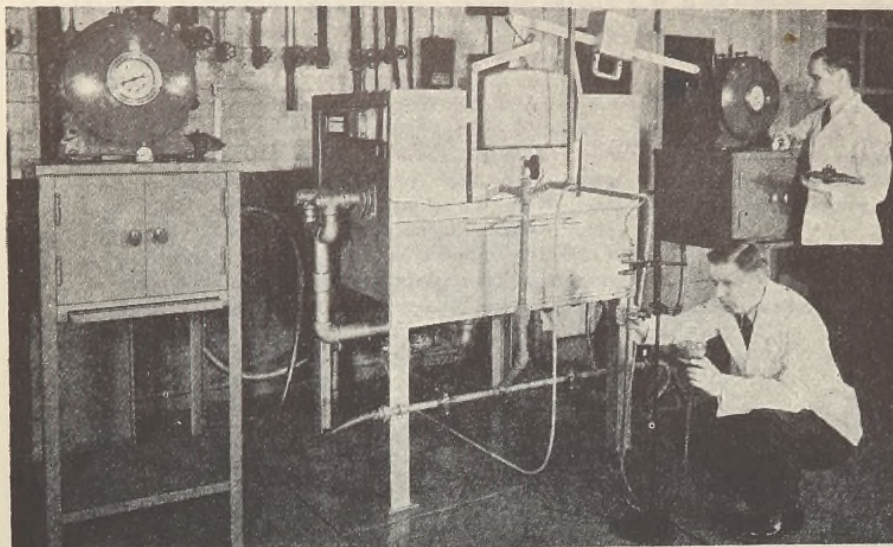
Figure 2 (*Left*). Test Furnace B, 2-Inch-Diameter Pipe with U-Tube inside the Heating Furnace

Figure 3 (*Below*). Test Furnace C, Commercial Gas Generator with Water-Cooled Combustion Chamber, Water-Jacketed Condenser, Spark Plug Ignition, and Special Catalyst; Air-Gas Ratio Apparatus at Right, Gas Sample Collector at Lower Left
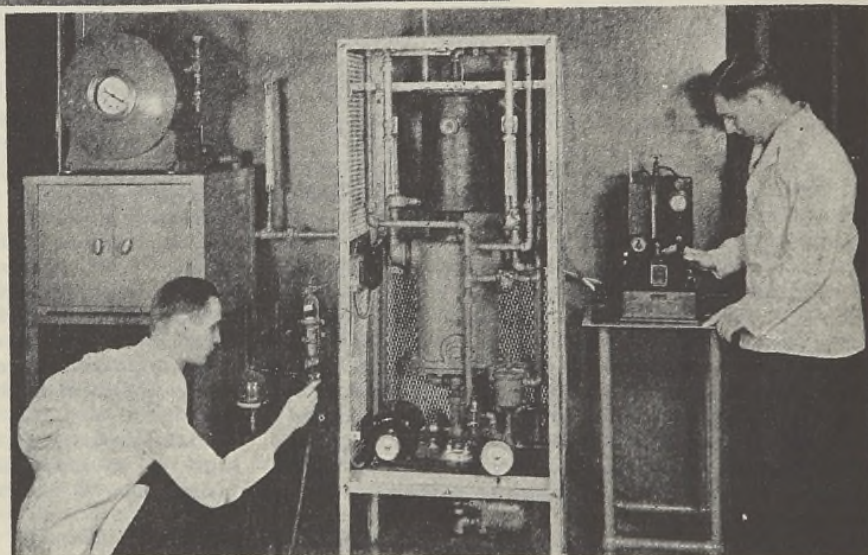
35% was determined by measuring the dew point.

Partial combustion of manufactured coke-oven gas with limited air supply gave the results shown in Figure 5. Flame could be maintained with this gas with decreasing percentages of air down to 53%. Below that figure down to 10% air, it was necessary to supply external heat. In these tests a temperature of 1800° F. was maintained as gas-air mixture passed over a nickel-impregnated ceramic catalyst. Below 10% air, excessive carbon deposition occurred. As air for combustion was decreased from 100 to 10%, carbon dioxide decreased from 10 to 0.2%, carbon monoxide increased from 0 to 21.5%, hydrogen increased from 0 to 52.5%, and methane increased from 0 to 2.2%. By referring to the curves shown, the composition of flue products at any aeration from 100 to 10% can be predicted. For example, at 10% air the combustion reaction yields a flue gas mixture consisting almost entirely of carbon monoxide and hydrogen with a trace of carbon dioxide and some methane.

The limits of flame combustion reported here for natural and manufactured gases lie close to the upper explosive limit for these gases. However, additional study would be necessary before a more general statement of possible relationship between these values could be made.

As butane gas is burned with decreasing percentages of air from that needed for complete combustion, the resultant composition of constituents for any given aeration from 100 to 20% is shown in Figure 6. Flame was maintained without external heating, provided not less than 60% of the air needed for complete combustion was available. From 60 down to 20% aeration, external heating as outlined for natural and coke-oven gas was applied.

TABLE II. ANALYSES OF PRODUCTS OF INCOMPLETE COMBUSTION FROM NATURAL, COKE-OVEN, AND BUTANE GAS

Fuel Gas	Natural				Coke-Oven			Butane		
Aeration, %	84.2	67.5	29.4[a]	29.2	49.5	29.2[a]	29.3	49.0	29.3[a]	26.0
Test furnace temp., ° F.	...	...	1800[a]	1000	...	1800[a]	1000	...	1800[a]	1000[a]
Analysis of flue products, % by vol.										
HCHO	0.000022	0.0133	0.000003	0.000216	0.00302	0.000004	0.000029	0.0842	0.000003	0.000009
CH₂CHO	0.00003	0.00008	....	0.0001	0.0002	0.00001	0.0003	0.0052	....	0.00004
(CHO)₂	....	0.0005	....	....	0.00009	....	....	0.0023	....	
HCOOH	0.00022	0.00282	....	0.0001	0.00097	0.00006	0.0003	0.0208	0.0004	0.00074
CH₃OH	0.00005	0.0004	....	0.0002	0.00025	0.00007	0.00002	0.006	....	
Combined N₂	0.000054	0.00106	0.00010	0.00018	0.00046	0.00223	0.00079	0.00106	0.00215	0.00024
Total	0.000376	0.01816	0.000103	0.000796	0.00499	0.002374	0.001439	0.11956	0.002553	0.001029

[a] External heat.
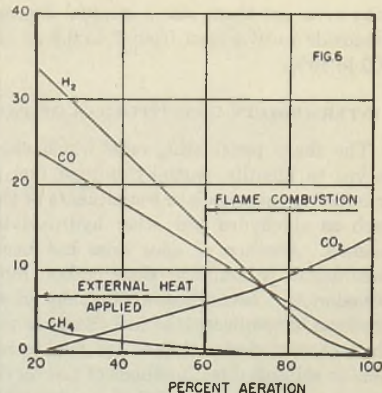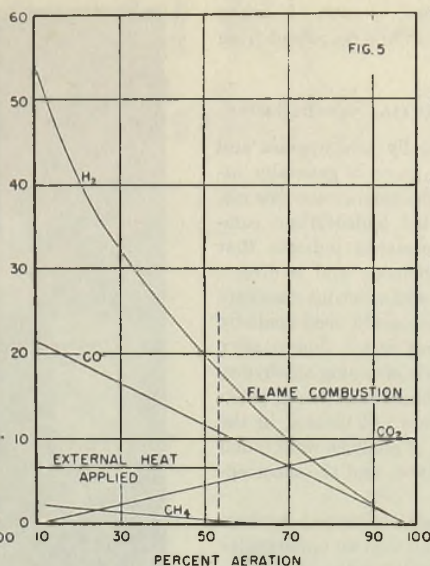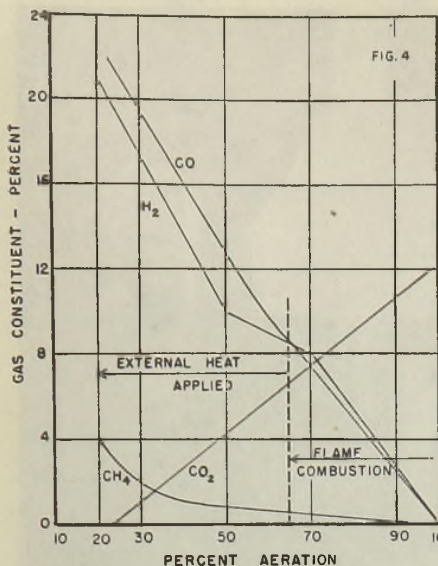
Figure 4. Composition of Gases Produced by Burning Natural Gas with a Deficiency of Air
Figure 5. Composition of Gases Produced by Burning Coke Oven Gas with a Deficiency of Air
Figure 6. Composition of Gases Produced by Burning Butane Gas with a Deficiency of Air

With decreasing percentages of air from 100 to 20%, the carbon dioxide content of resultant flue gases decreased from 14 to 0.2%, carbon monoxide content increased from 0 to 23.5%, hydrogen increased from 0 to 33.5%, and methane from 0 to about 3%.

Oxygen was not detected in the products of combustion of any of these tests until the flame was on the verge of extinction. At that point as much as 0.5% oxygen was observed. This was always accompanied by some unburned fuel gas as indicated by the presence of methane. If oxygen is encountered in burning gas with a deficiency of air, it can probably be attributed to too low a furnace temperature or escape of unburned air-gas mixture through the burner.

The work by Austin and Day (5) and others showed that, under actual furnace conditions, there is more or less equilibrium between the products undergoing treatment and the gases. In the analysis just discussed, this important factor was not introduced since it would be a variable depending upon each different metal undergoing treatment and the time and temperature involved. The data of Figures 4, 5, and 6 are the dry-basis analyses as obtained under the conditions outlined. They must not be interpreted as the percentage composition of all gases in a furnace since water vapor is omitted as explained in the introduction. It is well to bear this point in mind since the equilibrium constant applied to the data on the charts would yield apparently incorrect answers. When water vapor is properly taken into account, either by dew point measurement or computation, the data fall into proper pattern.

RATIO OF CO TO CO₂ AND CO TO H₂

Figure 7 shows the change in ratio of carbon monoxide to carbon dioxide for three fuel gases as the combustion reaction proceeds with decreasing amounts of air. The natural gas and butane gas curves practically coincide, the ratio of carbon monoxide to dioxide increasing rapidly from 0.3 to over 100 as air is decreased from 90 to 22%. For coke-oven gas the ratio of carbon monoxide to dioxide is less than for the other two gases for aerations below 70%. This is to be expected because of the difference in chemical composition. In addition to being useful in furnace atmosphere work, these curves can be utilized to estimate the composition of flue gases which may be expected in the case of other fuel gases having heating values between 534 and 3207 B.t.u. per cubic foot. Knowing the percentage of either
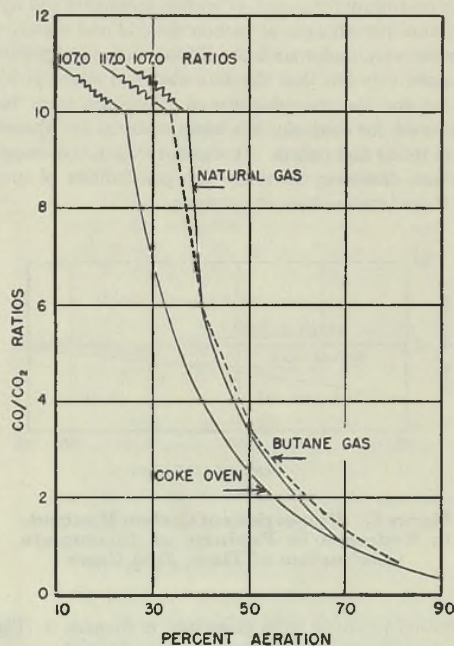
Figure 7. Proportion of Carbon Monoxide and Dioxide in Products of Incomplete Combustion of Three Fuel Gases

carbon monoxide or dioxide, the percentage of the other gas present can be closely approximated.

Another useful relation is the ratio of carbon monoxide to hydrogen in products of incomplete combustion. Figure 8 gives these ratios for natural, butane, and coke-oven gases. On natural gas the ratio carbon monoxide to hydrogen remains practically constant, varying only from 1 to 1.1 as air is decreased from 100 to 25%. This ratio on butane gas varies from the average curve from 1 to 1.1 as air for combustion is decreased from 100 to 86%, and then further decreases to 0.8 at 70% air where it remains practically constant as air is decreased to 20%. On

coke-oven gas there was a gradual decrease in ratio of carbon monoxide to hydrogen from 1 to 0.4 as air was decreased from 100 to 10%.

INTERMEDIATE CONSTITUENTS OF PARTIAL COMBUSTION

The sharp penetrating odor which usually accompanies and serves to identify partially burned fuel gases is generally attributed to intermediate constituents of the combustion process, such as aldehydes and other hydroxylated hydrocarbon compounds. Absence of odor does not necessarily indicate that combustion is complete since carbon monoxide and hydrogen are odorless. Identification of aldehydes and other intermediate products of combustion of fuel gases has generally been made by their characteristic odor or by qualitative test. Quantitative data or suitable direct methods of test for determining aldehydes, ketones, organic acids, alcohols, and combined nitrogen in products of incomplete combustion of gas were not located in the literature. However, numerous methods of analysis were found for the types of organic compounds involved, and the most applicable were selected and tried.

During the study of principal constituents of partial combustion of gas as previously discussed, it was felt that an opportunity was presented to determine quantitatively the amount of these intermediate oxidation compounds. In that study the objective was to secure as high a degree of incomplete combustion as possible with maximum formation of carbon monoxide and hydrogen and minimum percentages of carbon dioxide and water. Odors of aldehydes, etc., under such conditions were very pronounced. It was accordingly felt that the data obtained might yield useful information for the manufacture of chemicals from fuel gas. Formaldehyde, for example, is a basic material for phenol, urea, and casein resins and paints. It was not within the scope of this investigation, however, to study the possibilities of increasing yields of these intermediate compounds.
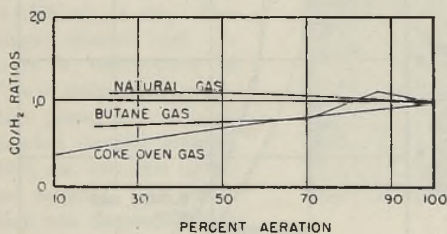
Figure 8. Proportions of Carbon Monoxide to Hydrogen in Products of Incomplete Combustion of Three Fuel Gases

Combustion products were generated in furnace A (Figure 1) with free-burning flame and limited pre-mixed air supply and also in unit B (Figure 2) consisting of a 2-inch diameter black iron pipe filled with ceramic pieces and nickel catalyst heated externally to 1000° and 2000° F. A special sampling apparatus (Figure 9) was designed for collecting condensate and soluble gases in water using 43 to 76 cubic feet of combustion products.

Existing methods of analysis reported in the literature were found to be primarily qualitative or suitable for fairly high concentrations. Those which seemed most adaptable for the present study were applied to known mixtures. The following six methods (4) were selected and appropriate modifications were made:

1. Fuchsin-sulfurous acid (Schiff or Schiff-Elvove reagent) method for determination of formaldehyde.
2. Silver precipitation method for total aldehydes.
3. Iodometric method for total aldehydes and methyl ketones.
4. Sodium hydroxide titration method for organic acid content.
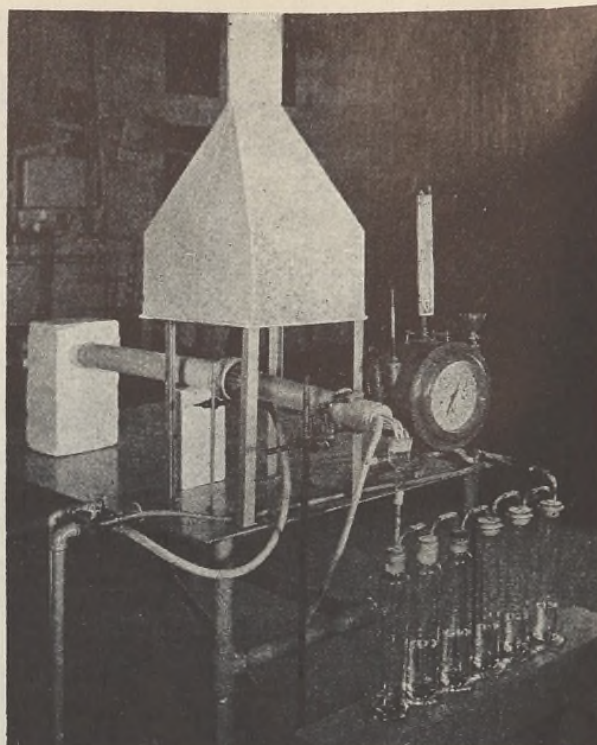
Figure 9. Apparatus for Generating and Collecting Intermediate Products of Incomplete Combustion

5. Analyses for alcohols by oxidation with dichromate in acid solution.
6. Kjeldahl determination for combined nitrogen.

Table II presents results in terms of percentage by volume, obtained on ten analyses. A study of the table reveals that:

1. Formaldehyde was identified in each of the ten tests; maximum percentage found was 0.0842, minimum 0.000003.
2. Acetaldehyde was detected in eight out of ten samples, maximum being 0.0052%, minimum 0.00001%.
3. Glyoxal or other dialdehydes were shown in three of the ten samples, maximum being 0.0023%.
4. Total aldehydes attained a maximum for any one test of 0.0917% on butane, 0.01388% on natural, and 0.00331 on coke-oven gas.
5. Organic acid, reported as formic acid, was detected in nine out of ten samples, maximum percentage being 0.0208%.
6. Methyl alcohol appeared to be present in seven of ten samples, but it is doubtful if data are within experimental error; maximum percentage found was less than 0.006%.
7. Combined nitrogen was found in all samples from traces up to 0.00223%.
8. Total maximum percentage of above intermediate products of combustion was 0.01816 from burning natural gas, 0.00499 from coke-oven gas, and 0.11956 from butane gas.

Results reported should not be regarded as exact figures but rather as an indication of the relative magnitude of those constituents present.

LITERATURE CITED

(1) Am. Gas Assoc., *Research Bull.* 11 (1940) and 15 (1942).
(2) *Ibid.*, 15, p. 16.
(3) *Ibid.*, pp. 31, 47.
(4) *Ibid.*, pp. 79–90.
(5) Austin, J. B., and Day, M. J., IND. ENG. CHEM., 33, 23 (1941).
(6) Cline, C. R., and Segeler, C. G., *Ibid.*, 33, 46 (1941).

Vapor-Liquid Equilibria in Mixtures of Volatile Paraffins

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Two five-component mixtures were prepared of volatile paraffin hydrocarbons having critical temperatures of approximately 100° F. and critical pressures of about 2000 pounds per square inch absolute. Vapor-liquid equilibrium determinations were made on these two mixtures at 100° F. and at pressures up to that of the single phase. Equilibrium constants at 100° F. from these two mixtures have been compared with equilibrium constants from a binary and a ternary mixture, each of which has a critical temperature of 100° F. and a critical pressure of approximately 2000 pounds per square inch absolute. Within the limits of experimental error it appears that the equilibrium constants of the volatile paraffin hydrocarbons in binary or complex mixtures of paraffins may be defined by specifying the temperature, pressure, and "convergence pressure" corresponding to the temperature of the equilibrium. The convergence pressure is the critical pressure of a mixture at its critical temperature. At any other temperature the convergence pressure is the pressure at which the equilibrium constants appear to converge to unity.

THE convenient Raoult's law for making equilibrium calculations in multiple component mixtures has served well for many years and is still satisfactory for ideal solutions, such as the volatile paraffin hydrocarbons at low pressures. As higher pressures are used in industrial fractionation, new relations of wider applicability are required for estimating the equilibrium relations. The use of the equilibrium constant $K = y/x$, suggested about twelve years ago (10), has been found more satisfactory than Raoult's law, but a simple, convenient method of estimating its value at high pressures in different mixtures is not available.

According to the phase rule, the number of independent variables that must be fixed in order to define the compositions of the two co-existing equilibrium vapor and liquid phases is equal to the number of components in the mixture. A binary system existing in two phases has two degrees of freedom. When the temperature and pressure are fixed, the compositions of the equilibrium liquid and vapor phases are fixed. When a ternary system is considered, it is necessary to fix the temperature, pressure, and a third phase-rule variable in order to define the compositions of the equilibrium liquid and vapor phases. In the presentation of vapor-liquid equilibrium data for a ternary system, Carter, Sage, and Lacey (3) used the variables temperature, pressure, and a parameter, $x_a/(x_a + x_b)$, based on mole fractions in the liquid phase. In calculating equilibrium relations it would be convenient if the equilibrium constant $K = y/x$ for each component could be estimated without advance specific information concerning the composition of the equilibrium liquid.

In 1933 (6) attention was called to the fact that, since the compositions of both equilibrium phases are identical at the critical point, the equilibrium constants of all components in any mixture are unity at the critical temperature and pressure of the mixture.

In the case of binary mixtures the values of K for either component are functions of temperature and pressure only and are independent of the proportion of the two components present in the mixture. Therefore, the isothermal values of $\log K$ plotted against $\log P$ (Figure 3) will always converge to unity ($K = 1$) at the critical pressure corresponding to the temperature for that binary system. In estimating equilibrium constants, the binary mixture may be identified by a convergence pressure at any desired temperature. The mixture may go into a single phase at a pressure below convergence, but use of the convergence pressure appears adequate to identify the K curves.

Recently (4) this property was used to estimate the values of K in binary systems without experimental data at high pressures to define the curve of $\log K$ plotted against $\log P$. A similar pro-
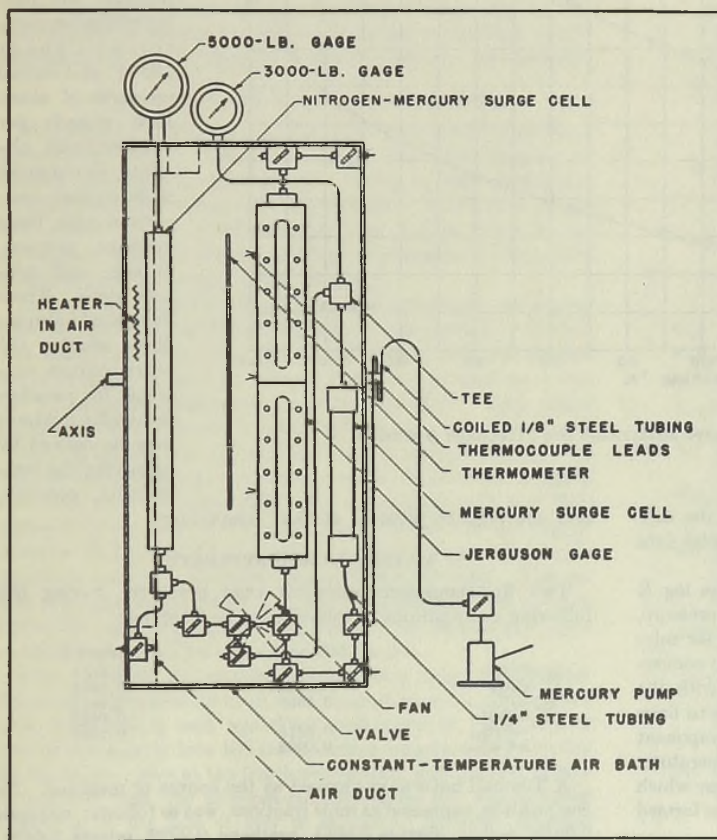
Figure 1. Equilibrium Apparatus

- 5000-LB. GAGE
- 3000-LB. GAGE
- NITROGEN-MERCURY SURGE CELL
- HEATER IN AIR DUCT
- AXIS
- TEE
- COILED 1/8" STEEL TUBING
- THERMOCOUPLE LEADS
- THERMOMETER
- MERCURY SURGE CELL
- JERGUSON GAGE
- MERCURY PUMP
- 1/4" STEEL TUBING
- FAN
- VALVE
- CONSTANT-TEMPERATURE AIR BATH
- AIR DUCT
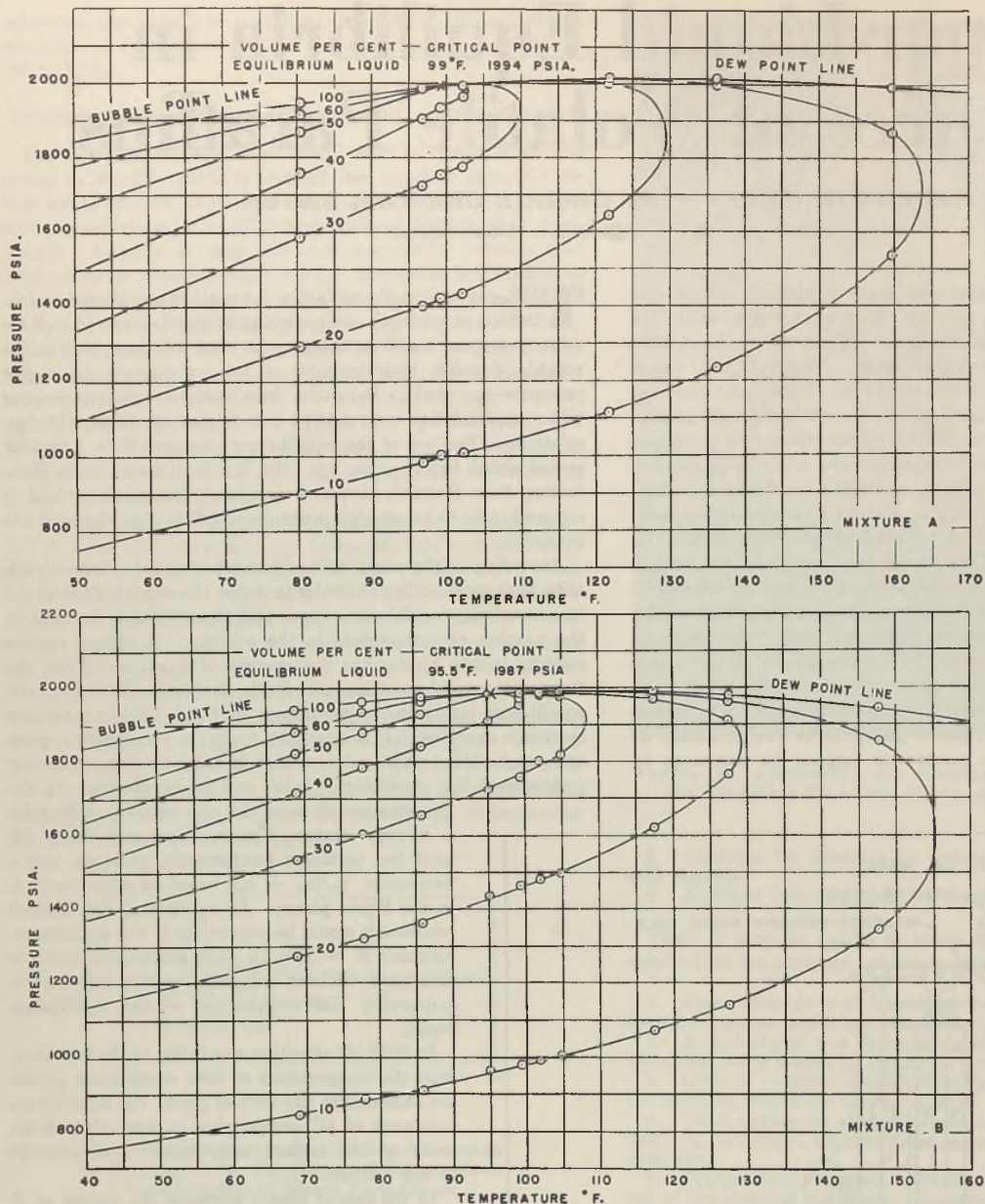
Figure 2.   Pressure-Temperature Phase Diagrams for Mixtures A and B

butane binary system, having a convergence pressure of 1912 pounds per square inch absolute at 100° F., are available (9). The equilibrium constants for methane in a methane–propane–n-pentane ternary mixture having a convergence pressure of 1912 pounds per square inch absolute at 100° F., can be obtained from published triangular diagrams (3). The K values for methane from these mixtures agree, within the experimental error, with an average deviation of about 2%. Additional equilibrium data on more complex mixtures containing methane, propane, n-butane, and n-pentane, and having critical temperatures of about 100° F. and critical pressures of about 1900 pounds per square inch absolute, would make an interesting comparison with these methane, propane, butane, and pentane data. These data would also indicate whether the equilibrium constants for paraffins in paraffin mixtures may be defined by specifying the temperature, pressure, and convergence pressure at that temperature.

cedure was suggested for complex mixtures (11), and the estimated equilibrium constants agreed well with experimental data at high temperatures.

To determine whether a component follows the same log K curve in different mixtures with the same convergence pressure, it is necessary to have experimental equilibrium data for mixtures of three or more components which have the same convergence pressure and at least one component in common with the binary or ternary mixture. Apparently it is impossible to have two binary paraffin systems which have a common component and a common convergence pressure at the same temperature. A ternary system does not have convergence pressures which overlap with those of the three binary systems that can be formed from the components of the ternary system.

The equilibrium constants for methane in the methane–n-

MATERIALS AND APPARATUS

Two five-component mixtures were prepared, having the following compositions expressed as mole fractions:

	Mixture A	Mixture B
CH_4	0.6626	0.7057
C_2H_6	0.1093	0.0669
C_3H_8	0.1057	0.0413
$n-C_4H_{10}$		0.0508
$n-C_5H_{12}$	0.0616	0.1353
$n-C_6H_{14}$	0.0608	. . .

A Tomball natural gas served as the source of methane. Its composition, expressed as mole fractions, was as follows: nitrogen 0.0043, carbon dioxide 0.0051, methane 0.9320, ethane 0.0425, propane 0.0161. The purity of the ethane (supplied by Carbide

and Carbon Chemicals Corporation) was given as 97.5%, the remainder being principally ethylene with small amounts of propane and heavier. The propane, n-butane, and n-pentane were research-grade materials (obtained from Phillips Petroleum Company). The propane contained less than 0.1% of other hydrocarbons, probably ethane and isobutane. The purity of the n-butane and n-pentane was given as 99+ mole %. The diluents in the n-butane amounted to about 0.2% isobutane and 0.1% isopentane. The n-pentane contained about 0.5% isopentane. The n-hexane was technical-grade material (Phillips Petroleum Company), and its purity was given as 95+ mole %, the principal diluent being methylcyclopentane.

The experimental apparatus (Figure 1) was a modification of that used by Kurata and Katz (7) to determine the critical points of volatile hydrocarbon mixtures. The principal unit was a double Jerguson gage with a volume of about 150 cc., which served as the equilibrium cell. The nitrogen-mercury surge cell was used to displace samples at equilibrium pressure. These two units, along with the necessary valves and transfer lines, were located in a constant-temperature air bath maintained at 100° F. by a 250-watt heater located in an air duct and providing temperature control of the air bath within about 0.5° F. A uniform temperature was maintained throughout the bath by an electric fan. Thermocouples embedded in the body of the equilibrium cell enabled the operator to know when the heavy metal parts were at the same temperature as the air bath. The pressure in the equilibrium cell was indicated by a 3000-pound Duragage which permitted direct readings to 25 pounds and estimated readings to 5 pounds. The pressure gage was calibrated with a dead weight tester. The entire unit rested upon an axis permitting rotation of the bath through an angle of 270°.

The analyses of the equilibrium vapors and liquids were carried out in a low-temperature Podbielniak fractionating column. Before a sample entered the fractionating column, its pressure was reduced by means of a needle valve, and it was then passed through a unit containing calcium chloride, ascarite, and Drierite.

PREPARATION AND CHARGING OF SAMPLE

Mixtures A and B were prepared in a storage bomb which had a capacity of 750 cc. The bomb and its associated valves and transfer lines were so arranged that it was possible to displace samples from the unit at constant pressure. Mixtures A and B were stored in and transferred from the storage bomb to the equilibrium cell as a single-phase fluid at pressures between 2500 and 3000 pounds per square inch absolute.

Before vapor-liquid equilibrium studies were made, the critical point of each mixture was determined by the method of Kurata and Katz (7) as the intersection of all lines of constant volume per cent liquid (Figure 2). The critical point of mixture A was 99° F., and 1994 pounds per square inch absolute. The critical point of mixture B was 95.5° and 1987 pounds.

After a sample was transferred from the storage bomb to the equilibrium cell, the unit was maintained at equilibrium temperature and pressure overnight. The equilibrium cell was then agitated by rotation on its axis; the movement of the slug of mercury in the equilibrium cell caused the vapor and liquid phases to come into intimate contact with each other. The cell was then allowed to stand in a vertical position for 30 minutes before the vapor sample was taken, to allow the equilibrium liquid to drain from the sides of the equilibrium cell.

Prior to taking the sample of equilibrium vapor, the transfer line from the equilibrium cell to the needle valve at the Podbielniak fractionating unit was filled with mercury. The rate of flow of the sample into the fractionating column was controlled by the needle valve at the fractionating unit, and the rate of flow of mercury from the nitrogen-mercury surge cell was adjusted according to the rate of flow of sample to maintain constant pressure within 7 pounds per square inch. The vapor sample was taken until the vapor-liquid interface entered the sample transfer

line, when the needle valves were closed. The material in the sample line was vented.

Since the densities of the equilibrium liquids were desired, the method of taking liquid samples was somewhat different. The sample of equilibrium liquid was displaced into a pycnometer from which it was passed into the fractionating unit and analyzed. The densities of the equilibrium liquids have already been reported (5).

When equilibria at low pressures were studied, the quantity of equilibrium vapor and liquid available for analyses was increased by displacing most of the equilibrium vapor into the fractionating column; additional mixture was added to the equilibrium cell, and equilibrium at the same temperature and pressure was again established. The second charge of equilibrium vapor was then displaced into the fractionating column, and both charges of equilibrium vapor were analyzed together. This experimental technique is based on the principle that the compositions of two phases in equilibrium are independent of the extent of either phase.

EQUILIBRIUM RESULTS

The experimental compositions of the equilibrium vapor and liquid phases from mixtures A and B and the experimental equilibrium constants are given in Tables I and II. To check the accuracy of the equilibrium determinations, material balance

Figure 3. Experimental Equilibrium Constants from a Binary and a Complex Mixture

Figure 4. Experimental Equilibrium Constants from a Ternary and Two Complex Mixtures

ponent whose concentrations in the two equilibrium phases are nearly equal. Ethane is that component for mixtures A and B at 100° F. and the pressures studied.

In connection with the equilibrium with mixture B at 1297 pounds per square inch absolute, if the molal concentration of ethane in the vapor phase had been 0.0629 instead of 0.0615, or if the concentration of ethane in the liquid phase had been 0.0785 instead of 0.0756, the material balance based on ethane would have agreed with the material balances based on the other components. When concentrations of components in the equilibrium phases are widely different, a material balance calculation is less sensitive in reflecting experimental errors. Figure 3 compares the experimental equilibrium constants for methane and n-butane in mixture B (open circles) with those in the methane-n-butane (9) binary system (solid line). The critical or convergence pressure for the binary system of methane and n-butane at 100° F. (1912 pounds per square inch absolute) is slightly less than the convergence pressure for mixture B which is about 2000 pounds. Figure 4 compares the experimental equilibrium constants for methane, propane, and n-pentane in mixtures A and B with those in a ternary mixture of methane, propane, and n-

TABLE I. EXPERIMENTAL COMPOSITIONS OF EQUILIBRIUM VAPOR AND LIQUID PHASES FROM MIXTURE A AT 100° F.

Pressure, Lb./Sq. In. Abs.	Component	Mole Fraction Vapor	Mole Fraction Liquid	$K = y/x$
1046	CH_4	0.7801	0.3042	2.564
	C_2H_6	0.1102	0.1311	0.841
	C_3H_8	0.0787	0.2026	0.388
	$n-C_5H_{12}$	0.0223	0.2021	0.110
	$n-C_6H_{14}$	0.0087	0.1600	0.054
1822	CH_4	0.7647	0.5574	1.372
	C_2H_6	0.1022	0.1222	0.836
	C_3H_8	0.0779	0.1369	0.569
	$n-C_5H_{12}$	0.0309	0.0851	0.363
	$n-C_6H_{14}$	0.0243	0.0984	0.247
1419	CH_4	0.7645	0.3858	1.982
	C_2H_6	0.1169	0.1314	0.890
	C_3H_8	0.0836	0.1755	0.476
	$n-C_5H_{12}$	0.0215	0.1449	0.148
	$n-C_6H_{14}$	0.0135	0.1624	0.083
1639	CH_4	0.7853	0.4512	1.740
	C_2H_6	0.1022	0.1308	0.781
	C_3H_8	0.0764	0.1490	0.513
	$n-C_5H_{12}$	0.0198	0.1256	0.158
	$n-C_6H_{14}$	0.0163	0.1434	0.114
1235	CH_4	0.8040	0.3472	2.316
	C_2H_6	0.1039	0.1325	0.784
	C_3H_8	0.0700	0.1893	0.370
	$n-C_5H_{12}$	0.0140	0.1613	0.087
	$n-C_6H_{14}$	0.0081	0.1697	0.048

TABLE II. EXPERIMENTAL COMPOSITIONS OF EQUILIBRIUM VAPOR AND LIQUID PHASES FROM MIXTURE B AT 100° F.

Pressure, Lb./Sq. In. Abs.	Component	Mole Fraction Vapor	Mole Fraction Liquid	$K = y/x$
1431	CH_4	0.8442	0.4199	2.010
	C_2H_6	0.0656	0.0752	0.872
	C_3H_8	0.0285	0.0681	0.419
	$n-C_4H_{10}$	0.0207	0.1055	0.196
	$n-C_5H_{12}$	0.0410	0.3313	0.124
517	CH_4	0.8398	0.1479	5.678
	C_2H_6	0.0663	0.0438	1.514
	C_3H_8	0.0331	0.0814	0.407
	$n-C_4H_{10}$	0.0267	0.1522	0.175
	$n-C_5H_{12}$	0.0341	0.5747	0.059
946	CH_4	0.8543	0.2866	2.981
	C_2H_6	0.0627	0.0718	0.873
	C_3H_8	0.0287	0.0780	0.368
	$n-C_4H_{10}$	0.0161	0.1323	0.122
	$n-C_5H_{12}$	0.0382	0.4313	0.089
1297	CH_4	0.8561	0.3838	2.231
	C_2H_6	0.0615	0.0756	0.813
	C_3H_8	0.0277	0.0705	0.393
	$n-C_4H_{10}$	0.0215	0.1129	0.190
	$n-C_5H_{12}$	0.0332	0.3572	0.093
1736	CH_4	0.8270	0.5251	1.575
	C_2H_6	0.0609	0.0727	0.838
	C_3H_8	0.0288	0.0597	0.482
	$n-C_4H_{10}$	0.0279	0.0840	0.332
	$n-C_5H_{12}$	0.0554	0.2585	0.214

calculations were made on each component. When the composition of the charge to the equilibrium cell and the compositions of the equilibrium liquid and vapor phases are known, it is possible to make a separate material balance for each component to determine the moles of equilibrium vapor, or liquid, per mole of mixture. The results of these calculations are given in Table III. If all of the operations in the equilibrium determination were executed perfectly, the calculated fraction of equilibrium vapor, or liquid, would be the same irrespective of the component on which the calculations were based. Table III shows that the agreement is reasonably good for all components except ethane. Furthermore, the agreement of the material balances in the cases of methane, propane, n-butane, and n-pentane is within about 5% for all equilibrium determinations except the first three with mixture A which were carried out while experience was being acquired.

The irregularities in connection with ethane are probably due in part to impurities in the ethane used in the construction of mixtures A and B. However, a material balance calculation is a sensitive test of the accuracy of the data concerning that com-

TABLE III. MOLES OF EQUILIBRIUM VAPOR PER MOLE OF MIXTURE CALCULATED BY A MATERIAL BALANCE ON THE INDICATED COMPONENT AT 100° F.

		Pressure, Lb./Sq. In.				
		1046	1822	1419	1639	1235
Mixt. A	CH_4	0.753	0.507	0.731	0.633	0.690
	C_2H_6	1.043	0.645	1.524	0.752	0.811
	C_3H_8	0.782	0.529	0.760	0.596	0.701
	$n\text{-}C_5H_{12}$	0.781	0.434	0.675	0.605	0.677
	$n\text{-}C_6H_{14}$	0.656	0.507	0.682	0.650	0.674

		Pressure, Lb./Sq. In.				
		1431	517	946	1297ᵃ	1736
Mixt. B	CH_4	0.674	0.806	0.738	0.682	0.598
	C_2H_6	0.865	1.027	0.538	0.617	0.492
	C_3H_8	0.677	0.830	0.744	0.682	0.595
	$n\text{-}C_4H_{10}$	0.645	0.808	0.701	0.679	0.592
	$n\text{-}C_5H_{12}$	0.675	0.813	0.753	0.685	0.607

pentane, having a critical temperature of 100° F. and a critical (convergence) pressure of about 2000 pounds per square inch absolute (3).

Figures 3 and 4 present equilibrium constants from published correlations by Robinson and Gilliland (8), by Brown (1, 2), and as modified by White and Brown (11). The equilibrium constant curves from Brown are represented as reliable only for conditions unaffected by the critical, which should always be modified at high pressures. Figures 3 and 4 give an equilibrium constant curve for methane for a convergence pressure of 2000 pounds per square inch absolute at 100° F. from an unpublished correlation by the authors. This correlation of methane equilibrium constants from binary paraffin systems was made on the basis of convergence pressure.

In connection with the binary and ternary mixtures the authors (3, 9) report that no uncertainties in the compositions of the equilibrium phases greater than 0.005 mole fraction are to be expected except in the immediate vicinity of the critical state. This uncertainty is of the same order of magnitude as the uncertainty in the compositions of the equilibrium phases from mixtures A and B. Within the limits of experimental error, it appears that the curves of log K against log P for a paraffin in paraffin mixtures having the same convergence pressure at a given temperature can be considered coincident.

LITERATURE CITED

(1) Brown, *Petroleum Engr.*, 11, No. 8, 25 (1940).
(2) *Ibid.*, 11, No. 9, 55 (1940).
(3) Carter, Sage, and Lacey, *Trans. Am. Inst. Mining Met. Engrs.* 142, 170 (1941).
(4) Gilliland and Scheeline, IND. ENG. CHEM., 32, 48 (1940).
(5) Hanson, Kuist, and Brown, *Ibid.*, 36, 1161 (1944).
(6) Katz and Brown, *Ibid.*, 25, 1373 (1933).
(7) Kurata and Katz, *Trans. Am. Inst. Chem. Engrs.*, 38, 995 (1942).
(8) Robinson and Gilliland, "Elements of Fractional Distillation", 3rd ed., p. 45, New York, McGraw-Hill Book Co., 1939.
(9) Sage, Hicks, and Lacey, IND. ENG. CHEM., 32, 1085 (1940).
(10) Souders, Selheimer, and Brown, *Ibid.*, 24, 517 (1932).
(11) White and Brown, *Ibid.*, 34, 1162 (1942).

Thermodynamic Properties of Methane at Low Temperature

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I**N THE** solution of many engineering problems the use of detailed thermodynamic data is very convenient. Frequently such data are not readily available and must be obtained from measured physical and thermal properties by lengthy calculations. Thermodynamic properties of methane above 70° F. have been tabulated by several authors. Corresponding information for temperatures below 70° F. is not so easily available. Keesom and Houthoff (4) presented a temperature-entropy diagram for methane covering the temperature range from 100° to 270° K. and the pressure range from 1 to 40 atmospheres. The thermodynamic quantities were determined by utilizing information from a single source (5). The results are given in metric units and no tabulated data are shown. Subsequent experimental work has afforded increased information on the physical and thermal properties of methane.

It has, therefore, seemed desirable to utilize the more recent methane data in preparing a temperature-entropy diagram for the low temperature region, in terms of English units. The thermodynamic properties of methane from 70° to −230° F. and from

atmospheric pressure to 1400 pounds per square inch absolute have been derived from data existing in the literature and are presented in tabular and graphical form.

METHODS

Molal heat capacities at zero pressure were determined from fundamental vibrational frequencies given by Vold (9). At zero pressure the isobaric heat capacity is given by the equation:

$$C_{P_0} = ab\left[\frac{3}{2} + \frac{3}{2} + 1 + \sum_{i=1}^{i=n} \frac{\left(\frac{\theta_i}{T}\right)^2 e^{\frac{\theta_i}{T}}}{\left(e^{\frac{\theta_i}{T}} - 1\right)^2}\right] \quad (1)$$

The first two terms within the bracket are concerned with translational and rotational energy, respectively; the third term is related to the difference between the isobaric and isochoric heat capacities. The characteristic temperature θ_i is obtained by multiplying the vibrational frequency by hc/k in consistent units. Since the methane molecule has five atoms, it possesses nine degrees of vibrational freedom and hence the limits for the last term

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Figure 1. Temperature-Entropy Diagram of Methane in Low-Temperature Region
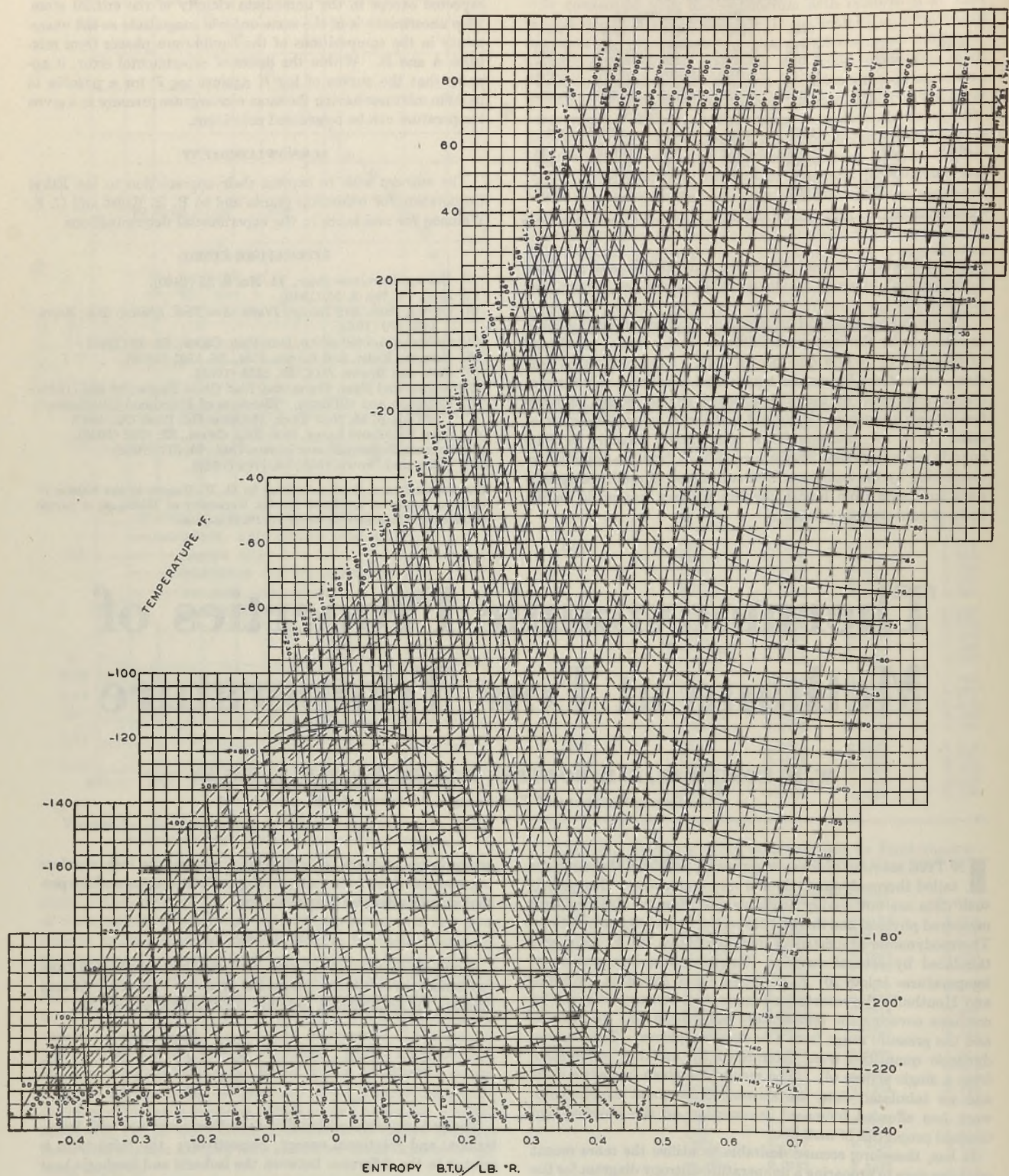
TABLE I. THERMODYNAMIC PROPERTIES OF METHANE IN THE SINGLE-PHASE REGION[a]

P	70° F. H	70° F. V	70° F. S	40° F. H	40° F. V	40° F. S	10° F. H	10° F. V	10° F. S	−20° F. H	−20° F. V	−20° F. S	−50° F. H	−50° F. V	−50° F. S	−80° F. H	−80° F. V	−80° F. S	−110° F. H	−110° F. V	−110° F. S
0	5.26		1.0086	−10.44		0.9794	−25.67		0.9472	−41.32		0.9133	−56.50		0.8774	−71.58		0.8390	−86.50		0.7976
14.696	4.80	24.064	0.9439	−10.93	22.701	0.9130	−26.53	21.310	0.8808	−41.94	19.935	0.8468	−57.21	18.552	0.8107	−72.45	17.173	0.7721	−87.52	15.775	0.7305
25	4.45	14.122	0.9130	−11.30	13.311	0.8259	−26.96	12.502	0.7934	−42.40	11.689	0.7592	−57.72	10.873	0.7227	−73.04	10.053	0.6836	−88.21	9.225	0.6413
50	3.70	7.040	0.8571	−12.18	6.637	0.7744	−28.90	6.219	0.7417	−43.50	5.808	0.7072	−58.97	5.390	0.6704	−74.52	4.974	0.6308	−89.50	4.548	0.5880
75	2.90	4.677	0.8058	−13.85	4.408	0.7374	−29.90	4.125	0.7046	−44.60	3.847	0.6697	−60.19	3.564	0.6325	−76.04	3.281	0.5924	−91.60	2.987	0.5487
100	2.15	3.496	0.7694	−15.60	3.290	0.6846	−31.90	3.079	0.6512	−45.70	2.869	0.6157	−61.48	2.655	0.5778	−77.55	2.438	0.5365	−93.34	2.208	0.4916
150	0.60	2.317	0.7166	−17.40	2.174	0.6464	−33.90	2.031	0.6125	−47.98	1.887	0.5763	−64.07	1.739	0.5376	−80.55	1.587	0.4950	−96.99	1.4289	0.4478
200	−1.00	1.7256	0.6685	−21.07	1.619	0.5999	−38.08	1.509	0.5559	−50.25	1.397	0.5182	−66.78	1.283	0.4776	−83.81	1.165	0.4321	−100.69	1.0390	0.3809
300	−4.18	1.1356	0.6245	−24.60	1.062	0.5499	−42.25	1.062	0.5138	−55.09	0.9072	0.4744	−72.35	0.8254	0.4323	−90.57	0.7398	0.3985	−109.00	0.6535	0.3258
400	−7.25	0.8407	0.5848	−28.17	0.7888	0.5169	−46.40	0.7243	0.4796	−60.08	0.6022	0.4385	−78.16	0.5967	0.3939	−97.65	0.5268	0.3411	−118.39	0.4570	0.2749
500	−10.35	0.6639	0.5525	−31.80	0.6170	0.4889	−50.70	0.5148	0.4503	−65.02	0.5148	0.4073	−84.23	0.4589	0.3603	−105.06	0.3985	0.3036	−129.04	0.3412	0.2217
600	−13.50	0.5468	0.5256	−39.05	0.5059	0.4422	−68.60	0.4624	0.4005	−70.15	0.4164	0.3538	−90.38	0.3669	0.3002	−112.81	0.3117	0.2262	−141.93	0.2518	0.0287
800	−19.95	0.4005	0.4812	−46.57	0.3674	0.4031	−78.25	0.3317	0.3579	−80.85	0.2933	0.3058	−103.47	0.2501	0.2355	−133.11	0.1922	0.1321	−200.48	0.1088	−0.0655
1000	−26.25	0.3137	0.4441	−54.10	0.2851	0.3688	−87.80	0.2540	0.3187	−92.21	0.2188	0.2587	−121.66	0.1714	0.1771	−163.64	0.1178	0.0599	−212.79	0.0635	−0.0907
1200	−32.60	0.2560	0.4124	−61.55	0.2305	0.3381		0.2022	0.2838	−105.87	0.1693	0.2191	−139.41	0.1829	0.1350	−186.98	0.0935	0.0222	−239.60	0.0505	−0.1075
1400	−38.85	0.2149	0.3845		0.1923			0.1674		−117.61	0.1394		−152.50	0.1081		−198.19	0.0776		−242.66	0.0490	

P	−140° F. H	−140° F. V	−140° F. S	−170° F. H	−170° F. V	−170° F. S	−200° F. H	−200° F. V	−200° F. S	−230° F. H	−230° F. V	−230° F. S
0	−101.44		0.7523	−116.33		0.7026	−131.19		0.6475	−146.03		0.5851
14.696	−102.59	14.386	0.6846	−117.76	12.950	0.6347	−132.91	11.455	0.5787	−148.45	9.891	0.5135
25	−103.40	8.401	0.5948	−118.71	7.505	0.5439	−134.05	6.581	0.4858	−150.05	5.587	
50	−105.42	4.115	0.5406	−121.08	3.630	0.4883	−136.97	3.141	0.4271			
75	−107.50	2.681	0.5005	−123.50	2.353	0.4464	−139.89	2.021	0.3844			
100	−109.55	1.970	0.4418	−125.95	1.723	0.3846	−142.89	1.481				
150	−113.85	1.264	0.3953	−131.05	1.1124	0.3356						
200	−118.41	0.9242	0.3213	−136.51	0.8115							
300	−128.76	0.5789	0.2510									
400	−141.35	0.3989										

[a] P = pressure, lb./sq. in. abs.; H = enthalpy, B.t.u./lb.; V = specific volume, cu. ft./lb.; S = entropy, B.t.u./(lb.)(° R.)

in Equation 1 are from $i = 1$ to $i = 9$. The values for the vibrational heat capacity as a function of θ_i/T are given by Wenner (10).

Enthalpies of methane at zero pressure were calculated by integrating graphically the differential relation between C_{P_0} and T, and arbitrarily setting the enthalpy equal to zero at a datum state corresponding to zero pressure and 60° F. To obtain enthalpy values at various pressures and temperatures, isothermal enthalpy changes for pressure intervals of 10 kg./sq. cm. given by Eucken and Berger (3) were utilized. Enthalpies of saturated gas and saturated liquid methane were taken from Wiebe and Brevoort (11) and converted to the basis of the given reference point. Vapor pressures were obtained from data presented by Eucken and Berger (3). The critical constants were determined with the assistance of the law of rectilinear diameters as applied to plots of H vs. T and H vs. P. These plots were smoothed simultaneously by reference to the vapor pressure curve. It is believed that the uncertainty in the enthalpy values should not be greater than 0.5 B.t.u./lb.

From a plot of enthalpy vs. pressure at constant temperature, values of $-(\partial H/\partial P)_T$ were read, and $(\partial Z/\partial T)_P$ was calculated using the following expression, which may be obtained by combining the definition of compressibility factor with a suitable thermodynamic equation of state (6):

$$-\left(\frac{P}{bT^2}\right)\left(\frac{\partial H}{\partial P}\right)_T = a\left(\frac{\partial Z}{\partial T}\right)_P \quad (2)$$

A plot of $(\partial Z/\partial T)_P$ against temperature was utilized for integration to give isobaric changes in the compressibility factor, Z.

Compressibility factors at 70° F. in the pressure range from 0 to 1500 pounds per square inch were obtained from the values of Sage, Budenholzer, and Lacey (7). Using calculated values of ΔZ, the compressibility factors for temperatures from 70° to −80° F. and pressures from 0 to 1400 pounds per square inch were determined. It was not believed desirable to extend compressibility factor calculations below a temperature of −80° F. because of the uncertainty in $(\partial H/\partial P)_T$ resulting from the rapid variation of H with respect to P at the higher pressures.

Specific volumes of methane for temperatures down to −80° F. were calculated from the compressibility factors. Specific volumes of the gas at saturation were obtained by combining saturated liquid densities (5), vapor pressures (3), and smoothed values of the latent heat of vaporization (11) in the Clapeyron equation. To bridge the gap in specific volume values from −80° F. to saturation, a plot of P against T at constant even values of V was prepared from an isothermal plot of log P vs. log V. By nearly linear interpolation of the even-volume P vs. T plot between −80° F. and saturation, the remainder of the specific volumes for the given pressure range were obtained. Sufficient care was taken in graphical integration and interpolation that uncertainty in specific volume at any point should not be greater than 0.5% of the value.

Entropies in the temperature region from 70° to −80° F. were determined from a relationship involving the isobaric residual volume-temperature derivative and the specific heat. The isobaric residual volume-temperature derivative was obtained from the equation:

$$a\left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T + a\underline{V}\right] \quad (3)$$

The equation for change in entropy can be written in the following form:

$$dS = \frac{C_P dT}{T} + a\left(\frac{\partial \underline{V}}{\partial T}\right)_P dP - \frac{abdP}{P} \quad (4)$$

TABLE II. THERMODYNAMIC PROPERTIES OF SATURATED-GAS AND SATURATED-LIQUID METHANE

Temp., °F.	P	Saturated Gas H	V	S	Saturated H	V	Liquid S
−230	43.42	−152.9	3.076	0.4378	−361.0	0.040	−0.4720
−220	62.58	−150.0	2.158	0.4095	−354.0	0.041	−0.4435
−210	86.94	−147.3	1.613	0.3881	−346.8	0.042	−0.4162
−200	117.33	−145.1	1.243	0.3591	−339.2	0.043	−0.3885
−190	154.21	−143.4	0.979	0.3372	−331.3	0.045	−0.3602
−180	198.61	−142.4	0.784	0.3149	−323.2	0.046	−0.3315
−170	249.23	−142.2	0.634	0.2923	−314.4	0.048	−0.3024
−160	308.18	−142.9	0.513	0.2683	−305.0	0.050	−0.2726
−150	375.84	−145.1	0.413	0.2420	−294.4	0.052	−0.2396
−140	453.11	−149.2	0.327	0.2130	−281.5	0.055	−0.2011
−130	541.38	−156.3	0.252	0.1765	−265.0	0.061	−0.1530
−120	638.70	−173.6	0.175	0.1140	−239.7	0.072	−0.0805
−116.5	673.0	−205.4	0.116	0.0186	(critical values)		

Since values of C_P at zero pressure had been calculated, the change in entropy was obtained by integration from 60° F. and 1 atmosphere to the desired state at T and P:

$$\Delta S = \int_{519.69}^{T} \frac{C_P dT}{T} + a \left[\int_{14.696}^{0} \left(\frac{\partial V}{\partial T}\right)_P dP + \int_{0}^{P} \left(\frac{\partial V}{\partial T}\right)_P dP - b \ln \frac{P}{14.696} \right] \quad (5)$$

$[P = 0] \qquad [T = 519.69] \qquad [T = T]$

The datum value of S was taken as 1 at 60° F. and 1 atmosphere.

At pressures below 500 pounds per square inch and temperatures below −80° F., entropies were obtained by utilizing values of ΔS at constant pressure, calculated from the relation:

$$\Delta S = \int_{T_1}^{T_2} \frac{1}{T} \left(\frac{\partial H}{\partial T}\right)_P dT \quad [P = \text{constant}] \quad (6)$$

Since the variation of enthalpy with temperature was essentially linear in the region considered, the uncertainty in the entropy calculations was minimized.

Below −80° F. and above 500 pounds per square inch a plot of $(\partial P/\partial T)_V$ against V at constant temperature was used for graphical integration to obtain values of ΔS. Values of entropy at dew point were obtained by application of the following equation:

$$\left(\frac{dS}{dT}\right)_d = \frac{1}{T}\left[\left(\frac{dH}{dT}\right)_d - aV\left(\frac{dP}{dT}\right)''\right] \quad (7)$$

The saturation dome was completed by use of the relationship:

$$\Delta S_{vapor} = \frac{\Delta H_{vapor}}{T} \quad (8)$$

In calculating heat capacities at zero pressure, a value of 1.4386 cm.° K. was used for hc/k, the molecular weight of methane was taken as 16.042, and the value 0.66898 was used for the specific gas constant b.

RESULTS

Table I lists calculated thermodynamic data for methane in the single-phase region. Table II gives the thermodynamic properties of saturated gas and saturated liquid, as well as critical constants. Figure 1 is a temperature-entropy diagram of methane in the low-temperature region. The diagram shows lines of constant pressure, enthalpy, volume, and quality.

It was possible in some instances to compare the calculated thermodynamic properties of methane with those of other investigators. In this way an additional measure of the uncertainty in the data was obtained. Calculated values of C_{P_0} are in close agreement with those presented in the literature.

In the superheated region, comparison with enthalpy values obtained by Sage, Lacey, and co-workers (1, 7, 8) from Joule-Thomson studies and P-V-T measurements, and values calculated by Edmister (2) from P-V-T data indicate a maximum uncertainty of 1 B.t.u./lb. in the enthalpy values.

Comparison of the superheated vapor volumetric data with those of Edmister (2) showed good agreement, but no volumetric data near the critical point were available for comparison. Entropies in the superheated gas region agree with those calculated by Edmister (2) to within 0.01 B.t.u./(lb.)(° R.).

Using temperature and volume as independent variables, a comparison of data was made with the diagram presented by Keesom and Houthoff (4). The comparison between the two sets of data was inconvenienced by the absence of tabulated thermodynamic properties in the publication by Keesom and Houthoff (4). It was found that the pressures differ by about 3%. Average deviations in enthalpies of about 4 B.t.u./lb. and in entropies of 0.01 B.t.u./(lb.)(° R.) were observed. Three typical points of comparison in the superheated region are given in Table III.

TABLE III. COMPARISON OF VALUES

Temp., ° F.	Sp. Vol., Cu. Ft./Lb.	Pressure, Lb./Sq. In. Authors	Keesom & Houthoff
10	0.5671	500	540
−110	0.4570	400	416
−170	3.630	50	53.4

NOMENCLATURE

a = conversion factor = 0.185184; (B.t.u.)/(lb./sq. in.)(cu. ft.)
b = specific gas constant, (lb./sq. in.)(cu. ft./lb.)/° R.
c = velocity of light
C_P = heat capacity at constant pressure, B.t.u./(lb.)(° R.)
C_{P_0} = heat capacity at zero pressure, B.t.u./(lb.)(° R.)
C_V = heat capacity at constant volume; Btu./(lb.)(° R.)
e = base of natural logarithms
H = enthalpy, B.t.u./lb.
h = Planck's constant
i = integer
k = Boltzmann's constant
n_g = weight fraction of a system in gas phase
P = pressure, lb./sq. in. absolute
S = entropy, B.t.u./(lb.)(° R.)
T = thermodynamic temperature, ° R. = ° F. + 459.69
V = specific volume, cu. ft./lb.
$\underline{V}$ = residual specific volume $(bT/P - V)$, cu. ft./lb.
Z = compressibility factor
θ_i = "characteristic temperature", ° R.
Subscript d = a system which is at dew point (saturated gas)
Superscript $''$ = a system in which two phases are present

LITERATURE CITED

(1) Budenholzer, Sage, and Lacey, IND. ENG. CHEM., 31, 1288 (1939).
(2) Edmister, Ibid., 28, 1112 (1936).
(3) Eucken and Berger, Z. ges. Kälte-Ind., 9, 145 (1934).
(4) Keesom and Houthoff, Commun. Phys. Lab., Univ. Leiden, Suppl. 65 (Sept., 1924–April, 1928).
(5) Keyes, Taylor, and Smith, J. Math. Phys., 1, 211 (1922).
(6) Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances", p. 134, New York, McGraw-Hill Book Co., 1931.
(7) Sage, Budenholzer, and Lacey, IND. ENG. CHEM., 32, 1169 (1940).
(8) Sage and Lacey, Ibid., 31, 1497 (1939).
(9) Vold, J. Am. Chem. Soc., 57, 1192 (1935).
(10) Wenner, "Thermochemical Calculations", New York, McGraw-Hill Book Co., 1941.
(11) Wiebe and Brevoort, J. Am. Chem. Soc., 52, 622 (1930).

Manufacture of Concentrated Superphosphate

EFFECT OF MIXING AND CURING CONDITIONS ON CONVERSION

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CONCENTRATED superphosphate is made at the TVA Fertilizer Works at Wilson Dam by mixing 78% phosphoric acid from the electric furnace process with rock phosphate and curing the fresh superphosphate by storage in large piles for several weeks; the cured superphosphate is then ground, screened, and bagged for shipment. The results of laboratory studies of the effects of the principal operating conditions on the composition of concentrated superphosphate were published some years ago (10). In general, good agreement was found between the laboratory data and plant operating data. However, an apparently small but unmistakable difference was noted between the conversion of plant superphosphate and that predicted from the laboratory results.

The percentage conversion as reported in this paper was computed from analysis of the rock and of the superphosphate, according to the following formula:

$$\% \text{ conversion} = \left[1 - \frac{(\text{insol. } P_2O_5)_s (CaO)_r}{(P_2O_5)_r (CaO)_s} \right] 100$$

where

(CaO)$_s$ = % CaO in superphosphate
(CaO)$_r$ = % CaO in rock
(P$_2$O$_5$)$_r$ = % P$_2$O$_5$ in rock
(insol. P$_2$O$_5$)$_s$ = % P$_2$O$_5$ in superphosphate insoluble in a solvent designed to indicate availability to plants

The percentage conversion calculated according to this formula actually indicates the net increase in soluble P$_2$O$_5$ on acidulation of the rock, assuming that all of the P$_2$O$_5$ initially in the rock is insoluble and all of the P$_2$O$_5$ in the acid is soluble, expressed as a percentage of the P$_2$O$_5$ in the rock.

To determine the exact magnitude of the difference of plant results and laboratory predictions under average plant operating conditions, control experiments were made in which superphosphates were prepared in the laboratory to correspond with respect to kind and proportion of raw materials to plant superphosphate made over a period of 3 years. As a result, differences in conversion between the laboratory and plant superphosphates were

Concentrated superphosphate is made in the TVA plant by mixing 78% phosphoric acid with finely ground rock phosphate, curing in large piles for about 12 weeks, grinding, screening, and bagging. Data on the conversion of rock phosphate P$_2$O$_5$ to available P$_2$O$_5$ for plant superphosphate made from Tennessee and Florida rock phosphate were obtained for a period of several years and compared with corresponding data for control superphosphates prepared in the laboratory. The conversion of the plant superphosphate was lower than that of the control; this behavior was due to differences in thoroughness of mixing, temperature of mixing, and temperature of curing. The effect on conversion of reactant temperature over the range 32° to 200° F. and of curing temperature from 80° to 190° F. was determined in laboratory experiments on Tennessee rock phosphate; both low mixing temperatures and low curing temperatures favor high conversion for superphosphate made with acid stronger than 70% H$_3$PO$_4$. By improving thoroughness of mixing, lowering reactant temperature, and lowering curing temperature, considerable increase in conversion can be obtained. It was also found that under certain conditions there are significant differences between conversions indicated by the MacIntire-Shaw-Hardin method of analysis and those indicated by the A.O.A.C. method.

ascribed to differences in thoroughness of mixing, mixing temperature, and curing temperature. A study was then made in the laboratory to determine quantitatively the effects of mixing and curing temperature on conversion over wide temperature ranges and to indicate whether thoroughness of mixing is an important factor in determining conversion. Since soluble P$_2$O$_5$ in concentrated superphosphate is determined by the MacIntire-Shaw-Hardin method of analysis (7) rather than by the A.O.A.C. method (1) at the TVA Fertilizer Works, in the present work conversions were determined by both methods.

Little information has been reported on the effect of mixing and curing temperature on the composition of concentrated superphosphate, made with phosphoric acid. Marshall, Rader, and Jacob (8) determined the effect of mixing temperature for superphosphates made with phosphoric acid in the range 21 to 64% H$_3$PO$_4$; they found that fresh superphosphate mixed at 140° F. (60° C.) had higher conversion by 2 to 12% than superphosphate mixed at room temperature. They also found that for superphosphate made with 47% phosphoric acid the maximum conversion of the fresh material was obtained with a mixing temperature of 140° F. in experiments covering the range 86° to 212° F. (30° to 100° C.). Copson, Newton, and Lindsay (2) concluded that temperature of mixing had no great effect upon the chemical composition of cured superphosphate, based on experiments with 74 to 78% H$_3$PO$_4$ and acid temperatures in the range 68° to 171° F. (20° to 77° C.). Previous laboratory work indicated that the principal effects of curing are decrease in weight (principally due to loss of water and carbon dioxide), decrease in free acid, and increase in conversion (8, 10). However, no data have been published on the effects of curing under conditions closely approximating those in the TVA plant curing piles, or on mixing and curing in the plant-scale manufacture of concentrated superphosphate.

Similarly, little information has been reported on the effects of mixing and curing temperature of normal superphosphate, made with sulfuric acid. Williams (13) claimed that, by artificially lowering the temperature of the reacting mixture of acid and rock, increased conversion resulted. Cooling freshly prepared
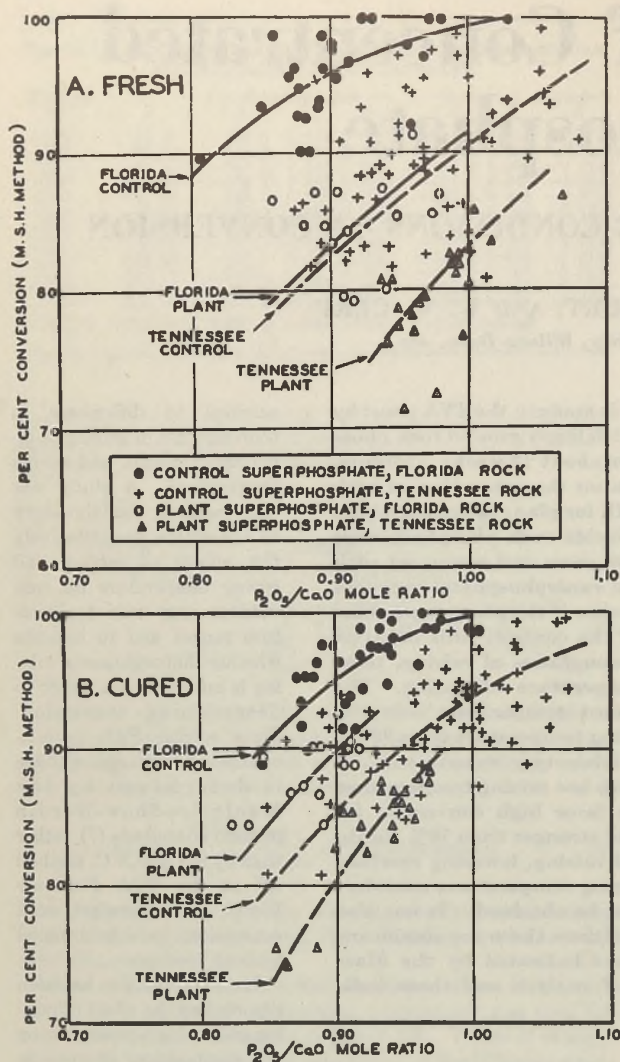
Figure 1. Comparison of Conversions of Plant and Control Superphosphates Made from Florida and Tennessee Rocks

Figure 2. Effect of Thoroughness of Mixing on Conversion of Cured Superphosphate

normal superphosphate and using low curing temperatures have been said to reduce reversion of soluble P_2O_5 (9, 11, 12).

TVA MANUFACTURING PROCESSES

The manufacture of concentrated superphosphate at the TVA Fertilizer Works and previous TVA laboratory studies relating to its manufacture were described previously in some detail (2–5, 10). Only a brief summary of the methods of manufacture is presented here.

The phosphoric acid used is made by the electric furnace process and is diluted to approximately 78%. The rock phosphate is dried and ground so that about 80% passes a 200-mesh sieve. Acid and rock are mixed in either batch or continuous mixers. In the batch method, acid and then rock are introduced into sigma-blade mixers. Agitation is continued until the superphosphate is sufficiently dry and crumbly to be discharged from the mixer. The total mixing cycle is about $2\frac{1}{2}$ minutes, and about 1500 pounds of superphosphate are made per batch. The superphosphate is conveyed to curing piles by a system of slat conveyors, elevators, and monorail cars.

In the continuous method, acid and rock (normally between 150° and 200° F.) are introduced simultaneously at a constant rate into a funnel-shaped mixing bowl. The acid is introduced into the bowl tangentially at several points around its top, and the rock phosphate dust is introduced at the center of the bowl. The bowl contains no high-speed mixing blades such as those described in an earlier paper (3); it has been found that mixing is reasonably satisfactory without moving blades, which are a source of mechanical difficulty. While it is still fluid, the mixture is discharged from the bowl onto a moving conveyor belt, and further mixing occurs on the belt because of turbulence. The superphosphate quickly becomes solid on this belt, and by the time it reaches the end of the belt (about 2 minutes after discharge onto the belt), it is about as dry as that from the batch mixers. The superphosphate is then sent to storage piles by the conveyor system used for the batch-mixed superphosphate.

Two curing piles extend the length of the storage building. Each completed pile is about 36 feet high, 90 feet wide, and 600 feet long. The piles are built continually by dumping the fresh superphosphate, starting at one end of the building and progressing toward the other. For convenience in keeping records of the time of storage, each pile is divided into sections about 25 feet long by markers; there are no separating walls between the sections, however. About 7 days are required to fill a section,

TABLE I. COMPOSITION[a] OF RAW MATERIALS FOR SUPERPHOSPHATE MANUFACTURE, 1941–43

Year	Source of Rock	Size of Rock, % of −200 Mesh	Moisture, % (wet basis)	Composition of Rock						P₂O₅/CaO mole ratio	Composition of Acid[c], %		
				Dry basis, %							H₃PO₄[d]	CaO	F
				P₂O₅	CaO	SiO₂[b]	Fe₂O₃	Al₂O₃	F				
1941	Fla.	79	0.9	34.2	48.8	6.2	0.8	0.9	3.67	0.277	77.8	0.04	0.03
1942	Fla.[e]	79	0.6	33.9	48.5	7.4	1.4	1.4	3.58	0.276	78.9	0.04	0.03
1942	Tenn.[e]	86	1.2	32.7	45.4	7.9	2.7	2.7	3.37	0.284	79.2	0.10	0.03
1942	Av.	84	1.0	33.1	46.4	7.7	2.3	2.4	3.44	0.282	79.1	0.08	0.03
1943	Tenn.	84	0.9	31.8	43.6	10.4	2.5	3.0	3.36	0.288	78.3	0.20	0.04

[a] Average weighted on basis of superphosphate produced each month. [b] Determined as perchloric acid–insoluble material.
[c] In addition, there are a number of other minor constituents. A typical sample of plant acid contained 0.18% K, 0.14% Ca, 0.004% Pb, 0.01% Fe, 0.001% As, 0.001% Mn, 0.02% Si, 0.003% C, and 0.004% S.
[d] Total P₂O₅ by chemical analysis, expressed as per cent H₃PO₄. [e] Florida rock used during 3 months; Tennessee rock used in other months.

TABLE II. COMPOSITION[a] OF SUPERPHOSPHATE MANUFACTURED IN TVA PLANT, 1941–43

Year	Source of Rock	Fresh Superphosphate[b], %				Cured Superphosphate[c], %				
		Free acid	P₂O₅		CaO	Moisture[e]	Free acid	P₂O₅		CaO
			Total	Sol.[d]				Total	Sol.[d]	
1941	Fla.	5.8	49.1	47.0	20.8	2.8	1.2	49.8	48.2	22.2
1942	Fla.[f]	5.8	49.1	46.2	21.2	2.6	1.0	49.1	46.4	23.1
1942	Tenn.[f]	7.0	48.1	44.9	19.7	2.4	1.0	48.9	46.0	21.4
1942	Av.	6.6	48.4	45.2	20.2	2.5	1.0	49.0	46.1	21.9
1943	Tenn.	6.8	47.4	44.8	19.1	3.0	1.1	48.1	45.9	20.3

[a] Average weighted on basis of superphosphate production each month. [b] Shift samples analyzed within 8 to 12 hours after end of shift on which sample was taken. [c] Data for superphosphate made in corresponding year. [d] By MacIntire-Shaw-Hardin method of analysis. [e] Determined by drying over concentrated sulfuric acid for 24 hours in an evacuated desiccator at room temperature. [f] Florida rock used during 3 months; Tennessee rock used in other months.

which contains about 1200 tons of material; however, on occasion, as few as 3 or as many as 20 days may be needed, depending on operating conditions. The superphosphate remains in piles for at least 12 weeks. Cured superphosphate is dug from the piles, ground, screened to −4 mesh, and bagged for shipment.

During the curing period a high temperature is developed in the piles. A 60-day study of a pile during curing showed that the maximum temperature (about 190° F.) was near the center and that this temperature persisted throughout the entire period. At a point 3 feet below the top of the 36-foot pile, the temperature was about 120° F. during the entire period, and at points 3 feet from the bottom and 13 feet from the top of the pile the temperature decreased from 180° to 160° F. during the 60 days.

PLANT MANUFACTURING DATA

Table I gives yearly averages of the composition of rock and acid used for superphosphate manufacture over the three-year period studied (1941–43). Compositions of rock and acid are averages of the results of duplicate analyses of monthly composites of samples taken during each shift. Table II shows yearly averages of the composition of superphosphate made in the plant over the corresponding three-year period. Soluble P₂O₅ was determined by the MacIntire-Shaw-Hardin method (7). Fresh superphosphate was analyzed 8 to 12 hours after it was mixed; the samples were taken from the discharge of the bucket elevator and were kept in closed containers until they were analyzed. The samples of cured superphosphate were taken just before the superphosphate was bagged for shipment. All the values in Table II are averages of individual analyses made for each shift during the year. The analyses for the cured superphosphate correspond to those of the fresh material shown in the same year. The compositions of the cured superphosphates were made to correspond to those of the fresh superphosphates by grouping and averaging the shift analyses according to storage section, and then averaging the section average analyses for each year.

The yearly averages in Tables I and II are weighted according to the tonnage of superphosphate made, which varied from 1000 to 12,000 tons per month.

The most important single factor that determines the con-

version of superphosphate is acidulation, the best measure for which is perhaps the ratio of acid P₂O₅ to rock P₂O₅; therefore any comparison of other factors affecting conversion must be made on the basis of equal acidulation. However, in the present work such a comparison was made by plotting conversion against the P₂O₅/CaO mole ratio calculated from analysis of the superphosphates (Figure 1); this is a satisfactory measure of acidulation when all the rocks involved have essentially the same P₂O₅/CaO ratio, as was the case for the Florida and Tennessee rocks used. Although there is considerable scattering of the points in Figure 1, the curves are drawn to represent the trends indicated by the data, and certain definite conclusions still may be made. The scattering of the points indicates that factors other than acidulation also influenced conversion. That the scattering was more pronounced for fresh than for cured superphosphate can be explained by the fact that the composition of the fresh superphosphate changes rapidly during the first few hours after it is made, and the fresh materials were not analyzed at precisely the same age.

The cured plant superphosphate apparently had a lower P₂O₅/CaO ratio than the fresh plant superphosphate (see later section on Comparison of Plant and Control Data). Carefully controlled laboratory experiments showed that no P₂O₅ would be volatilized under the plant curing conditions. (This is indicated also by the laboratory experiments on curing at high temperatures, described later in the paper.) The apparent change in P₂O₅/CaO ratio is therefore attributed to errors in sampling of the fresh superphosphate. There is a tendency for the plant operators to hand-pick the samples so as to get a highly acidulated sample. This is possible because the fresh superphosphate is not perfectly homogeneous but contains some lumps that are more highly acidulated than others. No opportunity exists, however, to hand-pick samples of the thoroughly mixed cured superphosphate. The P₂O₅/CaO ratios of the cured material are therefore believed to represent actual acidulations. Typical acidulation actually used in the plant for Florida rock is equivalent to a P₂O₅/CaO mole ratio of about 0.90, and for Tennessee rock, about 0.95; in terms of pounds of 78% acid per pound of rock, these acidulations are about 1.36 for Florida rock containing 34.2% P₂O₅ and 1.29 for Tennessee rock containing 31.8% P₂O₅. All comparisons of the conversions of fresh superphosphate with those of cured superphosphate were made on the basis of equal P₂O₅/CaO ratios. In this way the effect of errors in sampling was eliminated.

Examination of Figure 1 and Tables I and II leads to the following conclusions regarding superphosphate made in the plant:

1. A greater acidulation was required for Tennessee rock than for Florida rock to obtain equal conversion. In the operating acidulation range (Figure 1B), about 10% more acid P₂O₅ per unit of rock P₂O₅ was required for Tennessee rock than for Florida rock for equal conversion of cured plant superphosphate. The differences between conversion of Tennessee and Florida rock for equal P₂O₅/CaO ratios were from 6 to 10% for cured superphosphate in the operating acidulation range.

2. There is an increase in conversion on curing of about 6 or 7% for superphosphate made from Florida rock and about 8 or 9% for superphosphate made from Tennessee rock.

3. The free acid content of the superphosphate (expressed as P_2O_5) made from both Florida and Tennessee rock decreased from about 4–8% to about 1% on curing.

4. The moisture content of the superphosphate made from both Florida and Tennessee rock decreased to 2.5–3.0% on curing. The moisture content of the fresh superphosphate was not determined for the entire 3-year period, but it is usually about 8 to 10%.

5. A loss in weight occurred on mixing and curing, due to volatilization of certain constituents, principally moisture, carbon dioxide, and fluorine. The losses in weight during mixing and curing were calculated from a comparison of the total P_2O_5 content of the superphosphate after mixing and after curing with that calculated from the composition of the raw materials; these calculations were based on acidulations equivalent to the P_2O_5/CaO ratio of the cured superphosphates, and the total P_2O_5 contents of the fresh superphosphates were corrected to the same P_2O_5/CaO ratio as the cured superphosphates. The results indicate a 4.1% loss of weight on mixing and a 2.0% loss of weight on curing for the superphosphates made from Florida rock, and a 3.1% loss of weight on mixing and a 2.3% loss of weight on curing for the superphosphate made from Tennessee rock. The greater mixing loss for the Florida rock was probably due to a higher carbonate content of this rock.

Because of the scattering of the points in Figure 1, the quantitative interpretation in conclusions 1 and 2 is subject to some error, but qualitatively these conclusions are without question.

Attempts were made to discover any differences in the composition of the superphosphate made in the batch mixers from that made in the continuous mixer and also any differences due to the time of year in which the superphosphate was made, but any such differences were not apparent.

CONTROL EXPERIMENT DATA

To have a standard of comparison for the plant superphosphate, control superphosphates were prepared in the laboratory from the monthly composite samples of the acid and rock used in manufacturing the plant superphosphates (Table I). Five pounds of the rock were introduced into a laboratory sigma-blade batch mixer, and the acid was added. The mixer bowl had a volume of 6 gallons, and the two blades rotated at 60 and 90 r.p.m., respectively. Both the rock and the acid were at room temperature (about 80° F.). After 3 minutes of mixing, the superphosphate was discharged, forced by hand through a screen with 1/2-inch openings, and ground in a laboratory disk mill to −14 mesh. A 1-ounce sample was obtained for analysis by riffling the pulverized superphosphate. The bulk of the pulverized material was placed in an open paper bag, covered loosely to prevent contamination by dust, and cured for 30 days at room temperature. Analyses were made of the control superphosphates about 12 hours after mixing and after the 30-day curing period. Some of the control superphosphates were analyzed after 60-day curing; no further change in composition was apparent, an indication that 30-day curing was sufficient in the laboratory.

Soluble P_2O_5 was determined by the MacIntire-Shaw-Hardin method (7), in which the extract of a citrated ammonium nitrate solution is analyzed for P_2O_5 directly, and by the A.O.A.C. method (1), in which the P_2O_5 in the insoluble residue from a neutral ammonium citrate solution extraction is subtracted from the total P_2O_5 in the sample. A number of superphosphates of different acidulations were made for each month. The control superphosphate having the P_2O_5/CaO ratio that corresponded most closely to that of the cured plant superphosphate was compared with the plant superphosphate for a particular month.

Table III presents yearly averages (weighted) of the composition of control superphosphates. Conversion (monthly averages) vs. P_2O_5/CaO mole ratio of control superphosphates. is shown in Figure 1, plotted on the same coordinates as the plant superphosphate data for comparison. Table III shows yearly averages for the control superphosphates that had P_2O_5/CaO ratios nearest those of the cured superphosphates; Figure 1 includes monthly averages for all the control superphosphates prepared. The following conclusions regarding the control superphosphates may be made from Tables I, II, and III and Figure 1:

1. On the average, the control superphosphates made from Tennessee rock show only about a 3% increase in conversion on curing; those from Florida rock show practically no increase. This apparent difference in behavior is undoubtedly explained by the fact that the conversions of most of the fresh Florida rock superphosphates were high (about 95%), and consequently there was less opportunity for an increase in conversion on curing. Conversions of the fresh Tennessee rock superphosphates, on the other hand, were mostly between 80 and 90%.

2. The difference between conversions of cured control superphosphates prepared from Florida and Tennessee rock was about 6 to 10%, the same as for plant superphosphates.

3. The free acid contents of the fresh control superphosphates (about 2.8%) were, on the average, considerably lower than those of the fresh plant superphosphates (about 6.4%); on curing, the free acid contents of the control superphosphates reached a slightly lower value (about 0.8%) than those of the cured plant superphosphates (about 1.1%).

4. The moisture content of the fresh control superphosphates was about 6%; on curing, this decreased to about 1% for the Florida rock superphosphates and to 1.5–2.0% for the Tennessee rock superphosphates, which are somewhat lower than the moisture content of cured plant superphosphate (2.5–3.0%).

5. Calculations based on changes in total P_2O_5 content indicate that the loss of weight on mixing was 4.5% and on curing was 3.3% for the superphosphate made from Florida rock. The loss of weight on mixing was 3.5% and on curing was 3.2% for the superphosphate made from Tennessee rock. These figures are somewhat higher than the corresponding ones for the plant superphosphates, primarily as a result of a greater loss of water by the control superphosphates. This loss is indicated by the lower moisture contents of the cured control superphosphates.

6. On the average, the MacIntire-Shaw-Hardin method indicated 2 to 4% greater conversion than the A.O.A.C. method.

Because of the scattering of the control points in Figure 1, conclusions 1 and 2 are subject to the same reservations as the corresponding conclusions for the plant superphosphates.

TABLE III. COMPOSITION[a] OF CONTROL SUPERPHOSPHATES

Year	Source of Rock	Fresh Control Superphosphate, %							Cured Control Superphosphate[b], %									
		Mois-ture[c]	Free acid	P_2O_5			CaO	F	Mois-ture[c]	Free acid	P_2O_5			CaO	F	SiO_2[d]	Fe_2O_3	Al_2O_3
				Total	M.S.H. sol. (7)	A.O.A.C. sol. (1)					Total	M.S.H. sol. (7)	A.O.A.C. sol. (1)					
1941	Fla.	6.2	2.2	49.2	48.6	48.1	21.8	1.63	0.9	0.6	50.9	50.0	49.8	22.3	1.70	3.0	0.4	0.7
1942	Fla.[e]	4.6	1.6	49.7	48.9	48.4	22.1	1.61	1.0	0.6	51.1	50.1	49.8	21.7	1.59	3.6	0.7	0.6
1942	Tenn.[e]	5.3	3.3	48.4	46.8	46.4	20.1	1.53	2.0	1.3	49.7	48.8	48.3	20.3	1.44	4.1	1.4	1.0
1942	Av.[e]	5.0	2.8	48.8	47.4	47.3	20.7	1.55	1.7	1.1	50.1	49.2	48.9	20.7	1.48	3.9	1.1	0.8
1943	Tenn.	5.8	3.3	47.2	45.5	45.0	19.7	1.57	1.7	0.7	49.0	47.7	47.4	20.3	1.53	5.3	1.2	1.4

[a] Average weighed on basis of superphosphate production each month.
[b] Cured 30 days in paper bags at room temperature.
[c] Determined by drying over concentrated sulfuric acid for 24 hours in an evacuated desiccator at room temperature.
[d] Determined as perchloric-acid-insoluble material.
[e] Florida rock used during 3 months; Tennessee rock used in other months.

TABLE IV. COMPARISON OF CONVERSIONS OF PLANT AND CONTROL SUPERPHOSPHATES

Month Made	Source of Rock	Rock P₂O₅ % (dry basis)	Rock P₂O₅/CaO mole ratio	Acid[b] as % H₃PO₄	% made in Cont. mixer	% made in Batch mixer	Curing time, weeks	Plant Superphosphate Fresh Total P₂O₅ %	Fresh P₂O₅/CaO mole ratio	Fresh M.S.H. conv. %	Cured[c] Total P₂O₅ %	Cured P₂O₅/CaO mole ratio	Cured M.S.H. conv. %	Control Superphosphate[a] Fresh Total P₂O₅ %	Fresh P₂O₅/CaO mole ratio	Fresh M.S.H. conv. %	Fresh A.O.A.C. conv. %	Cured Total P₂O₅ %	Cured P₂O₅/CaO mole ratio	Cured M.S.H. conv. %	Cured A.O.A.C. conv. %
								1941													
Jan.	Fla.	34.4	0.276	79.0	0	100	12	49.4	0.90	84	50.3	0.90	88	..	..	..	..	50.8	0.88	89	88
Feb.	Fla.	34.2	0.279	78.5	52	48	11	49.6	0.96	86	50.2	0.91	90	..	..	..	..	50.4	0.87	93	90
March	Fla.	33.7	0.279	78.0	66	34	15	48.8	0.90	85	49.0	0.84	89	48.7	0.90	98	95	51.3	0.93	90	97
April	Fla.	34.5	0.278	76.3	87	13	17	48.3	0.98	87	49.5	0.90	92	49.0	0.86	99	94	51.0	0.94	99	97
May	Fla.	34.4	0.276	77.4	88	12	18	48.5	0.98	88	49.2	0.80	90	49.0	0.90	97	96	51.3	0.93	99	97
June	Fla.	34.6	0.278	77.1	100	0	22	48.2	0.94	88	49.9	0.80	90	49.7	0.85	93	84	50.7	0.88	95	91
July	Fla.	34.3	0.278	77.4	100	0	29	48.2	0.86	87	49.7	0.87	86	50.7	0.88	94	87	50.9	0.87	91	94
Aug.	Fla.	34.3	0.276	77.4	100	0	25	48.6	0.88	85	49.8	0.87	86	50.9	0.89	93	87	50.9	0.90	97	94
Sept.	Fla.	34.3	0.276	77.4	100	0	24	48.0	0.91	87	50.0	0.89	86	49.0	0.91	95	90	50.8	0.89	98	97
Oct.	Fla.	34.3	0.274	80.0	100	0	22	49.0	0.89	84	50.1	0.92	89	50.7		100		51.4	0.94		
Nov.	Fla.	34.5	0.275	79.1	100	0	18	49.0	0.91	92	50.0	0.91	84	50.1	0.97	98	95				
Dec.	Fla.	34.7	0.274		100	0			0.96		50.3	0.91	93								
Weighted av.[d]	Fla.	34.2	0.277	77.8	65	35	16	49.1	0.93	86	49.8	0.89	80	49.2	0.89	98	93	50.9	0.90	95	93
								1942													
Jan.	Tenn.	33.5	0.275	78.4	100	0	17	48.6	0.95	81	49.3	0.91	85	49.4	0.91	84	93	50.2	0.89	92	91
Feb.	Fla.	33.6	0.280	78.0	100	0	17	49.3	0.94	80	49.5	0.80	84	49.4	0.89	96	94	50.2	0.91	94	90
March	Fla.	33.9	0.272	78.5	96	4	17	49.1	0.91	80	49.3	0.83	83	50.1	0.89	90	94	51.6	0.96	96	95
April	Fla.	34.1	0.278	78.5	98	2	17	48.3	0.92	80	48.6	0.82	84	50.1	0.88	91	85	51.2	0.91	91	92
May	Tenn.	33.1	0.284	79.0	95	0	18	48.3	0.98	73	48.6	0.85	75	48.9	0.95	92	83	49.6	0.98	96	92
June	Tenn.	33.2	0.280	78.4	35	65	18	48.9	0.95	71	49.0	0.86	74	48.5	0.95	91	91	50.0	0.98	94	92
July	Tenn.	31.9	0.282	80.0	15	85	15	47.6	1.02	77	49.3	0.89	75	47.3	1.02	89	83	49.5	1.00	91	94
Aug.	Tenn.	31.6	0.290	80.3	50	50	13	47.0	1.00	84	48.7	0.97	88	47.0	0.96	89	89	49.3	0.90	92	93
Sept.	Tenn.	33.1	0.288	80.2	0	100	13	48.5	0.94	76	48.5	0.94	84	48.5	0.93	87	81	49.3	1.00	85	89
Oct.	Tenn.	33.0	0.288	78.8	10	90	13	47.3	0.95	78	48.1	0.92	84	48.1	1.01	91	81	50.8	1.00	98	89
Nov.	Tenn.	33.1	0.294	78.7	11	89	13	48.7	0.99	82	48.6	0.94	88	48.6	0.94	90	83	50.8	0.99	91	87
Dec.	Tenn.	33.0					15	48.5	1.00	80	49.3	0.93	88	48.4				49.8	0.96	94	
Weighted av.[d]	Tenn.	33.1	0.282	79.1	69	31	16	48.4	0.96	78	49.0	0.88	82	48.8	0.93	91	88	50.1	0.96	93	92
								1943													
Jan.	Tenn.	32.2	0.291	77.0	3	97	15	48.3	1.00	81	48.5	0.94	86	48.5	0.97	90	90	50.0	0.99	95	91
Feb.	Tenn.	29.8	0.286	78.9	0	100	17	46.3	1.07	87	47.2	0.90	88	46.4	1.06	94	94	47.4	1.03	95	95
March	Tenn.	28.5	0.287	78.3	0	100	17	46.3	0.99	83	46.5	0.97	87	44.3	0.94	83	81	46.0	1.00	94	87
April	Tenn.	31.4	0.293	78.0	0	100	12	48.0	0.90	82	47.7	0.95	87	46.6	0.92	89	82	48.2	0.94	85	84
May	Tenn.	32.0	0.290	78.7	0	100	17	47.1	0.97	85	47.7	0.95	87	47.8	0.95	91	81	48.8	0.98	91	84
June	Tenn.	32.3	0.290	79.8	0	100	15	47.6	0.97	80	48.6	0.92	82	47.6	0.96	95	79	50.5	0.98	88	85
July	Tenn.	33.0	0.276	79.4	0	100	14	47.9	0.94	81	48.6	0.90	85	48.6	0.92	90	86	50.4	0.93	94	90
Aug.	Tenn.	33.0	0.285	77.3	0	100	14	47.0	0.99	83	48.1	0.91	80	47.4	0.93	86	87	50.4	0.90	93	93
Sept.	Tenn.	31.8	0.281	78.7	0	100	14	47.8	0.97	82	48.7	0.93	82	48.0	0.97	90	82	47.9	0.99	89	88
Oct.	Tenn.	31.8	0.294	78.7	0	100	14	47.2	0.99	80	47.8	0.95	85	45.5	0.93	90	81	48.4	0.95	89	88
Nov.	Tenn.	31.4	0.289	78.1	0	100	16	47.0	0.96	79	48.7	0.96	85	47.2	0.92	78	83	47.9	0.91	90	89
Dec.	Tenn.	31.5	0.290	78.0	0	100	16	47.1	0.90	78	48.0	0.94	87								
Weighted av.[d]	Tenn.	31.8	0.288	78.3	0.4	99.6	15	47.4	0.98	82	48.1	0.94	86	47.2	0.95	88	84	49.0	0.95	91	88

[a] Made from corresponding monthly composite samples of acid and dust used in the plant.
[b] Total P₂O₅ by chemical analysis expressed as per cent H₃PO₄.
[c] Data for superphosphate made in corresponding month.
[d] Weighted on basis of superphosphate production.

COMPARISON OF PLANT AND CONTROL DATA

Table IV compares plant superphosphates and the corresponding control superphosphates for the three-year period. Figure 1 shows that the conversion of the fresh control superphosphates was as much as 15% higher than that of the fresh plant superphosphates and as much as 7% higher than that of the cured superphosphates. Also, the differences in conversion between fresh control and fresh plant superphosphates were greater for Florida than for Tennessee rock. These conclusions were checked by plotting P_2O_5 solubilities against P_2O_5/CaO ratios of plant and control superphosphates. Calculation of P_2O_5 solubility (the ratio of soluble to total P_2O_5) does not involve the percentage of CaO in the superphosphate as does calculation of conversion; thus comparison of P_2O_5 solubilities is not subject to any possible constant analytical errors in CaO determination. The resulting plots (not shown) were similar to Figure 1, and the conclusions regarding differences in conversion between the plant and control superphosphates were substantiated.

These differences must be attributed to variations in mixing and curing conditions in the plant and in the laboratory, and not to variations in composition of the raw materials, since both control and plant superphosphates were made from the same materials. The differences in mixing and curing conditions considered most likely to influence conversion were in thoroughness of mixing, temperature of mixing, and temperature of curing. Another important difference is that in the
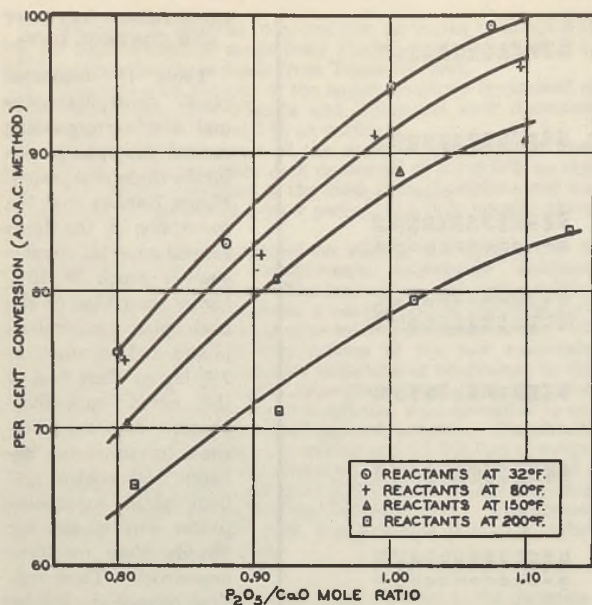
Figure 3. Conversions (A.O.A.C. Method) of Fresh Superphosphates Prepared at Various Temperatures

laboratory only a few pounds of superphosphate are cured so that rapid and more complete removal of volatile materials is possible; in the plant the curing piles are so large that diffusion of volatile materials from the interior is much slower, and their removal is consequently slower. However, in time, as much volatile material would probably be removed from superphosphate in the plant as in the laboratory.

EFFECT OF THOROUGHNESS OF MIXING

Superphosphates were made by three procedures, using Tennessee brown rock and plant phosphoric acid. The rock contained 0.6% moisture (wet basis) and the following constituents (dry basis): 32.7% P_2O_5, 46.0% CaO, 7.4% SiO_2 (determined as perchloric-acid-insoluble material), 3.2% Al_2O_3, 2.1% Fe_2O_3, and 3.5% F. The plant phosphoric acid contained 77.8% H_3PO_4 (based on total P_2O_5 content), 0.02% CaO, and 0.01% F.

In the first mixing procedure ("normal mixing"), the required quantity of acid was put in the laboratory sigma-blade mixer, 5 pounds of rock were added quickly while the mixer blades were turning, and mixing was continued until the superphosphate had set up to a dry, crumbly state; total mixing time was usually about 3 minutes. In the second procedure ("poor mixing") the required quantity of acid was placed in the mixer, 90% (4.5 pounds) of the total rock to be used was added while the blades were turning, mixing was continued for 10 minutes, the remaining 10% of the rock was added, and then the mixer blades were allowed to turn only two or three revolutions. This procedure was believed to simulate conditions in plant mixers when a crust of rock forms near the top of the mixer and is not mixed thoroughly, but is dumped as raw rock and mixed only superficially with the well-mixed portion of superphosphate. The third procedure ("hand mixing") was to dump the required quantity of acid and 5 pounds of rock simultaneously into a bucket and stir by hand with a wooden paddle. Total mixing time was about 3 minutes. This procedure produced a fairly homogeneous mixture, but mixing was not so thorough and intimate as in the normal procedure. Batches of fresh superphosphate were prepared for curing in the same way as were control superphosphates.

Superphosphates were made with four different acidulations, corresponding to P_2O_5/CaO mole ratios of 0.8, 0.9, 1.0, and 1.1.

The temperatures of the reactants and of curing were 80° F. in all experiments. The samples were cured in open paper bags except those cured only 1 day; in the latter case sealed containers were used so that the analysis would correspond as closely as possible to that of the freshly mixed material. Duplicate analyses were made of all samples.

Figure 2 shows that the poor mixing and hand mixing procedures gave about equal conversions; the normal mixing procedure gave about 4% greater conversion than the other two by the M.S.H. method and 3–6% greater by the A.O.A.C. There was no significant change in moisture, free acid, or fluorine content of the superphosphate mixed by the different procedures. As expected, the moisture and free acid in the cured superphosphates increased and the fluorine content decreased with increasing acidulation.

It was concluded that for maximum conversion the acid and rock should be brought together so that all of the rock is mixed with the acid while the mixture is still fluid, and that mixing should be as thorough and intimate as possible, especially before the mixture becomes plastic. These results indicate that the deleterious effect of poor mixing on conversion is not overcome on curing of the poorly mixed superphosphate at 80° F. However, there is evidence (given in the section on Cumulative Effects) that at plant curing temperatures at least part of the deleterious effect of poor mixing is overcome on curing.

Improvement in thoroughness of mixing in the plant mixers is largely a mechanical problem of mixer design, although care in operation will also influence the degree of mixing obtained. It is believed that opportunity for improving the thoroughness of mixing is greater with the continuous than with the batch mixer; in the former the rock and acid are brought together more quickly and uniformly and thus permit all of the rock particles to be wetted by the acid before setting-up begins.

EFFECT OF MIXING AND CURING TEMPERATURE

Five pounds of phosphate rock and the corresponding amount of 78% phosphoric acid to give the desired P_2O_5/CaO ratio were added to the mixer simultaneously and quickly (approximately 5 seconds) while the mixer blades were turning. The same rock and acid were used as in the experiments on the effect of thoroughness of mixing on conversion. Since the reaction between acid and rock is exothermic, it was not possible to maintain a constant temperature throughout the mixing cycle in the laboratory sigma-blade mixer because the quantity of material was too great to be cooled quickly. The procedure adopted was to carry out experiments with the reactants and mixer at the same initial temperature for each experiment. The actual maximum temperature reached in the mixer was not determined, but the temperature of the fresh material immediately after being discharged was obtained in some cases by inserting a thermometer into the pile of fresh material from the mixer. For example, with reactants and mixer at room temperature (80° F.), the fresh material was at about 140° F. When the reactants and mixer were at higher temperatures, the temperature of the product varied considerably, depending on the acid-rock proportion.

As previously reported (3), the reaction between the rock and acid consists of a fluid stage, a plastic stage, and a dry stage. The time of each stage was greater, the greater the acidulation and the lower the reactant temperature. The fluid stage, in which most of the rock is mixed with the acid, lasted from about 6 seconds to $3\frac{1}{2}$ minutes. The plastic stage, in which some additional mixing took place and the reaction neared completion, lasted from about 1 to 11 minutes. The dry stage, in which the superphosphate broke up into lumps and evolution of vapors was greatest, lasted from about 2 to 6 minutes. Mixing was continued until the superphosphate reached a stage sufficiently dry for grinding in the disk mill. As the reactant temperature decreased, the change from one phase to the next became less distinct; in the mixes made with reactants at 32° F. the change

TABLE V. EFFECT OF MIXING AND CURING TEMPERATURE ON SUPERPHOSPHATE[a] CONVERSION

Reactant Temp., °F.	Curing Time, Days	Curing Temperature, 80° F.							Curing Temperature, 135° F.							Curing Temperature, 190° F.						
		Total	P2O5, % M.S.H. sol.	P2O5, % A.O.A.C. sol.	CaO, %	P2O5/CaO mole ratio	Conv. % M.S.H.	Conv. % A.O.A.C.	Total	P2O5, % M.S.H. sol.	P2O5, % A.O.A.C. sol.	CaO, %	P2O5/CaO mole ratio	Conv. % M.S.H.	Conv. % A.O.A.C.	Total	P2O5, % M.S.H. sol.	P2O5, % A.O.A.C. sol.	CaO, %	P2O5/CaO mole ratio	Conv. % M.S.H.	Conv. % A.O.A.C.
32	1[b]	46.4	42.6	43.2	22.9	0.80	77	76	48.5	44.2	44.5	23.9	0.80	75	76	48.8	43.7	44.5	24.2	0.80	70	75
	30	48.4	45.6	44.7	23.7	0.81	83	78	48.6	43.9	44.4	23.6	0.81	72	75	49.1	43.2	44.8	24.2	0.80	66	75
	60	48.4	46.4	44.8	23.7	0.80	79	77	48.5	44.0	43.9	23.8	0.81	73	73	48.9	43.4		24.0	0.80	68	
	120	48.1	44.6	44.3	23.8	0.80	79	78														
32	1[b]	47.2	45.4	44.7	21.0	0.88	88	83	49.3	46.6	47.1	21.8	0.89	83	86	50.0	46.8	47.8	21.8	0.90	79	86
	30	49.3	47.5	47.2	22.0	0.89	89	87	49.6	46.8	47.5	22.0	0.90	81	85	50.0	46.0	47.9	22.4	0.89	75	87
	60	48.8	47.2	46.7	21.4	0.90	90	86	49.6	46.8	47.2	22.2	0.88	82	85	49.8	46.4		22.2		78	
	120	49.4	48.1	47.3	22.4	0.87	92	87														
32	1[b]	48.6	48.0	48.0	19.2	1.00	96	95	50.0	49.4	49.7	19.7	1.00	96	98	51.4	50.9	51.2	20.2	1.00	97	99
	30	50.4	50.2	50.0	20.1	0.99	99	97	51.2	50.2	51.0	20.4	0.99	93	98	51.5		51.3	20.1	1.01	93	99
	60	50.0	49.5	49.6	20.1	0.98	99	97	50.6	50.2	50.4	20.1	1.00	97	99	51.2	50.2		20.4	0.99		
	120	50.3	49.6	50.0	20.5	0.97	95	98														
32	1[b]	49.4	49.1	49.3	18.2	1.07	98	99	50.4	50.2	50.4	18.3	1.09	98	100	52.9	52.8	52.9	18.8	1.11	99	100
	30	51.2	51.2	51.1	18.4	1.10	100	99	51.4	50.8	51.4	18.4	1.12	95	100	56.7	55.8	56.7	20.2	1.12		96
	60	51.2		51.1	18.4	1.10	100	99	51.3	50.6	51.3	18.4	1.10	94	99	56.3			20.4	1.09		
	120	51.3	51.3	51.2	18.8	1.08	100	99														
80	1[b]	47.5	43.0	43.3	23.3	0.80	73	75	49.2	44.3	44.5	23.8	0.82	71	72	49.8	43.8	45.0	23.9	0.82	65	72
	30	49.1	45.3	44.7	23.8	0.82	78	74	50.5	45.8	45.5	24.5	0.81	73	71	48.8	42.8	44.0	23.6	0.82	64	71
	60	51.2		43.2	23.8	0.78		75								49.3	44.0		24.1	0.81	69	
	120	50.0	46.2	45.8	24.4	0.81	78	76														
80	1[b]	48.1	45.8	45.5	21.0	0.90	85	83	50.6	48.3	48.0	21.5	0.93	85	83	50.5	47.3	48.3	22.1	0.90	80	86
	30	50.2	48.4	48.0	21.6	0.92	89	86	50.0	47.2	49.5	22.6	0.87	85	86	50.0	47.1	47.9	21.8	0.91	81	86
	60	49.1	47.4	46.3	22.4	0.87	89	86	52.0	49.0		23.1	0.89	81	85							
	120	51.4		49.3	22.2	0.92		87														
80	1[b]	49.0	48.0	47.8	19.6	0.99	93	91	51.4	50.6	50.9	20.2	1.01	94	96	51.9	50.3	51.5	20.5	1.00	89	97
	30	50.6	50.1	49.8	20.3	0.99	95	93	50.8	50.0	50.2	20.0	1.00	94	96	51.2	49.6	50.8	20.6	0.98	89	97
	60	50.8	49.6	49.7	20.4	0.98	93	94	52.8	51.9	52.3	21.0	0.99	94	97							
	120	52.6		51.7	20.6	1.01		94														
80	1[b]	49.9	49.4	49.4	18.0	1.10	96	96	52.4	51.4	52.4	18.7	1.11	96	100	53.5	52.5	53.5	19.7	1.11	93	100
	30	51.4	51.9	51.1	18.7	1.11	96	99	51.9	53.6	51.9	19.1	1.07	96	100	53.9	53.6	53.9	19.8	1.08	98	100
	60	53.3	51.1	53.1	18.9	1.08	98	99	54.2	53.6	54.2	19.2	1.11	98	99	54.6	54.2		19.8	1.09	100	
	120	52.8		53.1	18.8	1.12		99														
150	1[b]	47.7	42.0	42.7	23.6	0.81	72	70	48.5	43.9	43.1	23.8	0.80	73	68	48.6	43.4	43.5	23.8	0.81	69	70
	30	48.7	44.7	43.8	23.7	0.81	76	71	49.2	43.8	43.6	24.2	0.80	69	68	49.5	43.0	44.4	24.0	0.81	62	70
	60	48.5	44.0	43.4	23.8	0.80	73	70														
150	1[b]	49.1	46.7	46.2	21.2	0.92	79	84	50.0	50.6	47.6	22.0	0.90	84	85	50.6	46.8	48.2	22.0	0.91	76	85
	30	50.1	47.9	47.3	21.8	0.91	82	86	51.3	51.0	48.8	22.3	0.91	74	84	51.3	46.9	48.8	22.3	0.91	72	84
	60	49.8	47.4	46.8	21.8	0.90	81	85														
150	1[b]	50.2	48.9	48.6	19.7	1.01	91	89	51.2	50.6	51.2	20.1	1.02	93	97	52.5	51.4	52.1	20.8	1.00	93	97
	30	51.6	50.2	50.1	20.1	1.01	92	92	51.4	51.0	51.4	20.2	1.01	94	97	50.9	49.8	50.4	20.4	0.99	92	97
	60	51.6	50.4	50.4	20.1	1.02	92	92														
150	1[b]	51.6	50.5	50.4	18.6	1.10	92	91	52.3	51.8	52.4	18.4	1.12	96	98	54.1	53.6	54.1	19.0	1.13	96	100
	30	52.3	51.9	52.1	18.6	1.11	96	98	52.6	51.8		18.8	1.11	94	97	56.9	56.6	56.9	20.2	1.11	98	100
	60	52.0	51.0	51.6	18.6	1.10	92	97														
200	1[b]	48.3	43.7	42.6	23.5	0.81	71	66	49.5	44.6	44.2	23.8	0.80	72	69	50.6	44.1	45.2	24.4	0.82	63	69
	30	49.6	44.6	44.4	24.4	0.80	72	70	48.9	43.6	43.4	24.1	0.80	69	68	49.6	42.8	43.7	24.4	0.80	61	66
	60	48.5	43.8	43.0	24.0	0.80	72	68														
200	1[b]	49.7	46.5	45.3	21.4	0.92	79	71	50.8	47.7	47.4	22.1	0.91	81	78	50.6	44.1	47.8	22.4	0.90	78	79
	30	49.6	45.7	44.8	22.2	0.89	82	80	50.9	47.4	47.5	22.2	0.91	78	79	51.6	47.4	48.2	22.8	0.89	74	79
	60	50.2	47.2	46.7	22.3	0.89	81	78														
200	1[b]	50.7	48.5	47.8	19.7	1.02	84	79	52.1	50.3	50.4	20.4	1.01	88	88	54.2	52.3	52.5	20.7	1.00	88	90
	30	51.4	50.0	49.9	20.4	1.00	89	88	51.8	50.1	50.1	20.6	0.99	88	88	54.4	52.4	52.7	20.8	1.03	86	89
	60	51.6	50.0	49.7	20.5	0.99	90	88														
200	1[b]	51.6	50.0	49.6	18.0	1.13	88	84	53.0	52.3	52.5	18.9	1.11	95	96	55.7	55.3	55.7	19.5	1.13	96	99
	30	52.3	52.3	51.8	18.7	1.10	96	97	53.3	52.2	52.9	19.0	1.11	92	97	57.1	56.0	57.0	20.4	1.11	92	99
	60	52.2	51.1	51.7	18.0	1.15	91	96														

[a] Prepared from 32.7% P2O5 Tennessee sand and 78% H3PO4.

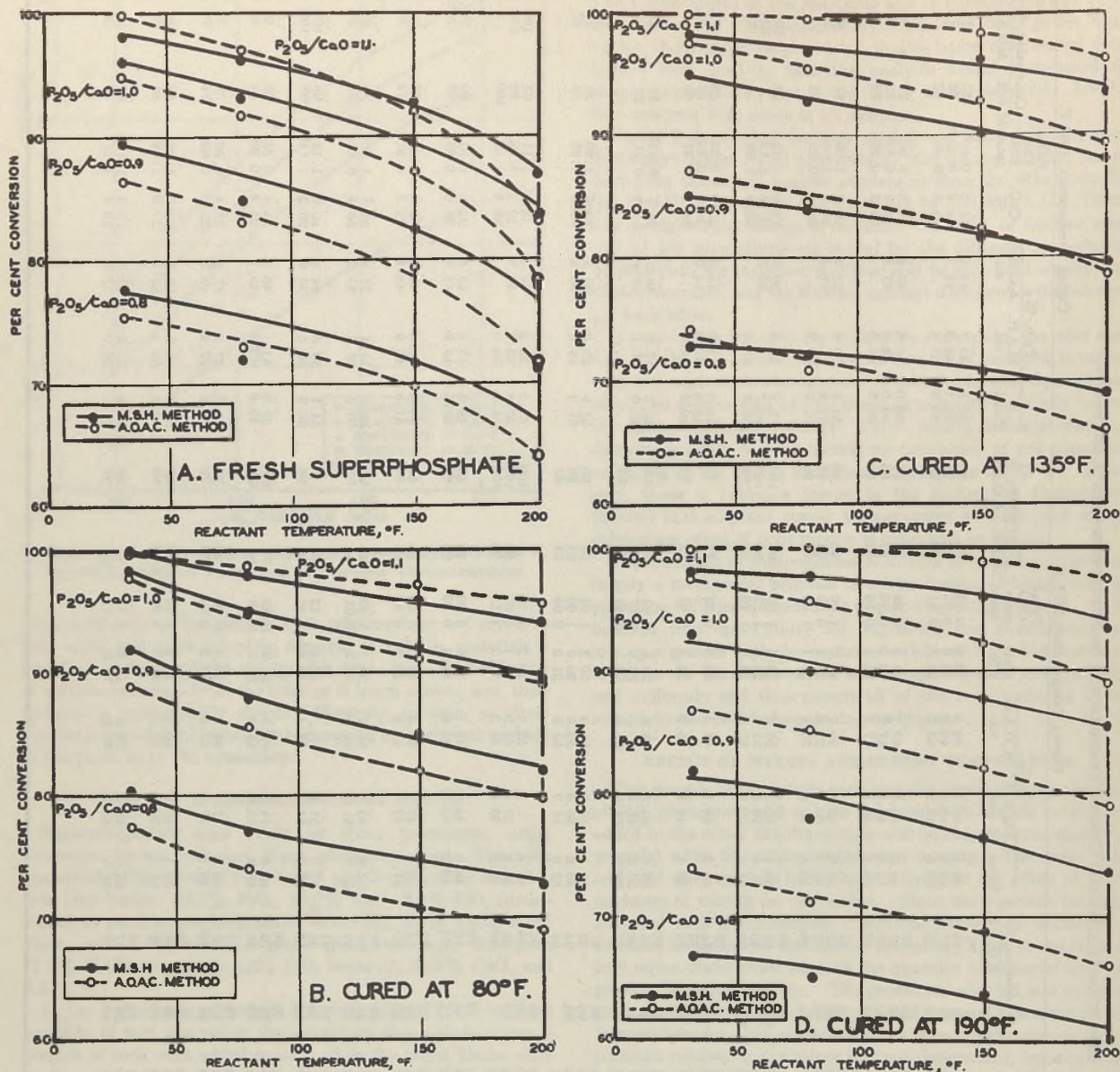[b] Samples taken from fresh batch and cured in sealed container.

Figure 4.   Effect of Reactant Temperature on Conversion of Fresh and Cured Superphosphates

from one phase to another was so gradual that the exact time the change occurred could be estimated only roughly.   In all mixes the evolution of vapors decreased as reactant temperature decreased, and in those mixes made with the reactants at 32° F. little vapor could be detected by sight or odor at any time.

Preliminary experiments showed that, when superphosphates were cured in open containers at elevated temperatures, conversion decreased rapidly and moisture and free acid contents became zero in only a few hours.   On the other hand, when superphosphates were cured in closed containers at elevated temperatures, conversions also decreased rapidly to values considerably below that obtained in the plant, but moisture and free acid contents remained much higher than those of plant-cured superphosphate.   The procedure finally developed consisted of curing the superphosphates in closed 1-quart Mason jars, provided with a thin gasket of glass wool instead of the usual rubber gasket. The jars were placed in a constant-temperature oven at the desired curing temperature.   By this method the superphosphates

did not dry out too rapidly, but it was possible for volatile constituents to diffuse from the jar during the curing period.   Equilibrium was reached in about 30 days of curing, and the materials could be cured for at least 120 days without further change in conversion.   This time is in contrast to the 12-week curing period required in the plant; the difference is undoubtedly due to the variation in quantity of material.   However, essentially equal conversions were believed to be obtained by this laboratory curing method and by the plant method.   Thermocouples placed inside the jars indicated that the temperature of the superphosphate did not rise appreciably above the oven temperature at any time during the curing period.

Superphosphates of four acidulations were prepared with reactant temperatures of 32°, 80°, 150°, and 200° F. and with curing temperatures of 80°, 135°, and 190° F.   These ranges were chosen to include the maximum mixing and curing temperatures likely to be encountered in the TVA plant and also the probable minimum mixing and curing temperatures that could be
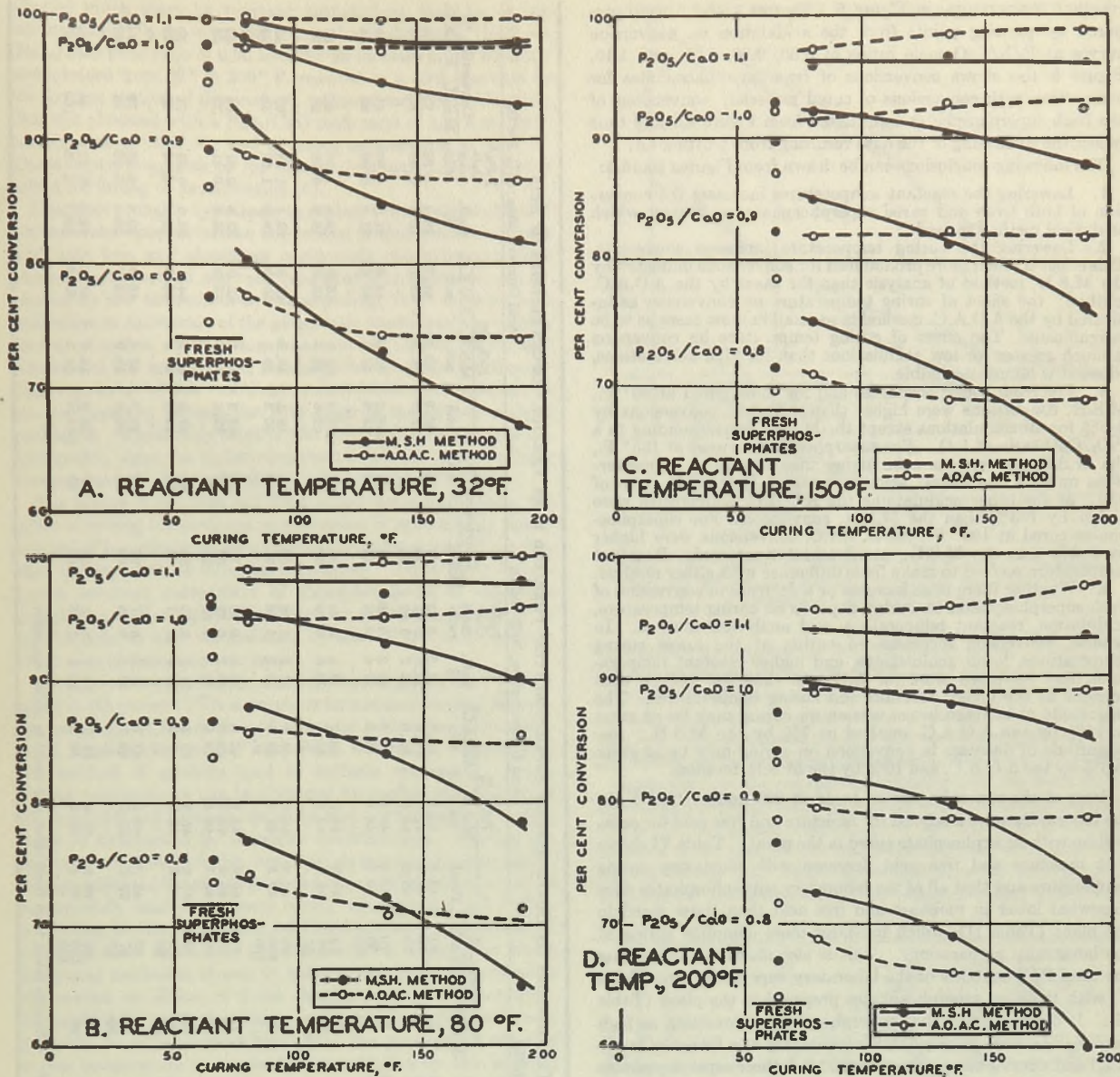
Figure 5. Effect of Curing Temperature on Conversion of Superphosphate at Various Reactant Temperatures

attained economically by artificial cooling. Samples were cured at 80° F. in open paper bags, and at 135° and 190° F. in ovens by the technique described previously. Although 30-day cure was sufficient for equilibrium conversion to be obtained, analyses were also made after 60-day curing as checks; in some cases where there was poor correlation of data after 60 days, the curing was extended to 120 days. Duplicate analyses were made of all samples.

Because the differences in conversion were relatively small in comparison with those caused by small differences in acidulation, it was not possible to compare individual superphosphates having the same nominal acidulation and different mixing or curing temperatures. Instead, such comparisons between superphosphates prepared at different mixing or curing temperatures had to be made by plotting curves of conversion against acidulation for all superphosphates prepared at each mixing or curing temperature. Because of the difficulty in obtaining homogeneous samples, the P_2O_5/CaO ratio obtained by analysis of the super-

phosphate was used as a measure of acidulation rather than acidulation calculated from weighed quantities of acid and rock.

Table V gives the data on mixing and curing temperatures, and Figure 3 is an example of conversion *vs.* acidulation curves. Although attempts were made to prepare superphosphates having P_2O_5/CaO ratios of exactly 0.80, 0.90, 1.00, and 1.10, there was considerable deviation from these ratios. Some of this deviation may have been analytical error, but most of it was probably due to the extreme difficulty in obtaining a homogeneous mixture of rock and acid; consequently, the 1-gram samples used for analysis did not always correspond exactly to the over-all acidulation of the entire batch of about 10 to 15 pounds. All the data for cured superphosphates were plotted on the same coordinates, since it had been found that there was essentially no change in conversion on curing after 30 days.

The effect of reactant temperature on conversion for the fresh superphosphates at each curing temperature is shown in Figure 4, and the effect of curing temperature on conversion for each

reactant temperature, in Figure 5. Figures 4 and 5 were prepared by plotting points from the acidulation vs. conversion curves at P_2O_5/CaO mole ratios of 0.80, 0.90, 1.00, and 1.10. Figure 5 also shows conversions of fresh superphosphates for comparison with conversions of cured material; conversions of the fresh superphosphates were taken from Figure 4A and thus reflect the smoothing of the data resulting from plotting 4A.

The following conclusions can be drawn from Figures 4 and 5:

1. Lowering the reactant temperatures increases the conversion of both fresh and cured superphosphate, no matter which analytical method is used.

2. Lowering the curing temperature increases conversion. This effect is much more pronounced for conversions indicated by the M.S.H. method of analysis than for those by the A.O.A.C. method; the effect of curing temperature on conversion as indicated by the A.O.A.C. method is so small in most cases as to be insignificant. The effect of curing temperature on conversion is much greater for low acidulations than for high acidulations, where it is almost negligible.

3. For fresh superphosphates and for those cured at 80° F., M.S.H. conversions were higher than A.O.A.C. conversions by 2-5% for all acidulations except the highest (corresponding to a P_2O_5/CaO ratio of 1.1). For superphosphates cured at 135° F., the M.S.H. conversions were higher than the A.O.A.C. conversions only at the lowest acidulation used (P_2O_5/CaO ratio of 0.8); at the other acidulations the A.O.A.C. conversions were higher by 1-3% than the M.S.H. conversions. For superphosphates cured at 190° F., the A.O.A.C. conversions were higher by 3-6% than the M.S.H., at all acidulations used. Reactant temperature seemed to make little difference with either method.

4. Whether there is an increase or a decrease in conversion of fresh superphosphates on curing depends on curing temperature, acidulation, reactant temperature, and analytical method. In general, conversion increases on curing at the lower curing temperatures, lower acidulations, and higher reactant temperatures, and increases more for A.O.A.C. than for M.S.H. conversions at the higher reactant and curing temperatures. The magnitude of increase in conversion on curing may be as great as 14% by the A.O.A.C. method or 7% by the M.S.H.; the magnitude of decrease in conversion on curing may be as great as 3% by the A.O.A.C. and 10% by the M.S.H. method.

Some of the superphosphates cured at 80° and at 190° F. in the laboratory were analyzed for moisture and free acid for comparison with superphosphate cured in the plant. Table VI shows that moisture and free acid decrease with increasing curing temperature and that all of the laboratory superphosphates were somewhat lower in moisture and free acid than those cured in the plant (Table II), which indicates more complete curing of the laboratory preparations. This is also shown by comparing the total P_2O_5 contents of the laboratory superphosphate (Table V) with those on superphosphates prepared in the plant (Table II). It is noteworthy that superphosphates containing as high as 57% P_2O_5 were prepared in the laboratory at a P_2O_5/CaO ratio of 1.1 and a curing temperature of 190° F.; these superphosphates did not contain objectionably high moisture and free acid contents (Table VI).

Figure 6 presents the influence of temperature on the fluorine content of the cured superphosphate. Fluorine content is

TABLE VI. EFFECT OF CURING TEMPERATURE ON MOISTURE AND FREE ACID CONTENT OF SUPERPHOSPHATE[a]

Curing Temp., °F.	P_2O_5/CaO Mole Ratio	Moisture[b], %	Free Acid as % P_2O_5
80	0.78	0.6	0.2
	0.87	0.8	0.3
	0.98	1.3	1.2
	1.08	2.3	3.2
135	0.82	0.6	0.2
	0.87	0.1	0.1
	1.00	0.2	0.2
	1.07	1.2	3.0
190	0.82	0.0	0.1
	0.91	0.0	0.1
	0.98	0.0	0.2
	1.08	0.2	0.7

[a] Reactant temperature, 80° F.; curing time, 60 days.
[b] Determined by drying over concentrated sulfuric acid for 24 hours in an evacuated desiccator at room temperature.

TABLE VII. EFFECT OF MIXING TEMPERATURE ON CONVERSION OF SUPERPHOSPHATE[a] PREPARED FROM VARIOUS CONCENTRATIONS OF ACID

Reactant Temp., °F.	Curing Time, Days	Acid Concentration, 60% H_3PO_4							Acid Concentration, 70% H_3PO_4							Acid Concentration, 85% H_3PO_4						
		Total	P_2O_5 % M.S.H. sol	P_2O_5 % A.O.A.C. sol	CaO %	P_2O_5/CaO ratio	Conv M.S.H.	Conv A.O.A.C.	Total	P_2O_5 % M.S.H. sol	P_2O_5 % A.O.A.C. sol	CaO %	P_2O_5/CaO ratio	Conv M.S.H.	Conv A.O.A.C.	Total	P_2O_5 % M.S.H. sol	P_2O_5 % A.O.A.C. sol	CaO %	P_2O_5/CaO ratio	Conv M.S.H.	Conv A.O.A.C.
80	1[b]	40.5	37.3	35.1	19.4	0.82	77	61	44.6	41.1	40.6	21.2	0.83	77	74	46.9	42.4	41.7	23.1	0.80	73	68
	30	46.6	43.6	43.2	21.8	0.84	81	79	47.6	44.9	43.8	23.0	0.82	84	77	47.5	44.2	43.1	23.2	0.81	80	73
	60	48.0	48.0	44.6	22.3	0.85	86	79	48.2	45.8	45.0	23.3	0.82	86	86							
80	1[b]	41.2	39.4	37.4	18.0	0.90	86	70	45.4	44.1	43.2	20.3	0.88	91	85	48.2	46.0	44.8	21.2	0.90	85	78
	30	48.1	47.0	46.5	20.4	0.93	92	89	49.1	48.6	47.5	21.4	0.91	97	90	48.9	47.8	46.4	21.4	0.90	93	84
	60	49.1	49.0	47.5	21.4	0.91	99	90														
80	1[b]	41.2	40.1	38.8	16.4	0.99	91	79	46.3	46.0	45.2	18.4	0.99	98	92	49.4	48.0	46.9	19.4	1.01	90	82
	30	48.0	48.4	47.8	18.7	1.02	100	96	49.9	49.8	49.6	20.0	0.99	99	98	49.8	49.3	48.8	19.8	0.99	96	93
	60	50.0	49.6	49.6	19.6	1.01	100	97														
80	1[b]	41.9	41.5	40.7	15.4	1.08	96	89	46.9	46.9	46.7	17.1	1.08	100	98	49.4	49.0	47.6	18.1	1.08	97	86
	30	49.0	48.0	48.2	17.5	1.05	98	100	49.5	49.4	49.5	18.2	1.08	99	100	50.2	50.0	50.0	18.2	1.09	98	98
	60	50.6		50.6	19.0	1.06		100														
150	1[b]	42.5	38.4	36.9	20.3	0.83	72	61	46.0	42.8	42.0	22.3	0.82	80	75	48.2	42.1	42.0	23.5	0.81	64	63
	30	47.4	44.0	44.2	22.8	0.82	79	80	48.2	45.6	44.9	23.1	0.82	85	80	48.4	44.2	43.0	23.6	0.81	75	68
	60	47.4	45.4	45.0	28.4	0.82	82	80	48.1					85	81							
150	1[b]	42.5	40.0	38.8	18.8	0.89	81	72	47.6	46.6	45.2	21.2	0.89	93	84	49.0	44.3	44.1	22.6	0.86	71	70
	30	48.0	47.8	46.9	21.3	0.90	96	90	49.5	48.8	47.9	21.4	0.91	95	90	49.7	47.0	46.3	22.7	0.86	83	79
	60	49.0	48.5	47.4	21.9	0.88	97	90														
150	1[b]	43.4	42.3	41.0	17.3	0.99	91	80	48.9	48.5	47.7	19.9	0.97	97	92	49.7	46.6	45.9	20.4	0.96	79	74
	30	49.6	49.1	49.2	20.0	0.98	96	97	50.2	50.2	49.7	20.2	0.98	100	96	50.4	49.6	48.6	20.3	0.98	94	88
	60	50.2	50.1	49.8	20.2	0.98	99	97														
150	1[b]	48.4	43.1	42.0	15.8	1.09	97	88	49.4	49.4	49.0	18.4	1.06	100	97	50.8	48.6	47.3	18.8	1.07	84	74
	30	48.9	48.7	48.9	18.1	1.07	98	100	50.4	50.6	50.3	18.4	1.08	100	99	51.2	51.2	50.8	18.7	1.08	100	97
	60	50.0		50.0	18.3	1.08		100														

[a] Prepared from 32.7% P_2O_5 Tennessee sand and cured at 80° F.   [b] Sample taken from fresh batch and cured in sealed container.

affected much more by reactant temperature than by curing temperature. In the operating range of acidulation for the plant (P_2O_5/CaO mole ratio of 0.90 to 0.95), an increase in the reactant temperature from 32° to 200° F. resulted in a 50% decrease in the fluorine content of the product. Almost complete defluorination was obtained with a P_2O_5/CaO mole ratio of 1.1, a reactant temperature of 200° F., and a curing temperature of 190° F. These superphosphates of low fluorine content should be well suited for liming or ammoniation (6).

The most probable hypothesis to explain the beneficial effect of low reactant temperature on conversion is that reactions of the acid with iron and aluminum compounds and other nonphosphatic constituents of the rock (so-called side reactions) are repressed by low temperatures; consequently, there is better acid utilization in conversion of the phosphatic constituents to soluble forms. Another contributing factor to the higher conversion obtained at low temperature, though probably of less significance than repression of side reactions, is that better mixing occurs at low temperature because the fluid stage of the mixing cycle is prolonged. Apparently most of the reactions during mixing are irreversible, since the higher conversions obtained at low mixing temperatures are not nullified by high-temperature curing.

The failure of the previous TVA experiments (2) to show the effect of mixing temperature on conversion is undoubtedly due to the use of less advanced experimental techniques and to the fact that the experiments were less exhaustive. These early experiments involved comparison of superphosphates of only one acidulation, and temperature effects on conversion are likely to be obscured in such comparisons because of the much greater effect of acidulation on conversion.

These results point to significant improvements that can be made in the present TVA superphosphate manufacturing process. By carrying out the mixing of rock and acid at lower temperatures, considerably greater conversion will result, regardless of the method of analysis used to indicate conversion. Lower mixing temperatures can be obtained by cooling one or both of the reactants and perhaps the mixer also. The degree of cooling must be determined by economic considerations. Cooling the reactants will also probably lower the curing temperature significantly, which is beneficial to conversion. Whether it would be economically feasible to lower curing temperatures still farther by cooling the freshly mixed superphosphate or by using a method of piling more conducive to heat liberation depends on which analytical method is chosen to indicate conversion (discussed in the section on Effect of Fresh Superphosphate Temperature). If the M.S.H. method is used, further cooling methods would probably be advantageous because of the pronounced effect of curing temperature on conversion as indicated by this method; but if the A.O.A.C. method is used, the effect of curing temperature on conversion is so slight that no additional expense to obtain lower curing temperatures would be permissible.

Use of lower curing temperatures in the plant would probably necessitate an increase in curing time, because the vapor pressure of the volatile constituents would be lower. The extent of this increase in curing time, which would probably not be excessive, can be determined only by plant experience.

CUMULATIVE EFFECTS OF POOR MIXING AND OF HIGH MIXING AND CURING TEMPERATURES

Experiments were made to determine whether the effects of poor mixing, high reactant temperature, and high curing temperature on conversion were cumulative. Superphosphates were made by the normal mixing procedure, with reactant and curing temperatures of 80° F., and by the poor mixing procedure, with reactant temperatures of 80° and 200° F. and with curing temperatures of 80° and 190° F. Duplicate analyses were made of all samples. The same rock and acid were used as in the experiments on the effect of thoroughness of mixing on conversion. The results for M.S.H. conversions are shown in Figure 7. Simi-
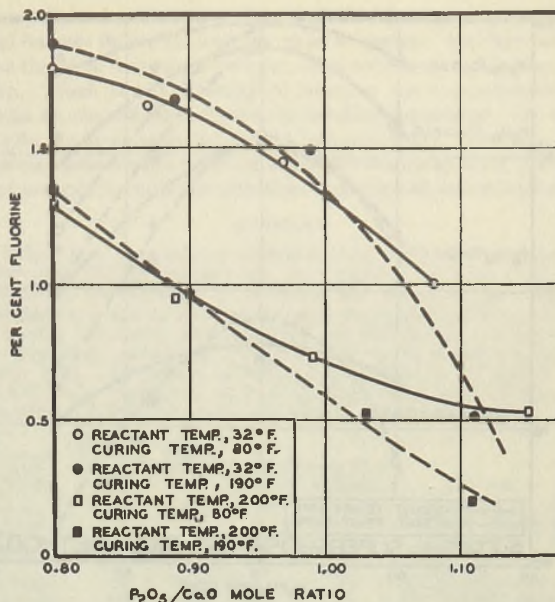
Figure 6. Effect of Reactant and Curing Temperatures on Fluorine Content of Cured Superphosphate Prepared from 78% H_3PO_4

lar results were obtained for A.O.A.C. conversions. The normal mixing procedure and the lower mixing and curing temperatures gave the highest conversion; poor mixing, high mixing temperature, and high curing temperature gave progressively lower conversions. It is concluded that the effects of thoroughness of mixing, mixing temperature, and curing temperature are cumulative.

Comparison of the conversions obtained with the most severe laboratory conditions (namely, poor mixing, reactant temperature of 200° F., and curing temperature of 190° F.) with conversions obtained in the plant shows that the severe conditions resulted in slightly (about 5%) lower conversions than the average plant conversions. Also, some of the conversions obtained with normal
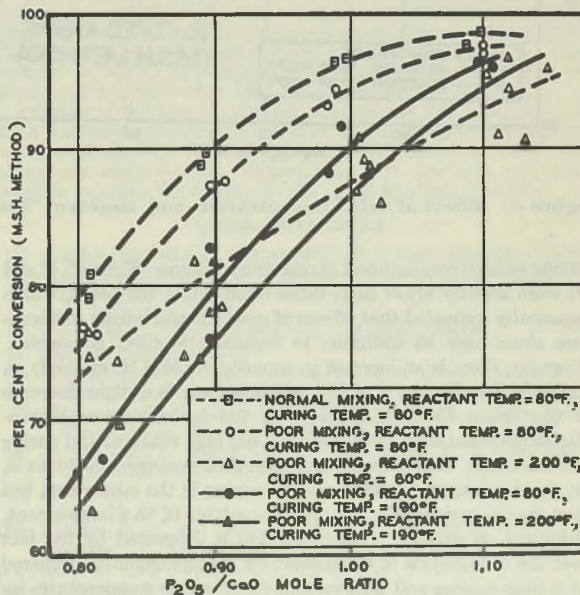
Figure 7. Cumulative Effects of Poor Mixing, High Mixing Temperature, and High Curing Temperature on Superphosphate Conversion (M.S.H. Method)
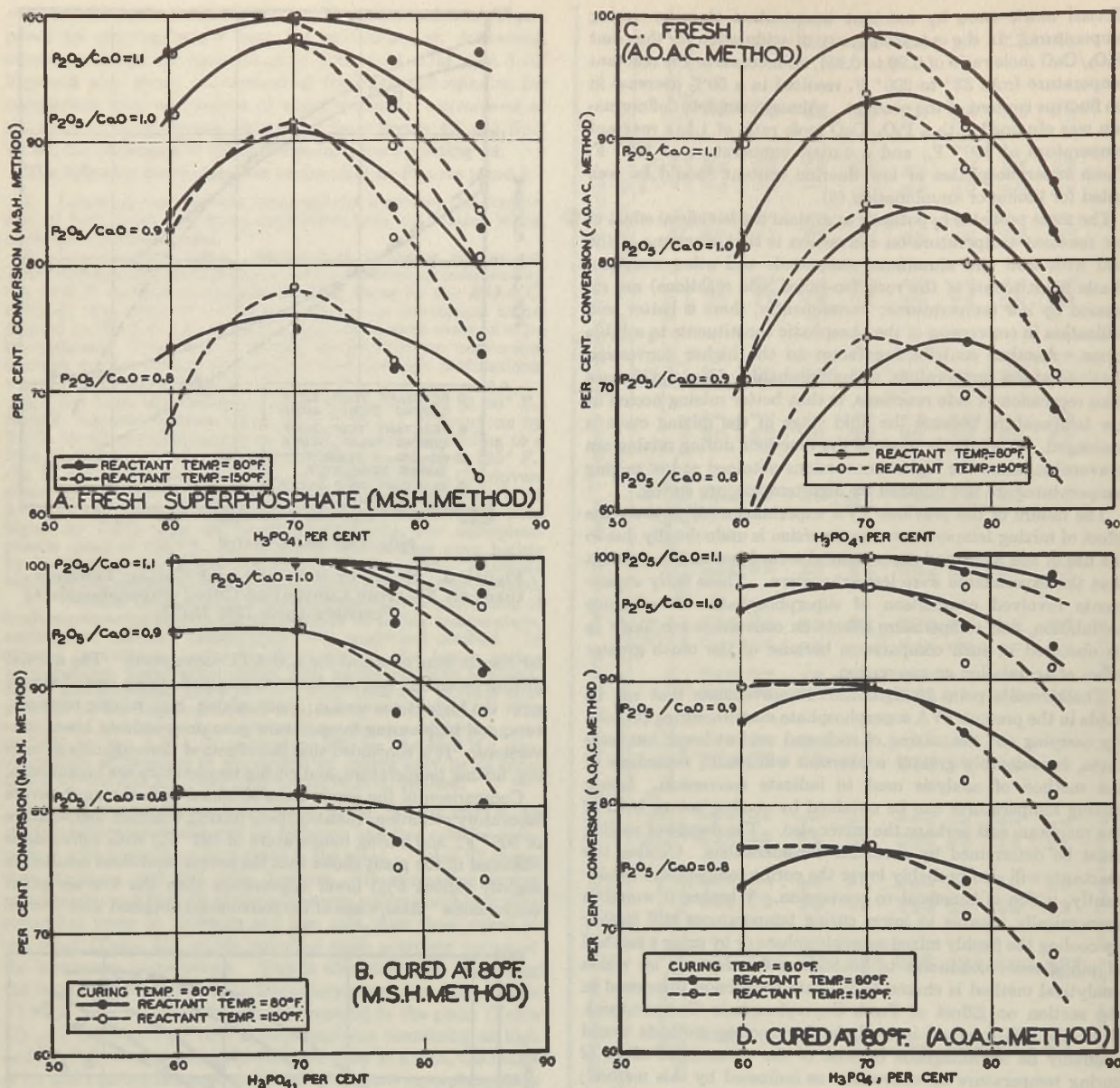
Figure 8. Effect of Acid Concentration and Reactant Temperature on Conversion of Fresh and Cured Superphosphates

mixing at high reactant and curing temperatures (Figure 5, *C* and *D*) were slightly lower than those obtained in the plant, which apparently indicated that effects of reactant and curing temperature alone may be sufficient to explain low plant conversion. However, there is an increase in conversion (M.S.H. method) on curing in the plant of 8 or 9%, whereas there is a slight decrease in conversion (M.S.H. method) of the laboratory superphosphates prepared with normal mixing and high reactant and curing temperatures; this behavior indicates that mixing in the plant is, on the average, poorer than normal mixing in the laboratory, but that the deleterious effect of this poor mixing is, to a large extent, overcome on curing. This conclusion is supported by the fact that the conversions of the laboratory superphosphates prepared with poor mixing and high reactant and curing temperatures increased considerably on curing, whereas the conversions of those made under the same conditions (except with normal mixing) did not increase on curing.

COOLING FRESH SUPERPHOSPHATE

An experiment was made to determine whether cooling freshly prepared superphosphate would lower its curing temperature appreciably under present TVA plant conditions. Insulated wooden boxes, each having a capacity of about 100 pounds, were filled with superphosphate directly from one of the plant batch mixers, which had a temperature of 149° F. Other boxes were filled with superphosphate that had been cooled in a rotary cooler with air to 84° F. The uncooled superphosphate reached a maximum of 201° F. (slightly higher than that attained in the plant curing piles) within $2\frac{1}{2}$ hours, whereas the cooled material attained a maximum temperature of only 111° F. within 14 hours. These experiments indicate, then, that considerable reduction in the curing temperature of the plant curing piles may be expected if the temperature of the fresh superphosphate is lowered.

EFFECT OF ORDER OF MIXING REACTANTS

Since the beneficial effect on conversion of low reactant temperature was considered to be due to repression of the side reactions, it was postulated that such a repression of these side reactions and consequent higher conversion would also be obtained by adding acid slowly to rock; an excess of rock would then be maintained throughout most of the mixing cycle. Experiments were made in which acid was added slowly to rock over a period of about 1 minute, rock was added to acid gradually for about 1 minute, and acid and rock were dumped quickly and simultaneously into the laboratory sigma-blade mixer. Superphosphates of four different acidulations (P_2O_5/CaO mole ratios of 0.8, 0.9, 1.0, and 1.1) were made with reactant temperature of 80° F. and with curing temperatures of 80° and 190° F. Results showed no appreciable difference in conversion between the three methods of adding rock and acid to the mixer.

EFFECT OF ACID CONCENTRATION

Because present results indicated that conversion was improved by lowering the reactant temperatures, whereas those of Marshall, Rader, and Jacob (8) indicated that a mixing temperature of 140° F. gave higher conversion than room temperature for superphosphates made with 21 to 64% phosphoric acid, experiments were made to determine whether these two apparently inconsistent conclusions could be explained by the difference in acid concentration. Mixing procedure was the same as that described for the experiments on effect of mixing and curing temperature on conversion. Superphosphates were made from 60, 70, and 85% phosphoric acid to supplement the data obtained with 78% acid. Reactant temperatures of 80° and 150° F. and curing temperature of 80° F. were used. The rock was the same as that in the previous experiments, and the acid was obtained by diluting plant phosphoric acid of the following composition: 94.0% H_3PO_4 (based on total P_2O_5 content), 0.06% CaO, and 0.09% F. The time of all three mixing stages increased with decreasing acid concentration as well as with decreasing acid temperature and increasing acidulation. The fluid stage lasted from about 6 seconds to 5 minutes; the plastic stage, from about 10 seconds to 15 minutes for all superphosphates except those made with 60% acid; the dry stage, from about 1 to 12 minutes for all superphosphates except those made with 60% acid. For those made with 60% acid, a dry stage was not reached after 30 to 60 minutes, and the superphosphates were discharged from the mixer in the plastic stage into shallow open pans, allowed to dry at room temperature overnight, and ground in the disk mill. For superphosphates made with 60% acid, 60 days were required for complete curing. Duplicate analyses were made of all samples.

As in experiments on the effects of reactant and curing temperature, results were plotted as conversion vs. P_2O_5/CaO ratio; from these curves, conversion vs. acid concentration curves were constructed (Figure 8). Table VII gives the data. Figure 8 shows that low reactant temperature has a beneficial effect on conversion only at acid concentrations greater than about 70%. At an acid concentration of 70%, reactant temperature in the range studied has no effect on conversion, and at lower acid concentrations a reactant temperature of 150° F. gives equal or greater conversion than does 80°, depending on the analytical method used. These results show that present data are consistent with those of Marshall, Rader, and Jacob (8) since their experiments were made in the range of acid concentration in which the higher reactant temperature favored conversion. Further experiments showed that decreasing the acid concentration from 85 to 60% H_3PO_4 decreased by approximately 5% the fluorine content of the superphosphate prepared at equal P_2O_5/CaO ratios.

These data indicate that for maximum conversion an acid concentration of about 70% should be used, which confirms the earlier TVA experiments (10). However, this is not considered feasible in the TVA manufacturing plant because the product

thus obtained is too wet to be handled without great difficulty and because the curing time would be increased. A compromise has therefore been made between these two factors and conversion. Much of the difficulty of handling wet superphosphate could be obviated by changes in handling equipment—for example, by more extensive use of belt conveyors. However, it appears more feasible to obtain higher conversion by lower mixing and lower curing temperatures than by lower acid concentrations.

SUMMARY

Laboratory experiments indicated that, with superphosphate made from 78% phosphoric acid, conversion in the plant could be improved considerably by lowering the reactant and curing temperatures and by improving the thoroughness of mixing. The following tabulation shows present and anticipated conversions for improved mixing and curing conditions for superphosphate made with 1.29 pounds of 78% phosphoric acid per pound of 31.8% P_2O_5 Tennessee rock (P_2O_5/CaO mole ratio of superphosphate, 0.95), the proportion used at present in the plant:

Thoroughness of Mixing	Equivalent Reactant Temp., ° F.	Curing Temp., ° F.	Conversion, %		Remarks
			M.S.H.	A.O.A.C.	
Present plant	150–200	190[a]	85[b]	88[c]	Present plant conditions for operation at capacity
Improved	100	140[d]	89	90	Water cooling of acid and rock
Improved	32	110[d]	93	94	Refrigeration of acid
Improved	32	80[d]	95	94	Refrigeration of acid and cooling of fresh superphosphate

[a] Maximum temperature reached in interior of pile; bulk of material probably reaches this temperature.
[b] Actual conversion for 1942–43 (Figure 1B) was slightly higher than 85% because operation during these 2 years was somewhat under plant capacity; consequently the mixing and curing temperatures were slightly lower than for capacity conditions.
[c] Estimated; data are not available because superphosphate manufacture has been greatly curtailed by the war, and operating conditions are not representative.
[d] Assumed as average curing temperature in pile.

The probable potential improvement is greater if the M.S.H. method of analysis is used because the M.S.H. conversion is affected by curing temperature considerably more than is the A.O.A.C. conversion. However, there is an advantage in using the A.O.A.C. method for present plant conditions of high mixing and curing temperatures. Use of lower curing temperatures would probably necessitate a somewhat longer curing time.

Lowering reactant temperatures has a beneficial effect on conversion only with acid greater than about 70% H_3PO_4; at lower concentrations, lowering reactant temperatures lowers conversion or does not affect it. Maximum conversion is obtained at about 70% H_3PO_4, but greater difficulty of handling and the longer curing time required for the resultant superphosphate make it more desirable to achieve improved conversion by using 78% H_3PO_4 and cooling the reactants than by using 70% H_3PO_4. The increase in curing time due to 70% H_3PO_4 would probably be considerably greater than that due to cooling the reactants.

Because of wartime conditions, superphosphate production at TVA has been greatly curtailed, most of the phosphorus produced being used directly for military purposes instead of for superphosphate manufacture. Consequently, it has not yet been possible to apply the results of this study to plant operation.

LITERATURE CITED

(1) Assoc. of Official Agr. Chem., Methods of Analysis. 5th ed., 1940.
(2) Copson, R. L., Newton, R. H., and Lindsay, J. D., IND. ENG. CHEM., 28, 923–7 (1936).
(3) Ibid., 29, 175–9 (1937).
(4) Curtis, H. A., Chem. & Met. Eng., 42, 320–4 (1935).
(5) Ibid., 42, 488–91 (1935).
(6) MacIntire, W. H., and Hardin, L. J., J. Assoc. Official Agr. Chem., 23, 388–98 (1940).
(7) MacIntire, W. H., Shaw, W. M., and Hardin, L. J., IND. ENG. CHEM., ANAL. ED., 10, 143–52 (1938).
(8) Marshall, H. L., Rader, L. F., Jr., and Jacob, K. D., IND. ENG. CHEM., 25, 1253–9 (1933).
(9) Nachfolger, F. L., and Lutjens, J., German Patent 112,151 (June 9, 1900).
(10) Newton, R. H., and Copson, R. L., IND. ENG. CHEM., 28, 1182–6 (1936).
(11) Sackett, A. J., U. S. Patent 2,028,413 (Jan. 21, 1936).
(12) Volfkovich, S. I., and Vladimirov, L. V., Trans. Sci. Inst. Fertilizers (U.S.S.R.), 55, 73–98 (1928).
(13) Williams, Rinaldo, U. S. Patent 1,003,681 (Sept. 19, 1911).

Corrosion Prevention by Controlled Calcium Carbonate Scale

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THE USE of controlled calcium carbonate scale for corrosion prevention in cooling tower systems serving steel equipment has been investigated at plants constructed for war production, when copper alloys were scarce. The study revealed factors that markedly affect the success of the treatment, which have hitherto had little recognition. If rising temperatures cause the actual pH of the water to drop at the same rate as the calcium carbonate saturation pH, scale of uniform thickness will be deposited over the entire temperature range. Conditions under which this occurs are described.

THE protection against corrosion of metals in recirculating fresh water cooling systems is a problem of enormous economic importance. The need for such protection has been greatly magnified in the various war industries because of the shortage of suitable corrosion-resisting metals and the serious impact on production of forced outages of critical equipment, imposed by failures resulting from corrosion. Of the many corrective measures tried, some have been partially or wholly successful in circulating systems, while others have been complete failures. A critical investigation of the conditions which have occurred will often reveal the basic reasons for the results obtained by such treatments.

In the final analysis, the protection of any metal from corrosion depends upon the creation and maintenance of a physical dam between the anodic or cathodic part of the metallic surface and the electrolyte (water). Such coatings may contain inorganic or organic substances or both; they may be the product of anodic or cathodic corrosion reactions or may be precipitated nonselectively on all areas from the liquid phase. For complete protection these deposits must be nonporous and continuous; and when this favorable condition is attained, all corrosive attack will be prevented, since there will be no possible contact of the vulnerable metal areas and the corroding medium.

It is not the purpose of this paper to attempt to survey the history of success or failure of all the treatments which are being offered by proponents of various chemical compounds or to evaluate their relative merits. This paper presents a summary of experiences and conclusions concerning the fundamental requirements for corrosion protection by the deposition of calcium carbonate scale and the specific control procedures which must be provided to ensure success. Some of the principles involved are equally applicable to other types of film inhibitors.

The deliberate production of a calcium carbonate scale to protect water distribution systems is carried out by many municipal water treatment plants and has been applied widely in industry. Of the several control methods available, the authors find it convenient to use the Langelier saturation index (*2, 3*) as determined by calculation with the aid of the curves shown in Figure 1 or by the marble test[1]. This method of corrosion prevention is attractive because the chemicals used are cheap, and both anodic

and cathodic areas are protected. It requires better control of more variables than is necessary for some other inhibitors.

Calcium carbonate has an excellent history of success, although there have been a number of failures. Some of the reasons for unsuccessful results have only recently been fully understood. They may be summarized as follows:

1. The presence of organic contaminants which prevent adherent impervious crystalline scale formation.
2. High sodium alkalinity or other dissolved solids which tend to increase the solubility of calcium carbonate.
3. Concurrent use of phosphates to prevent excessive scale on hotter surfaces.
4. Suspended matter or biological slimes which are mechanically bound up with the scale and make a porous, heavy deposit.
5. Erroneous selection of the chemical treatment used to obtain a positive saturation index—e.g., the use of caustic or soda ash when lime is required, or vice versa.
6. Mass precipitation of finely divided calcium carbonate instead of deposition as scale.
7. A high "index of uniformity of scaling", resulting in no protection of the cold surfaces and objectionably heavy scale on the hotter surfaces.

The last condition is the subject of·the commonest complaint against this method of protection and had led several plants to abandon it. In some cases the trouble actually resulted from mud, organic matter, and slimes, but was erroneously attributed to an inherent defect in the method of inhibition. The rate of increase in scale thickness with temperature depends on the composition of the water and is subject to control by manipulating the variables in the Langelier saturation index.

Finally, a sufficiently thin protective scale has been difficult to maintain in some cases where terminal temperature differences were small and over-all coefficient of heat transfer (*U* value) was inherently low, making bare metal surfaces practically imperative. An example is the cooling of hydrocarbon vapors and steam condensate to 105° F. with cooling water approaching 90°.

Before a scaling program is undertaken, the system should be thoroughly investigated to make sure that all of the sources of trouble discussed above can be corrected.

CONTROL OF SCALING RATE AND THICKNESS

Depending on the water composition, scale can be deposited or redissolved, or may not be affected either way by increases in water temperature. These possibilities occur because the actual pH of water decreases with rising temperature, and the rate of pH decrease depends on the relation between the methyl orange alkalinity and pH (as measured at 77° F.).

Figures 2 and 3 show the variation of actual pH with temperatures for water containing 25 and 100 p.p.m. of methyl orange alkalinity, as calculated according to the method of Amorosi and McDermet (*1*). If the saturation index is calculated as the difference between the saturation pH (pH$_s$) and the actual pH (pH$_a$) corrected for temperature, it may predict quite different behavior at elevated temperatures from what would be indicated

[1] The marble test is a measurement of the pH change resulting from saturating a sample with calcium carbonate (c.p. reagent grade), using a standard detention time, filtration procedure, temperature, etc
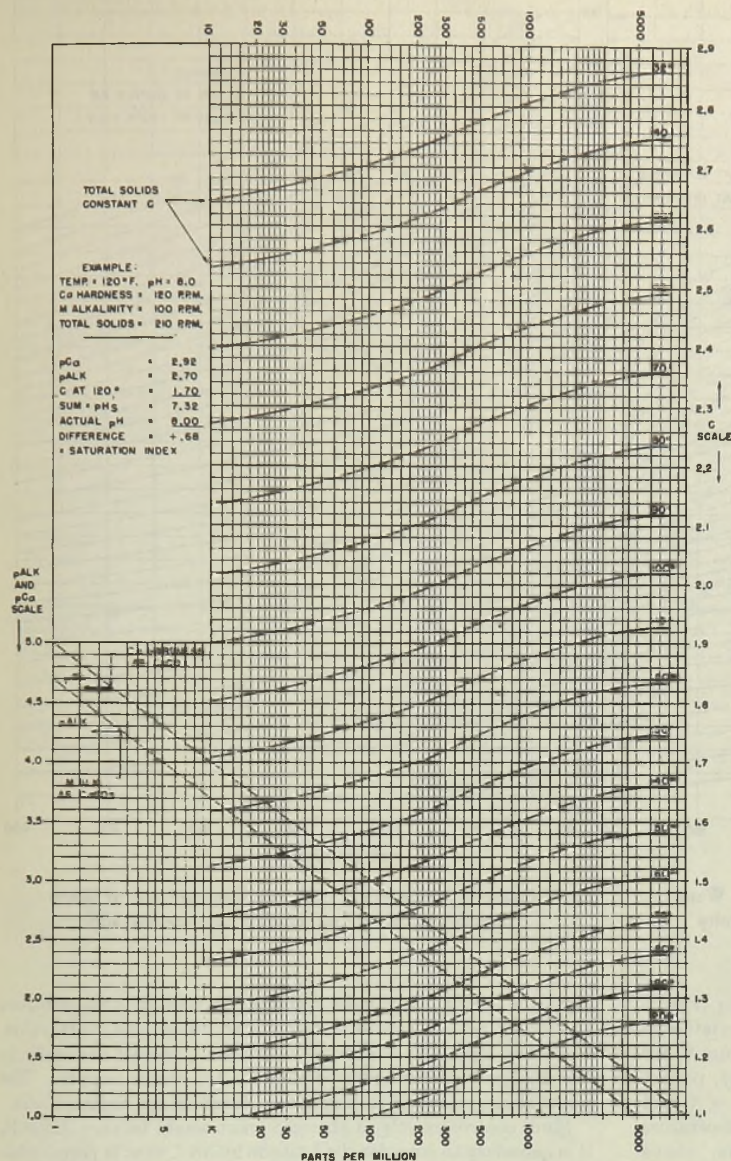
Figure I. Langelier Saturation Index Chart

each case. Comparable conditions have been seen many times in circulating cooling systems.

Figure 5B is a graph of the decrease in saturation pH (pH$_s$) against temperature; this is simply an expression of the change in constant C of the Langelier index, as shown by the distance between the parallel lines of Figure 1. Figure 5A shows four curves for actual pH (pH$_a$) against temperature, which are essentially parallel with the lower pH$_s$ curve. Waters having these pH-alkalinity relations and containing sufficient calcium to have a positive saturation index, will produce scale of about the same thickness at all temperatures because the actual pH decreases at the same rate as the saturation pH. Thus a thin protective film can be maintained on the colder surfaces without plugging the hotter passes of condensers if the correct relation between pH and alkalinity is maintained.

The obvious and immediate problem presented to operators is: How can scale of uniform thickness at all temperatures be maintained by adjusting water composition?

If the characteristics of the parallel curves shown in Figure 5 are plotted as in Figure 6, a curve is obtained which will indicate the necessary pH-alkalinity relations for the desired scaling control treatment. Figure 6 shows the pH for specific values of alkalinity at which the deposition of scale would be uniform on heat transfer surfaces at any temperatures. To control the treatment so as to deposit scale uniformly, it is first necessary to determine the optimum pH for the specific alkalinity from Figure 6. When using Figure 6, it should be remembered that the amount of scale deposited is still dependent on the saturation index value; by complying with the pH and alkalinity requirements of this figure the uniformity, but not necessarily the amount of scale deposition, is assured.

The preceding discussion, relating to calculations of the data shown in Figures 2 to 6, may suggest that the control procedure is unduly complicated for practical application. Actually, a scaling program can be successfully carried out if the water characteristics conform fairly well to the requirements indicated in Figure 6.

The change in saturation index with temperature predicts whether scale will be heavier, lighter, or uniform in thickness as temperature is increased, depending on whether its values are positive, negative, or zero. We have called this rate ΔS.I., the "coefficient of uniformity of scaling":

$$\Delta S.I. = S.I._{t_2} - S.I._{t_1}$$

where $t_2 > t_1$

The coefficient of uniformity of scaling will be zero if, for any given alkalinity, the pH (at 80° F.) conforms to the optimum value shown in Figure 6. At pH values below the curve, for any given alkalinity pH$_a$ becomes increasingly higher than pH$_s$ as the temperature rises, and the coefficient is positive; the saturation index and scale thickness increase. Thus, a protective scale treatment based on a high alkalinity, low pH, and a calcium hardness to suit (according to the conventional formula) may produce heavy scale at high temperatures. Conversely, if dependence is placed on a high pH and the alkalinity is too low, the hotter equipment may actually be corroded notwithstanding a theoretically correct calcium hardness.

by the conventional method; the latter uses the actual pH taken at room temperature. Such discrepancies have led to alternate methods of calculation, such as Ryznar's stability index (4). Ryznar describes three water supplies, having saturation indices of +0.54, +0.45, and +0.27 (at 80° F.), and points out that the saturation index does not predict the true nature of these waters. The first is corrosive to hot water heaters, the second deposits heavy scale in them, and the third is uniformly satisfactory in both cold and hot services.

The above discrepancy between expected performance and actual performance is explained when the effect of temperature on actual pH is taken into consideration and the change in saturation index is plotted over the range 80° to 150° F. (Figure 4). These data were taken from the three water supplies cited by Ryznar. It is obvious that the falling index (case A) predicts increased aggressiveness at high temperatures, the rising index (case B) predicts heavier scale, and the horizontal line (case C) predicts uniform protection. Figure 4 also shows that the conventional saturation index would predict increased scaling in
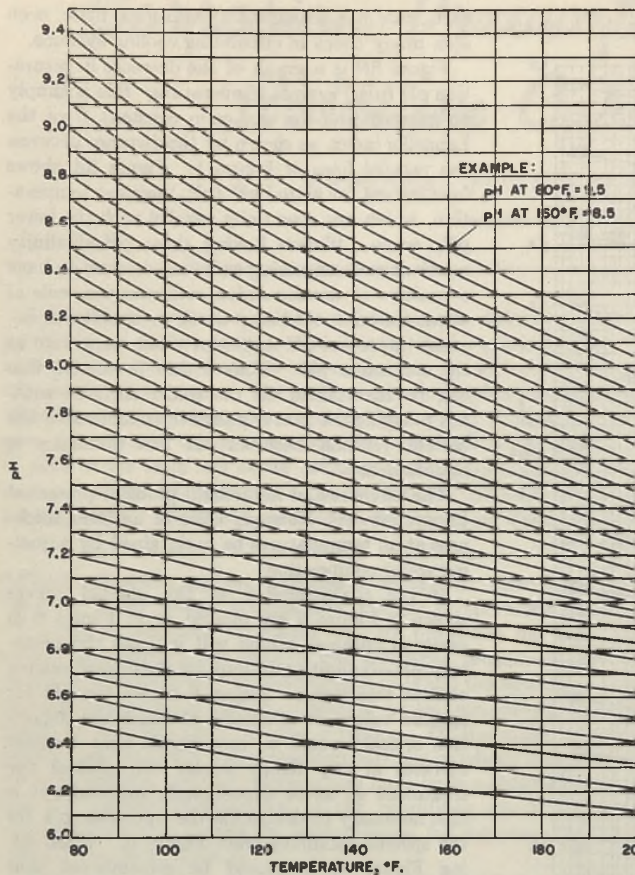
Figure 2. Actual pH (pH_a) vs. Temperature for Water Containing 25 P.P.M. Methyl Orange Alkalinity
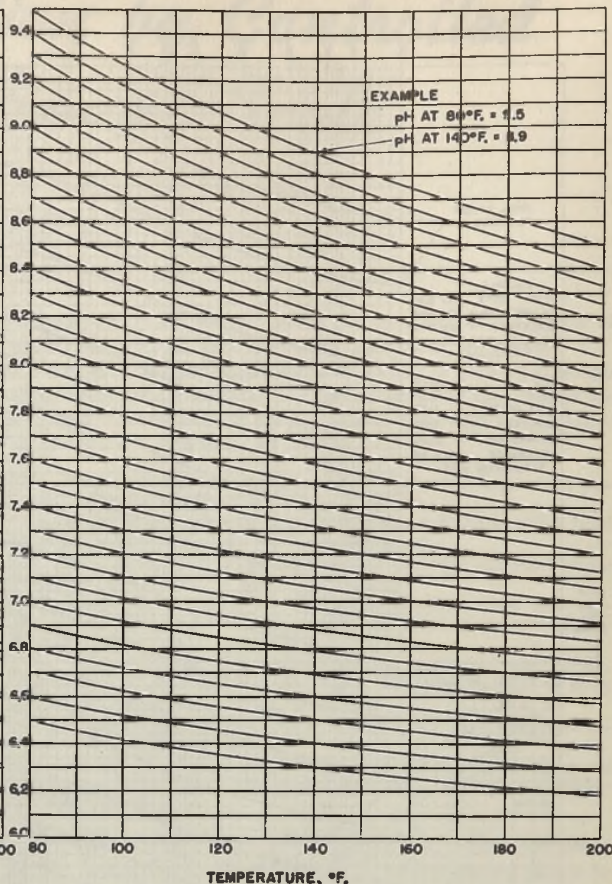
Figure 3. Actual pH (pH_a) vs. Temperature for Water Containing 100 P.P.M. Methyl Orange Alkalinity

The significance of the foregoing is shown by plotting (Figure 7) the coefficient of uniformity of scaling against the deviation in pH at 80° F. from the optimum values shown in Figure 6, for several values of methyl orange alkalinity. Obviously, perfect uniformity is predicted at the intersection of $\Delta pH = 0$ and $\Delta S.I. = 0$. Below and to the left of this point, rising temperature will be accompanied by corrosion or resolution of scale; above and to the right, by heavier scale.

For uniform scaling control by means of the curves shown in Figure 7, the optimum pH for the particular alkalinity in question should be determined from Figure 6 or the tabulation at the lower right of Figure 7. When the optimum pH is established, subtract the actual pH (measured at 80° F.) to obtain the ΔpH value. From this ΔpH on the abscissa of Figure 7, project vertically to the alkalinity curve corresponding to the water supply. The index of uniformity of scaling is now found on the ordinate axis.

Since control exactly at the zero point would be very difficult, it is necessary to consider the latitude in $\Delta S.I.$ that is permissible if acceptable results are to be obtained. The practical answer to this question, from observation of plants which are using the treatment, is reassuring. Table I gives the characteristics of cooling water supplies, including ΔpH and $\Delta S.I.$, for several cooling water systems with notes as to the degree of success experienced. These results are plotted on Figure 7. On this basis a zone of probable good performance is indicated by the shaded area. If the point of intersection between the ΔpH value and the alkalinity falls within this shaded area, the uniformity of scale deposition is likely to be satisfactory. For systems in which the water temperature differential is not greater than about 70° F., the additional chemicals and effort to control the treatment to achieve a zero

Table I. Saturation Index Data for Ten Cooling Water Systems

Plant	Protection	Uniformity	Methyl Orange Alkalinity	Calcium Hardness	Calcd. S.I.	Marble Test	Optimum pH	Actual pH	ΔpH	$\Delta S.I.$
A[a]	Good	Satisfactory	95	112	+1.2	n.d.	9.15	8.60	+0.55	+0.13
B[a]	Excellent	Excellent	90	119	+0.70	+0.30	9.10	8.50	+0.60	+0.15
C[a]	Good	Good	125	224	+0.46	+0.15	9.30	8.80	+0.50	+0.11
D[a]	Good	Satisfactory	136	204	+0.70	+0.50	9.25	8.50	+0.75	+0.17
E[a]	Good	Excellent	135	150	+1.00	+0.50	9.25	8.70	+0.55	+0.12
F[a]	Excellent	Excellent	107	105	+0.69	n.d.	9.20	8.62	+0.58	+0.13
G[b]	Good	Unsatisfactory	188	110	+0.69	n.d.	9.60	8.30	+1.30	+0.25
H[b]	Fair	Unsatisfactory	210	170	+1.30	n.d.	9.70	8.70	+1.00	+0.19
J[b]	Poor	Unsatisfactory	200	250	+1.10	+0.10	9.70	8.30	+1.40	+0.25
K[c]	Poor	Poor	67	90	+0.83	+0.26	8.70	9.00	+0.30	−0.04

[a] Plants A to F obtain protection of both hot and cold surfaces with slightly heavier scale on hot surfaces at those marked "satisfactory".
[b] Plants G, H, and J obtain very slight corrosion of cold equipment, and light to heavy scale in hot equipment; a higher saturation index and lower coefficient of uniformity are indicated.
[c] Plant K experiences scale on colder surfaces but corrosion of hot surfaces; a higher alkalinity to raise the optimum pH would bring the coefficient of uniformity within the positive range.
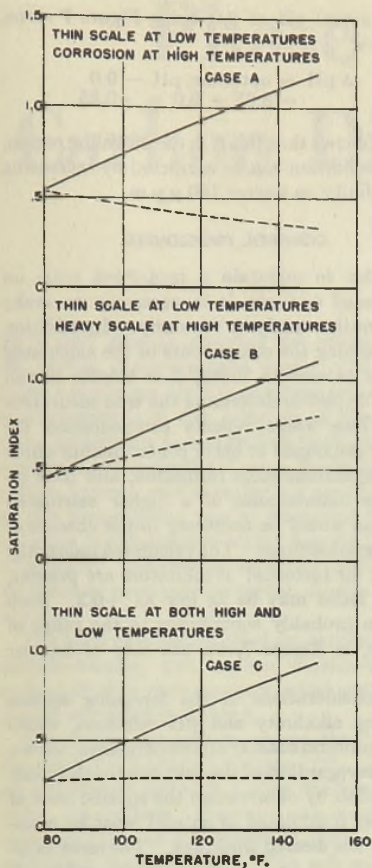
Figure 4. Conventional and Corrected Saturation Index vs. Temperature for Three Water Supplies of Different Chemical Characteristics

—— Saturation Index, 80° to 150° F., calculated from pH measured at 80° F.
· · · Saturation Index corrected for decrease in actual pH between 80° and 150° F.

ΔpH and ΔS.I. value is not always justified. Cases where the temperature differentials are extremely high may require maintenance of a ΔpH value which will result in a ΔS.I. of 0.1 or even less.

An inlet temperature of 80° F. and an outlet temperature of 150° were used as the basis for calculation of Figure 7, as this covers most cooling water systems. It makes no difference if this figure is used for a system with an inlet temperature other than 80° F. or an outlet temperature other than 150° F., as long as the actual pH used is measured at about 80° F.

To adjust the composition of cooling water for production of uniform scale, it may be necessary to vary the hardness with lime or reduce the alkalinity with acid. Frequently the use of caustic soda or soda ash to raise the saturation index gives unsatisfactory results and requires the substitution of lime for a sodium alkali to produce a dense, thin, and uniform scale.

Figure 8 shows the variation of saturation index with temperature for cooling waters at two plants listed in Table I where excellent results are being obtained. One plant produces low-boiling hydrocarbons, the other a copolymer. Both have steel
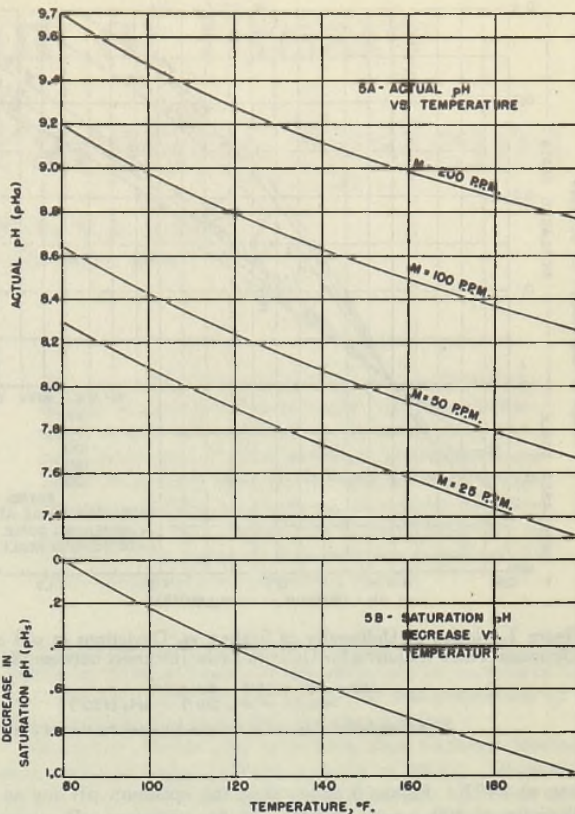

Figure 5. Temperature vs. Saturation pH Decrease and vs. Actual pH for Four Alkalinity Conditions Which Make These Changes Equal as Temperature is Increased

tubular heat exchangers and other water-jacketed equipment using water from a cooling tower. Both report good control of corrosion by a hard, dense scale which is slightly heavier in hotter units, but without significant loss of heat transfer.

EXAMPLES

The following example is given to illustrate the use of Figures 1, 2, and 3 in determining the conventional saturation index and also the corrected saturation index:

Assume a water of the following composition:

P.p.m. as CaCO₃	
Calcium hardness	200
Methyl orange alkalinity	100
Total solids	500
pHₐ at 80° F.	8.3

It is desired to know the S.I. at 80° F. and also at 150° F. From Figure 1:

	80° F.	150° F.
pCa	2.70	2.70
pAlk	2.70	2.70
Constant	2.12	1.50
pHₛ	7.52	6.90
pH at 80° F.	8.30	8.30
Conventional S.I.	+0.78	+1.40
pH at 150° F. (Fig. 3)	...	7.87
Corrected S.I. at 150° F.	...	+0.97

This would mean that from 80° to 150° F. the S.I. would increase +0.19 which would mean appreciably heavier scaling at 150° F

THIS CURVE HOLDS FOR ALL THICKNESSES OF SCALE DEPOSITS AND IS INTENDED TO INDICATE THE CONDITIONS FOR UNIFORM DEPOSITION REGARDLESS OF AMOUNT DEPOSITED.

SATURATION INDEX IS THE CONTROLLING FACTOR FOR THICKNESS.
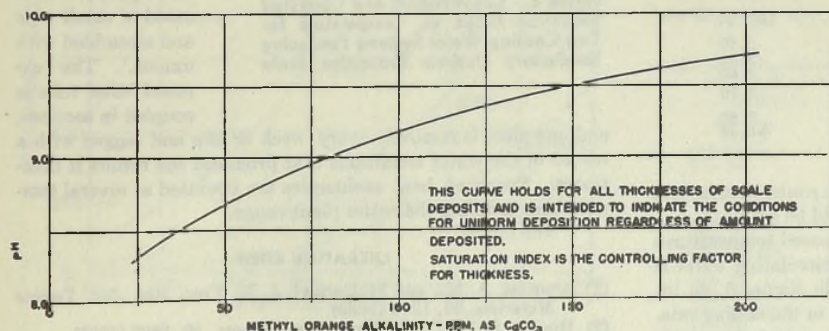
Figure 6. Optimum pH-Alkalinity Relations for Uniform Scale Deposition at All Temperatures
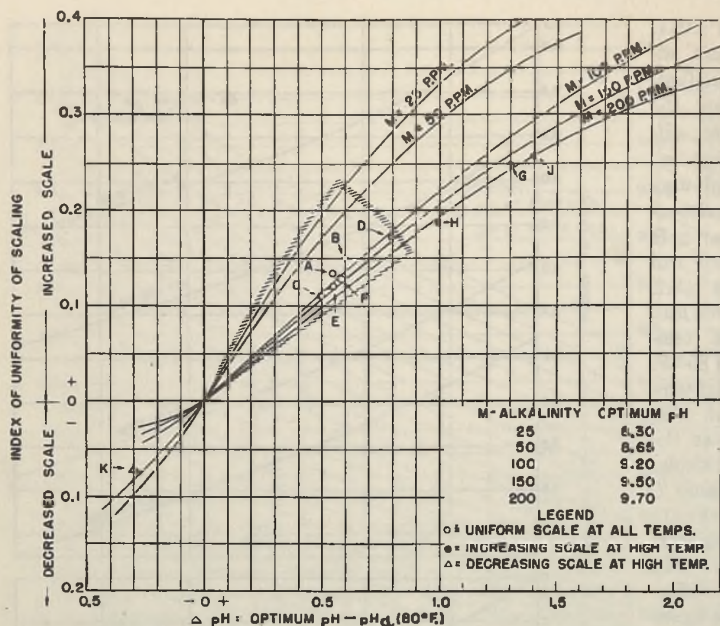
Figure 7. Index of Uniformity of Scaling vs. Deviations in pH at 80° F. from Optimum Value Required for Uniform Scale Thickness between 80° and 150° F.

$$\Delta S.I. = S.I. (150°) - S.I. (80°)$$
$$= 0.64 - pH_s (80°) + pH_s (150°)$$

(Good results are obtained in the area bounded by shaded lines.)

than at 80° F. Figure 6 shows that the optimum pH for an alkalinity of 100 p.p.m. is 9.20. If the optimum pH minus the actual pH at 80° F. is taken on Figure 7 (9.20 − 8.30 = +0.90), the point of intersection of this value (0.9) and the 100 p.p.m. alkalinity curve is at a $\Delta S.I.$ slightly above 0.2 in the increased scaling region.

This hypothetical condition could be corrected either by decreasing the methyl orange alkalinity value, by increasing the pH value, or by changing both conditions. It would be necessary, at the same time, to make some adjustment of the calcium hardness content of the water to keep about the same scaling rate.

If the alkalinity were decreased to 25 p.p.m., the S.I. difference at 80° and 150° F. would be zero and a uniform scale deposition would be expected.

The composition of the water would now be:

Calcium hardness, p.p.m.	320
Methyl orange alkalinity, p.p.m.	25
Total solids, p.p.m.	500
pH	8.3

From Figure 1:

	80° F.	150° F.
pCa	2.50	2.50
palk	3.30	3.30
Constant	2.12	1.50
pH_s	7.92	7.30
pH_a (Fig. 2)	8.30	7.68
S.I.	+0.38	+0.38

It is often impractical to change only one of the controlling factors and in such cases both pH and alkalinity should be adjusted.

Figure 7 shows that actual descaling at increased temperatures is possible. Whenever the actual pH of the circulating water is greater than the optimum pH values given in Figure 6, an increase in temperature will result in a decrease in the scaling rate. Without going through each step of the calculation, this behavior can be shown for a condition of 50 p.p.m. alkalinity

and an actual pH of 9.0, using Figure 7 alone, as follows:

$$\Delta \text{ pH} = \text{optimum pH} - 9.0$$
$$= 8.65 - 9.0 = -0.85$$

Figure 7 shows that this is in the descaling region, and the condition can be corrected by increasing the alkalinity to nearer 100 p.p.m.

CONTROL PROCEDURES

In order to maintain a protective scale on water-cooled surfaces, it is necessary to make simple routine analyses regularly. In addition to determining the components of the calculated Langelier saturation index, it is helpful to run the marble test to determine the true saturation index. This value reflects compensation for organic compounds or other contaminants which inhibit crystalline scale formation, and thus require the maintenance of a higher calculated index than would be necessary in the absence of inhibiting substances. The calculated index may be +1.0, for instance; if inhibitors are present, the true index may be as low as +0.2. Such inhibition probably contributes to the range of tolerance, in Figure 7, on the side of heavier scaling.

The considerations of the foregoing section concerning alkalinity and pH relations, which produce uniform scale at all temperatures, remain applicable regardless of the shift due to inhibitors. It is necessary to establish by observation the specific level at which the saturation index (calculated or actual) must be maintained to produce scale of the desired thickness. The most satisfactory guide is observation of the scale actually deposited on heat exchanger surfaces. Since such inspections require shutting down equipment and forced outages, this is often impractical and other control inspection techniques must be provided. Some operators have installed miniature single-tube heat exchangers, fabricated of small pipe and assembled with unions. The exposed inner tube is coupled in sections,

Figure 8. Conventional and Corrected Saturation Index vs. Temperature for Two Cooling Water Systems Producing Satisfactory Uniform Protective Scale

and one piece is removed every week or two and tagged with a record of the water conditions that produced the results it illustrates. Specimen heat exchangers are operated at several temperatures covering the entire plant range.

LITERATURE CITED

(1) Amorosi, A. M., and McDermet, J. R., *Proc. Am. Soc. Testing Materials*, 39, 1204 (1939).
(2) Hoover, C. P., *J. Am. Water Works Assoc.*, 30, 1802 (1938).
(3) Langelier, W. F., *Ibid.*, 28, 1500 (1936).
(4) Ryznar, J. W., *Ibid.*, 36, 472 (1944).

Phase Behavior of Binary Carbon Dioxide–Paraffin Systems

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IN 1897 Kuenen reported the critical behavior of the binary carbon dioxide–ethane system (*19, 20, 21*). This system forms a minimum-boiling azeotrope and has a critical locus which is characteristic of this behavior as Figure 1 shows. The azeotrope persists up to the critical locus giving a critical azeotrope containing 27 mole % ethane. Since the carbon dioxide–ethane system forms a minimum-boiling azeotrope, one of the purposes of this investigation was to determine the effect on the critical behavior of substituting higher paraffin hydrocarbons for ethane This study provides a basis for further examination of the equilibrium constants for carbon dioxide in complex hydrocarbon mixtures.

The binary systems studied are carbon dioxide–propane, carbon dioxide–butane, and carbon dioxide–pentane. Other binary carbon dioxide systems upon which critical data have been reported are listed in Table I.

The apparatus used to obtain the data was similar to that described by Katz and Kurata (*12*). It consisted primarily of an equilibrium cell with a glass window and suitable tubing and valve connections. Pressure was supplied by a hand pump, using mercury as the confining liquid, and was measured by a calibrated Bourdon gage. The cell was surrounded by an air bath which was agitated by a fan and heated by electric coils. The entire mechanism was mounted on a trunnion and rocked to ensure equilibrium, the mercury in the cell causing severe agitation of the liquid and vapor phases in the cell.

The vapor-liquid equilibria and critical loci of the binary carbon dioxide–propane, carbon dioxide–butane and carbon dioxide–pentane systems have been determined. The complete transition from the carbon dioxide–ethane system which forms constant-boiling mixtures to the carbon dioxide–pentane system which has normal behavior is shown. The experimental data are presented in both graphical and tabulated form.

The temperature was measured by a pair of calibrated copper-constantan thermocouples in series, embedded in the walls of the cell. The volume of the fluid in the cell was determined by a calibrated scale mounted beside the glass window.

The carbon dioxide used came from Pure Carbonic Incorporated and was stated to have a purity of 99.5%. Successive samples were completely absorbed in potassium hydroxide solution. The hydrocarbons were furnished through the courtesy of Phillips Petroleum Company. The propane was stated to have a purity of 99.9%; butane and pentane were 99.0% pure or better. The vapor pressures of the propane and butane checked those of the literature (*4, 5, 10, 11, 22, 25, 27*) to ±5 pounds per square inch, which is within the accuracy of the apparatus. The vapor pressures of pentane were taken from the literature (*3, 24, 26, 31*).

The gas mixtures were analyzed in an Orsat apparatus. The carbon dioxide was absorbed in a 35-40% solution of potassium hydroxide, and the hydrocarbon was determined by difference. The pentane gas mixtures were first diluted with a fixed volume of nitrogen before analysis to prevent the pentane from condensing after removal of the carbon dioxide. Most of the duplicate analyses checked within 0.2% and never differed more than 0.4%.

After the proper technique for taking data had been developed, the temperature of the cell was kept within ±0.5° F. of the value reported. Pressure observations were probably within ±5 pounds per square inch of the true value.

The procedure for charging the cell was as follows: The cell was first evacuated, the lines were flushed out with hydrocarbon,
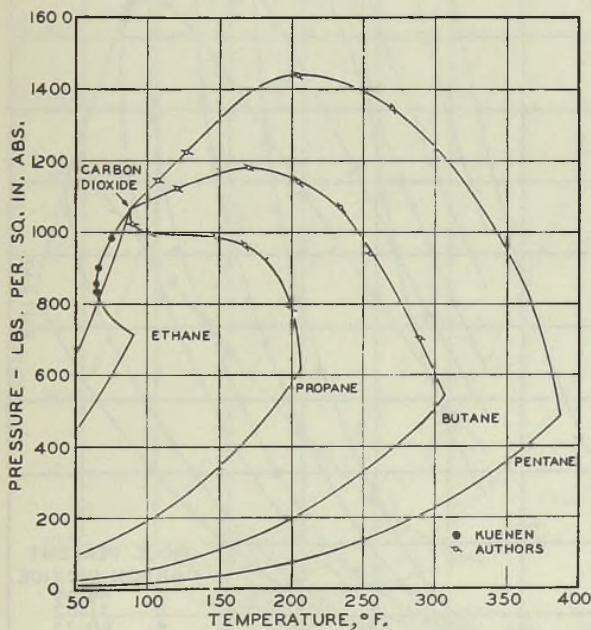
Figure 1. Critical Loci of Carbon Dioxide–Paraffin Systems

TABLE I. BINARY CARBON DIOXIDE MIXTURES

System	Investigators	Citation
CO_2–C_2H_2	Kuenen	(*19*)
CO_2–air	Cailletet	(*6*)
	Van der Waals	(*29*)
CO_2–C_2H_6	Kuenen	(*19, 20*)
	Kuenen and Robson	(*21*)
CO_2–H_2	Vershaffelt	(*28*)
CO_2–HCl	Ansdell	(*2*)
CO_2–CH_3Cl	Kuenen	(*18, 20*)
	Caubet	(*8*)
CO_2–N_2	Andrews	(*1*)
CO_2–N_2O	Caubet	(*8*)
CO_2–$C_6H_5NO_2$	Kohnstamm and Reeders	(*17*)
CO_2–O_2	Keesom	(*14, 15, 16*)
CO_2–SO_2	Caubet	(*7*)
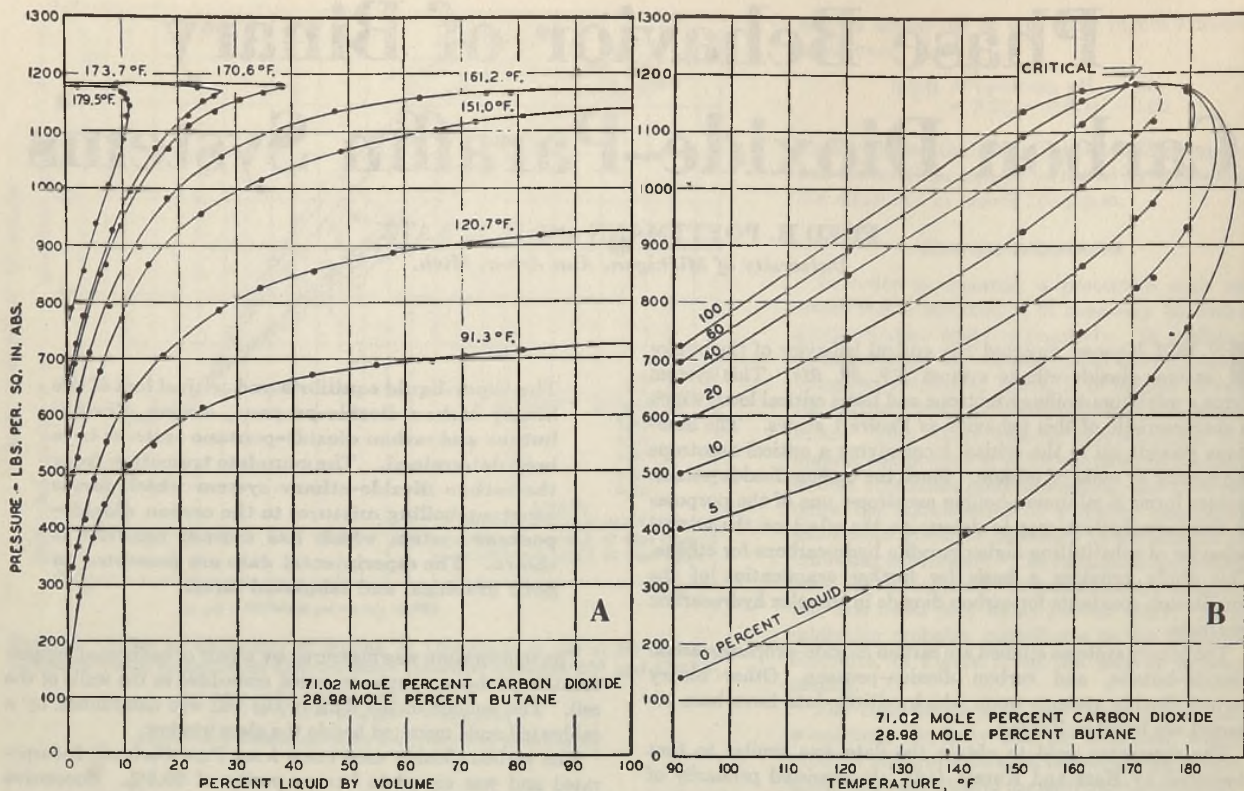
↑ **Figure 2**

↓ **Figure 3**   **Figure 4** →
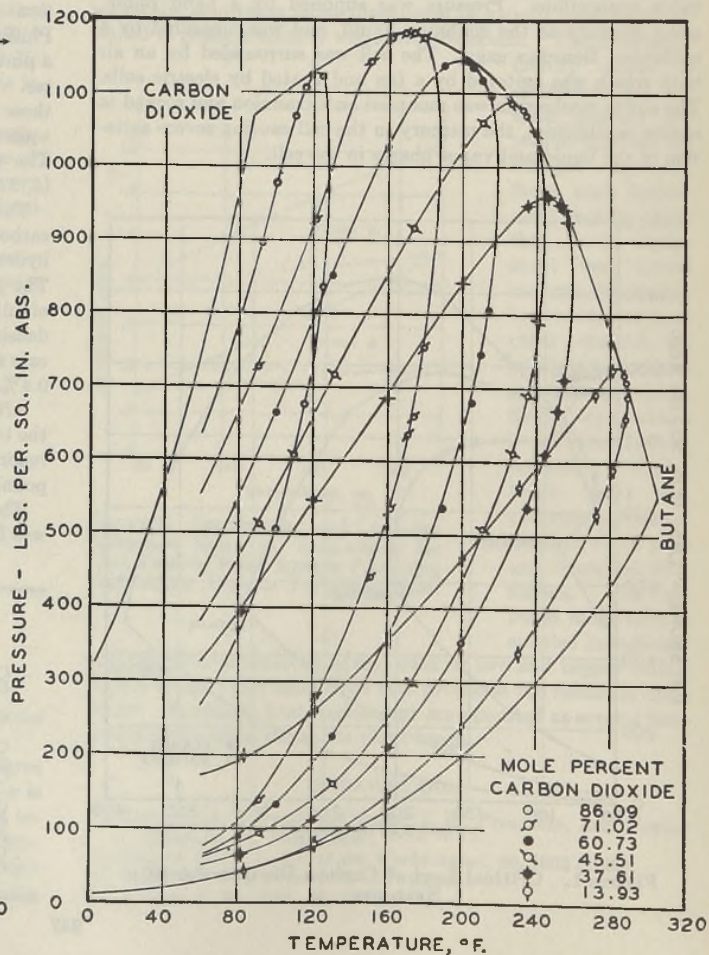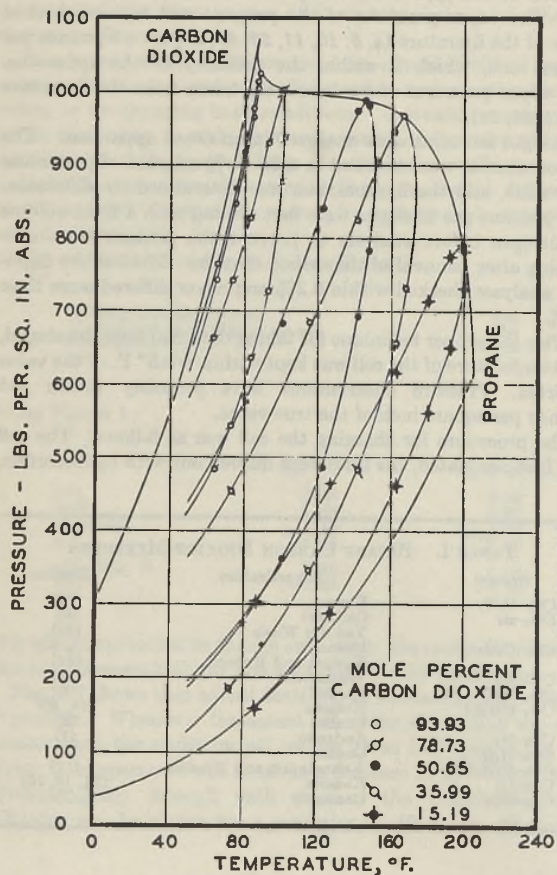
Figure 2.   Isotherms and Phase Diagram of Carbon Dioxide–Butane System

Figure 3.   Pressure-Temperature Diagram for Carbon Dioxide–Propane System

Figure 4.   Pressure-Temperature Diagram for Carbon Dioxide–Butane System

and the cell was filled with liquid hydrocarbon which was allowed to boil off slowly. The cell was again filled with liquid hydrocarbon which was allowed to partially boil off. Carbon dioxide was then added.

The cell was maintained at a constant temperature by a thermostatically controlled air bath. The material charged into the cell was compressed to a single phase by means of the mercury and hand pump. The pressure was then gradually reduced in small increments into the two-phase region by withdrawing

mercury. Observations were made as to the amount of single phase or of vapor and liquid phase at each pressure. The cell was agitated vigorously before the volume and pressure readings were made. Special care was taken to select isotherms which cover retrograde regions as completely as possible.

Three binary systems were studied: carbon dioxide–propane, carbon dioxide–butane, and carbon dioxide–pentane. Six mixtures were studied in both the carbon dioxide–propane and carbon dioxide–butane systems; five mixtures were studied in the carbon dioxide–pentane system.

Figure 2A is a plot of isotherms as pressure against per cent by volume liquid for a mixture containing 71.02% carbon dioxide and 28.98% butane. This diagram and the usual observations provided the bubble and dew point data in Table II (page 851). In most cases the determination of the dew and bubble points by this method gave values which are believed to be correct within the experimental error. However, for some butane and pentane mixtures the dew point may be off as much as 20 pounds per square inch as a result of the rapid change of pressure with very small changes in temperature or per cent liquid by volume.

Figure 2B is a cross plot of 2A and shows the phase behavior of this mixture and the method for locating the critical temperature and pressure by plotting lines of constant per cent by volume liquid.

Figures 3, 4, and 5 show the pressure-temperature diagrams of the three series of binary mixtures. The critical loci for these systems were added to that of the carbon dioxide–ethane system in Figure 1.

The change in the temperature composition diagram as pressure is increased and the change in the pressure-composition diagram as temperature is increased for the systems reported are plotted in Figures 6, 8, and 9. These plots provide the vapor-liquid equilibrium data for the systems.

It is apparent from the critical locus of the carbon dioxide–propane system that the forces tending to form a minimum-boiling azeotrope, as in the carbon dioxide–ethane system, have not yet completely disappeared. This is shown by the sharp downward curvature of the critical locus at the carbon dioxide end of the curve. Thus, the carbon dioxide–propane locus is an intermediate stage between that of the constant-boiling azeotrope type of carbon dioxide–ethane system and the normal systems of carbon dioxide with butane or pentane.

The purpose of Kuenen in studying the carbon dioxide–ethane system was to test the van der Waals theory (30) of binary mixtures. The theory worked very well in predicting the critical temperatures and pressures of carbon dioxide–ethane mixtures (20), but when applied to the systems of carbon dioxide with propane, butane, and pentane, the method was obviously inadequate since many of the calculated critical points did not fall within the range of the coordinates of Figures 3, 4, and 5. The cause
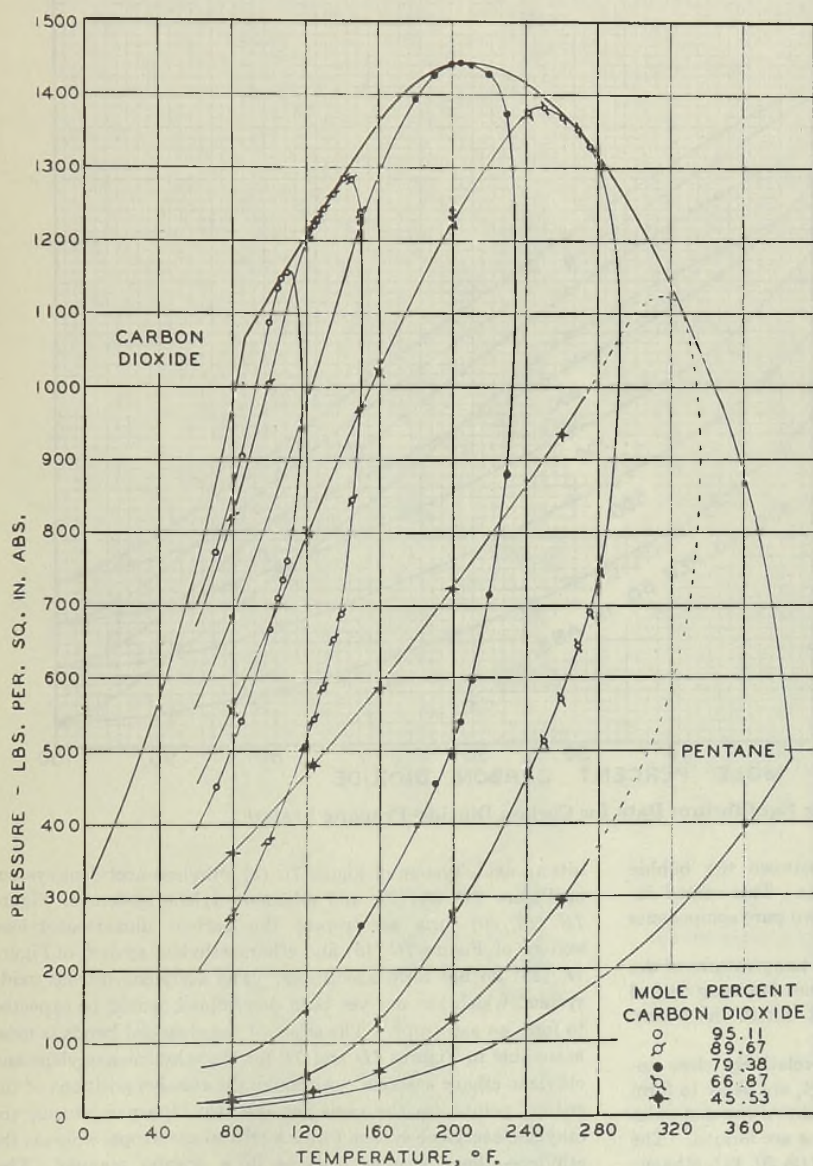
Figure 5.   Pressure-Temperature Diagram for Carbon Dioxide–Pentane System
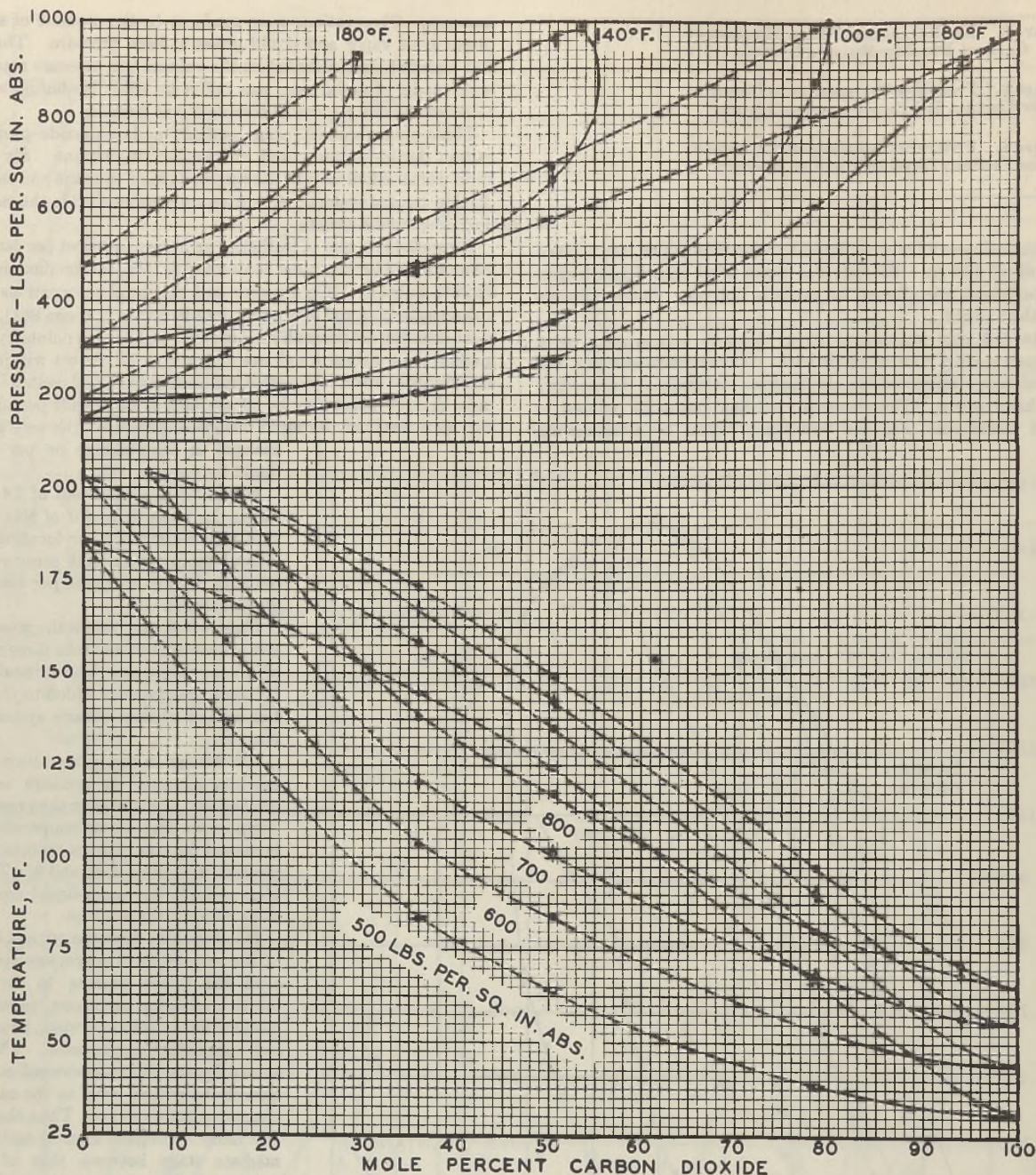
Figure 6. Vapor Equilibrium Data for Carbon Dioxide–Propane System

of this appears to be the great spread between the bubble and dew point curves of the latter mixtures. This spread increases as the vapor pressure curves of the two pure components become more divergent.

It seems that the farther apart the critical temperatures of the pure components are, the less will be the chance of forming critical azeotropic mixtures. This point is brought out in the binary carbon dioxide mixtures studied here.

Components with critical temperatures relatively close together, and those with critical pressures apart, are likely to form azeotropes but not necessarily, since the nature of the molecules and their bonds determine whether azeotropes are formed. The carbon dioxide–ethane system of Figure 7A (19, 20, 21), ethane–nitrous oxide system of Figure 7B (19, 20), carbon dioxide–

nitrous oxide system of Figure 7C (8), ethylene-acetylene system of Figure 7D (9, 13), and ethane-acetylene system of Figure 7E (19, 20) form azeotropes; the carbon dioxide–acetylene system of Figure 7C (15) and ethane-ethylene system of Figure 7F (23) do not form azeotropes. The acetylene–nitrous oxide system, which has not yet been determined, would be expected to form an azeotrope. The effect of the chemical bonds is most noticeable in Figures 7D and 7F for the ethylene-acetylene and ethylene-ethane systems. Although the relative positions of the critical points are the same for the two binary mixtures, the ethylene-acetylene system forms a critical azeotrope, whereas the ethylene-ethane system behaves in a normal manner. This difference is attributed to the nature of the acetylene molecule.

TABLE II. SUMMARY OF EXPERIMENTAL DATA

Compn., Mole %	Temp., ° F.	Pressure, Lb./Sq. In. Abs. Bubble point	Dew point
CARBON DIOXIDE–PROPANE			
78.73 CO_2–21.27 C_3H_8	63.1	661	484
	72.7	739	541
	83.7	825	635
	93.0	927	725
	100.6	996	876
	101.5	..	935, 1001.5
	101.4 (crit.)	1002	
35.99 CO_2–64.01 C_3H_8	72.4	452	182
	115.0	685	348
	141.8	824	483
	153.3	904	570
	162.0	944	655
	167.5	..	730, 967
	166.1 (crit.)	967	
50.65 CO_2–49.35 C_3H_8	80.1	575	275
	100.7	680	360
	122.7	837	485
	141.9	972	690
	147.8	..	982, 780
	146.9 (crit.)	986	
15.19 CO_2–84.81 C_3H_8	87.0	304	159
	127.7	464	288
	163.0	615	462
	180.3	712	560
	192.6	775	650
	200.1	..	783, 728
	199.4 (crit.)	790	
96.01 CO_2–3.99 C_3H_8	78.3	926	912
	84.0	994	979
	87.3	1031	1024
93.93 CO_2–6.07 C_3H_8	64.8	763	740
	75.1	865	846
	80.0	915	903
	85.1	976	963
	87.3	1012	1003
	88.0	1018	1010
	88.2 (crit.)	1022	
CARBON DIOXIDE–BUTANE			
45.51 CO_2–54.49 C_4H_{10}	90.2	512	96
	131.0	715	162
	172.8	915	298
	210.2	1059	508
	226.7	1087	612
	234.8	..	1072, 689
	240.2	..	1046, 790
	233.5 (crit.)	1077	
71.02 CO_2–28.98 C_4H_{10}	91.3	725	140
	120.7	925	278
	151.0	1139	445
	161.2	1173	535
	170.6	..	1183, 632
	173.7	..	1183, 663
	179.5	..	1178, 754
	169.0 (crit.)	1181	
86.09 CO_2–13.91 C_4H_{10}	92.6	895	445
	99.9	976	505
	110.0	1066	609
	115.4	1104	675
	120.2	..	1124, 748
	125.0	..	1122, 835
	119.5 (crit.)	1122	
60.73 CO_2–39.27 C_4H_{10}	80.1	540	88
	100.2	665	133
	130.8	850	224
	160.5	1025	363
	190.0	1135	536
	200.5	1143	636
	205.3	..	1132, 679
	210.1	..	1115, 745
	215.0	..	1095, 804
	203.0 (crit.)	1140	
37.61 CO_2–62.39 C_4H_{10}	81.8	393	65
	120.2	545	111
	160.5	683	209
	200.0	840	352
	236.3	945	536
	245.0	959	609
	251.7	946	668
	255.2	..	925, 711
	254.0 (crit.)	940	
13.93 CO_2–86.07 C_4H_{10}	83.4	198	42
	121.0	269	77
	160.3	355	144
	200.0	469	240
	230.5	565	340
	272.2	690	527
	281.0	725	590
	288.1	719	659
	289.8	..	704, 688
	288.8 (crit.)	709	
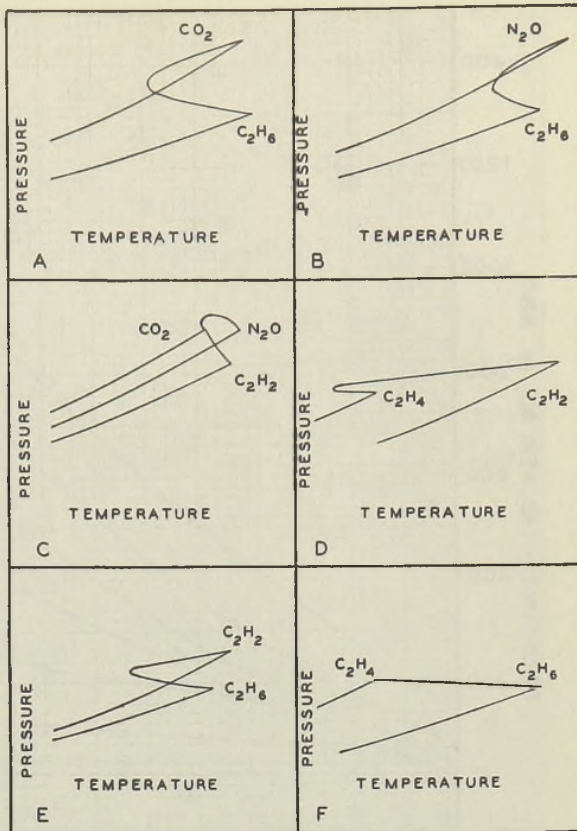
Figure 7. Critical Loci of Binary Systems

TABLE II (Continued)

Compn. Mole %	Temp. ° F.	Pressure, Lb./Sq. In. Abs. Bubble point	Dew point
CARBON DIOXIDE–PENTANE			
95.11 CO_2–4.89 C_5H_{12}	71.9	772	450
	85.3	904	541
	100.3	1086	668
	105.4	1134	710
	107.5	..	1150, 735
	110.0	..	1157, 760
	107.0 (crit.)	1148	
89.67 CO_2–10.33 C_5H_{12}	80.0	822	275
	100.0	1003	378
	120.0	1201	509
	125.0	1220	544
	129.9	..	1241, 586
	134.8	..	1264, 652
	140.3	..	1283, 688
	145.0	..	1283, 845
	150.3	..	1238, 972
	126.5 (crit.)	1228	
79.38 CO_2–20.62 C_5H_{12}	80.0	685	76
	120.0	970	145
	150.0	1225	260
	180.2	1391	400
	190.0	1429	455
	200.0	1441	490
	205.0	..	1441, 540
	210.1	..	1440, 597
	220.0	..	1431, 715
	229.9	..	1374, 880
	203.5 (crit.)	1441	
66.87 CO_2–33.13 C_5H_{12}	79.8	555	24
	121.1	799	55
	160.2	1017	124
	200.0	1223	272
	241.5	1378	470
	250.6	1383	512
	259.9	1368	570
	268.8	1353	645
	275.3	..	1330, 689
	280.8	..	1304, 747
	269.0 (crit.)	1352	
45.53 CO_2–54.47 C_5H_{12}	80.2	360	20
	123.8	480	35
	160.2	585	60
	200.0	721	180
	260.1	934	293

Figure 8.   Vapor Equilibrium Data for Carbon Dioxide–Pentane System

Figure 9.   Vapor Equilibrium Data for Carbon Dioxide–Butane System

LITERATURE CITED

(1) Andrews, *Trans. Roy. Soc.* (London), **178**, 45 (1887).
(2) Ansdell, *Proc. Roy. Soc.* (London), **34**, 113 (1882).
(3) Beall, *Refiner Natural Gasoline Mfr.*, **14**, 588 (1935)..
(4) Beattie, Kay, and Kaminsky, *J. Am. Chem. Soc.*, **59**, 1509 (1937).
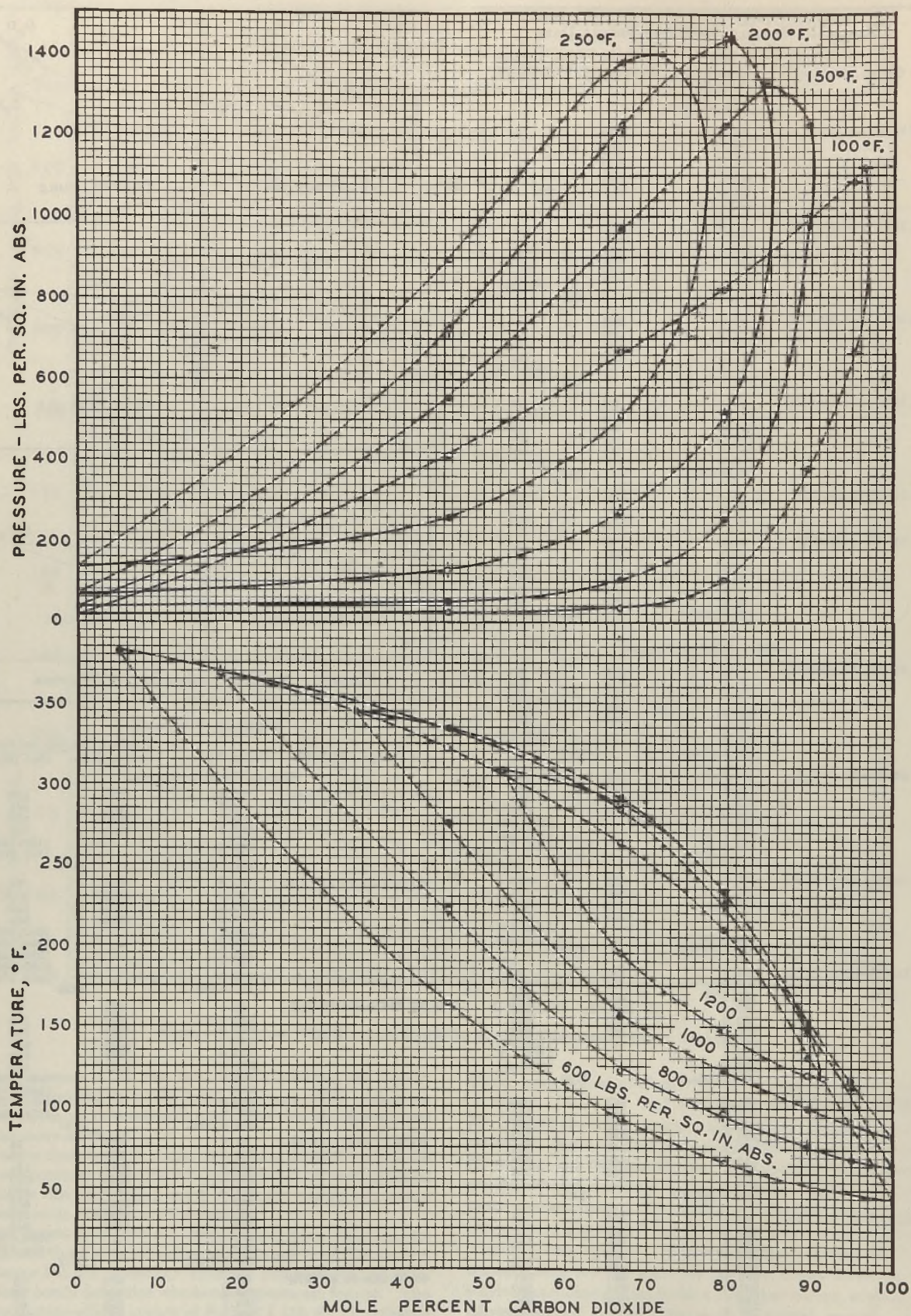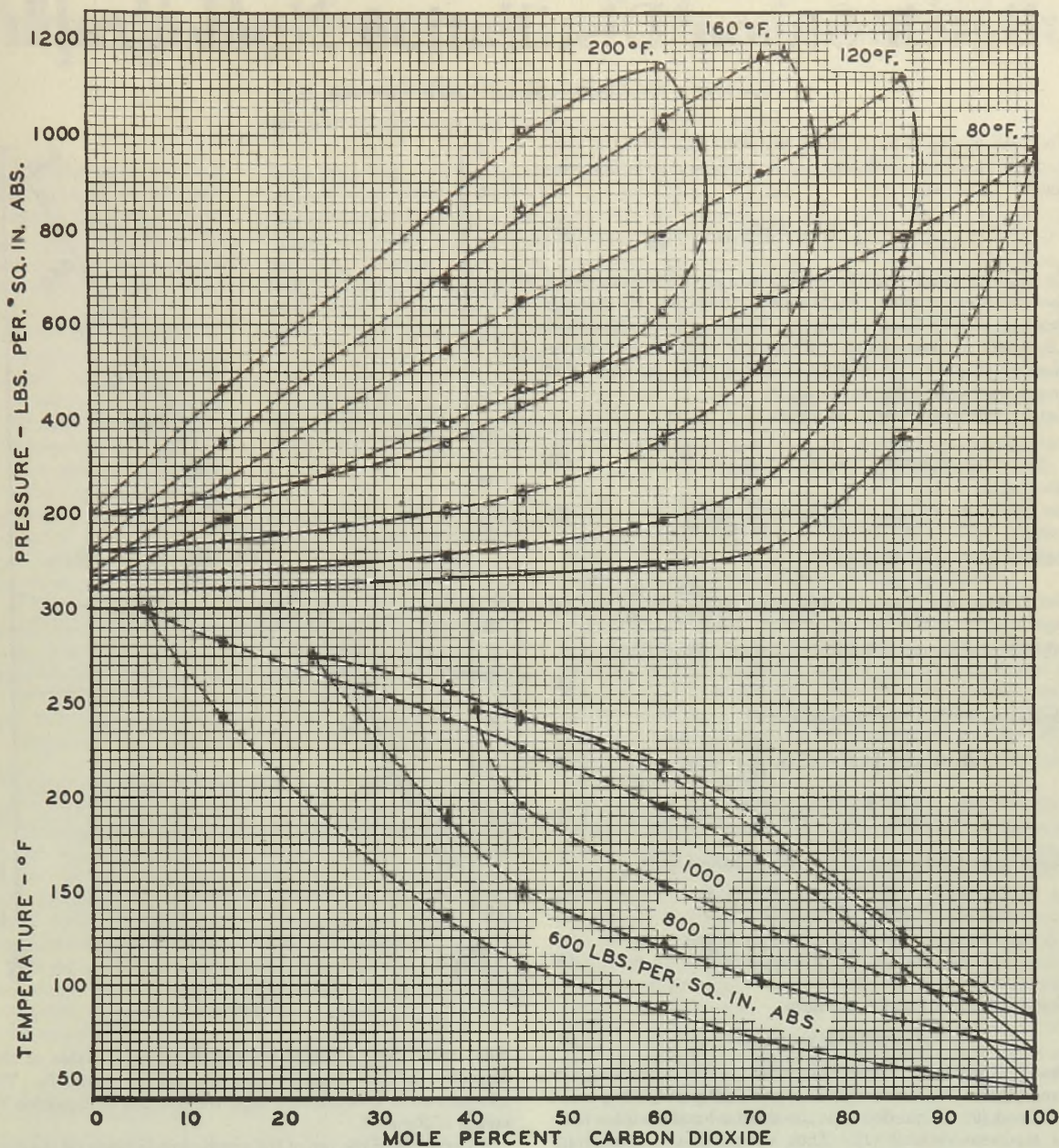(5) Beattie, Simard, and Gouq-JenSu, *Ibid.*, **61**, 25 (1939).
(6) Cailletet, *Compt. rend.*, **90**, 210 (1880).
(7) Caubet, *Z. physik. Chem.*, **40**, 257 (1902).
(8) *Ibid.*, **49**, 101 (1904).
(9) Churchill, Collamore, and Katz, *Oil Gas J.*, **39**, No. 28, 34 (1942).
(10) Dana, Jenkins, Burdick, and Timm, *Refrig. Eng.*, **12**, 387 (1926).
(11) Deschner and Brown, IND. ENG. CHEM., **32**, 836 (1940).
(12) Katz and Kurata, *Ibid.*, **32**, 817 (1940).
(13) Katz and McCurdy, *Ibid.*, **36**, 674 (1944).
(14) Keesom, *Commun. Phys. Lab. Univ. Leiden*, No. 88 (1903).
(15) Keesom, *Physik. Ber.*, [II] **60**, 668 (1904).
(16) Keesom, *Proc. Acad. Sci. Amsterdam*, **6**, 532 (1903).
(17) Kohnstamm and Reeders, *Arch. néerland. Sci.*, [IIIA] **2**, 63 (1912).

(18) Kuenen, J. B., *Commun. Phys. Lab. Univ. Leiden*, No. 4 (1892).
(19) Kuenen, J. B., *Phil. Mag.*, **44**, 174 (1897).
(20) Kuenen, J. B., *Z. physik. Chem.*, **24**, 667 (1897).
(21) Kuenen and Robson, *Phil. Mag.*, **4**, 116 (1902).
(22) Meyers and Van Duesen, *Bur. Standards J. Research*, **10**, No. **3** (1933).
(23) Quinn, D. Sc. thesis in chem. eng., Mass. Inst. Tech., 1940.
(24) Sage and Lacey, IND. ENG. CHEM., **34**, 730 (1942).
(25) Sage, Schaafsma, and Lacey, *Ibid.*, **26**, 1218 (1934).
(26) *Ibid.*, **27**, 48 (1935).
(27) Sage, Webster, and Lacey, *Ibid.*, **29**, 118 (1937).
(28) Vershaffelt, *Commun. Phys. Lab. Univ. Leiden*, No. 47 (1899).
(29) Waals, van der "Kontinentat der gasformigen und flussigen Zustandes", Orig. 1873, Leipzig, Barth, 1881;   English translation of Phys. Mem. I Phys. Soc. (London), 1888.
(30) Waals, van der, *Z. physik. Chem.*, **5**, 133 (1890).
(31) Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

Batch Steam Distillation Nomograph

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IN THE theory of batch steam distillation of a volatile component from its solution in a nonvolatile liquid, the following equation (2) appears:

$$S = \left(\frac{P}{EP_B} - 1 \right)(B_1 - B_2) + \frac{PO}{EP_B} \ln \frac{B_1}{B_2} \qquad (1)$$

This equation applies to the case of a nonvolatile component present in large amount, on the assumption that the volatile component follows Raoult's law. If Equation 1 is to be solved for B_2, a trial and error solution is required. This paper presents a nomographic solution which eliminates trial and error and permits rapid calculations to be made.

Let us define variables S_1 and S_2 as

$$S_1 = \left(\frac{P}{EP_B} - 1 \right) B_1 + \frac{PO}{EP_B} \ln \frac{B_1}{O} \qquad (2)$$

$$S_2 = \left(\frac{P}{EP_B} - 1 \right) B_2 + \frac{PO}{EP_B} \ln \frac{B_2}{O} \qquad (3)$$

Subtracting (3) from (2) gives

$$S_1 - S_2 = \left(\frac{P}{EP_B} - 1 \right)(B_1 - B_2) + \frac{PO}{EP_B} \ln \frac{B_1}{B_2} \qquad (4)$$

Comparison of Equation 4 with Equation 1 shows that

$$S = S_1 - S_2 \qquad (5)$$

Equations 2 and 3 can be rewritten as

$$B_1 = \frac{P}{EP_B} \left(B_1 + O \ln \frac{B_1}{O} \right) - S_1 \qquad (6)$$

$$B_2 = \frac{P}{EP_B} \left(B_2 + O \ln \frac{B_2}{O} \right) - S_2 \qquad (7)$$

or dividing both sides of each of these equations by O,

$$\frac{B_1}{O} = \frac{P}{EP_B} \left[\frac{B_1}{O} + \ln \frac{B_1}{O} \right] - \frac{S_1}{O} \qquad (8)$$

$$\frac{B_2}{O} = \frac{P}{EP_B} \left[\frac{B_2}{O} + \ln \frac{B_2}{O} \right] - \frac{S_2}{O} \qquad (9)$$

Equations 8 and 9 are of the form:

$$f(x) = F(x) \cdot \phi(y) + \psi(z) \qquad (10)$$

where B_1/O and B_2/O, respectively, play the role of variable x in (8) and (9), P/EP_B corresponds to y, and S_1/O and S_2/O represent z in (8) and (9). Equation 10 is the standard nomographic form for a recurrent variable (1). Thus, we can plot a nomograph consisting of three axes: B/O, S/O, and P/EP_B, which can be used once to represent Equation 2, and again to represent Equation 3. The resulting nomograph, Figure 1, may be used in either of the following ways:

If it is desired to calculate steam requirements for a given change in still composition, draw straight lines between the point on the P/EP_B axis and the two known points on the B/O axis. These two lines will intersect the S/O axis at two values, the difference between them representing the desired value of S/O. The steam requirement is found by multiplying this value by O.

If it is desired to determine the number of moles of volatile component B_2 remaining in the still after S moles of open steam have been used on a solution originally containing B_1 moles of volatile component, draw a line between P/EP_B and B_1/O. The intersection of this line with the S/O axis represents S_1/O. Subtract S/O, the ratio of moles of steam used to the number of moles of nonvolatile component, and thus determine S_2/O, another point on the S/O axis. The line connecting this latter
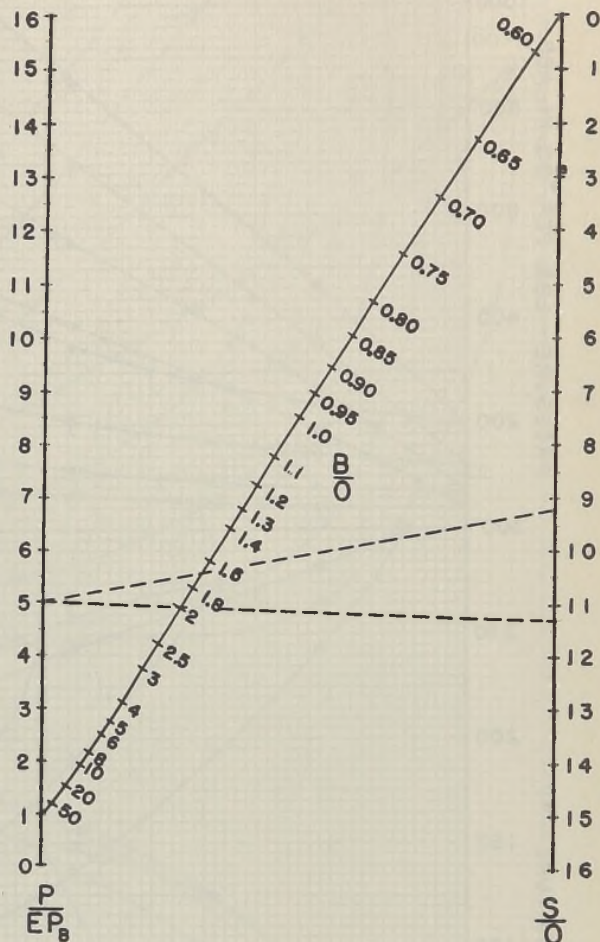
Figure 1

point with P/EP_B passes through the desired value of B_2/O. Multiply B_2/O by O and obtain the desired value, B_2. Thus, trial and error is eliminated from the solution of Equation 1 by means of Figure 1.

An example of the use of the nomograph is given by the dotted lines which indicate that, if $P/EP_B = 5.0$, $B_1 = 2.0$, and $S/O = 2.05$, then $B_2/O = 1.7$.

NOMENCLATURE

S = total moles of open steam used
B = total moles of volatile component present in still at any time
O = total moles of nonvolatile component in still (constant)
P_B = vapor pressure of pure volatile component
P = total pressure
E = vaporization efficiency = $\dfrac{(p_B) \text{ actual}}{(p_B) \text{ equilibrium}}$
p_B = partial pressure of volatile component

LITERATURE CITED

(1) Perry, J. H., Chemical Engineer's Handbook, 2d ed., p. 259 (1941).
(2) *Ibid.*, p. 1389.

Alkali Resistance of the Iron Blues

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New iron blues have appeared on the market, with increased resistance to alkaline environments, resulting from the addition of nickel salts during manufacture. Since iron blues have been formulated as salts of a polynuclear "berlinic acid", investigations were undertaken into the possibility of forming nickel and other metallic berlinates. No general stoichiometry was found for the latter; in fact, the usual formulas for the iron blues did not apply under the experimental conditions. A marked improvement in alkali resistance was obtained by nickel salt additions. A theory is advanced for the action of the latter. The literature on the constitution of the iron blues is reviewed and discussed briefly and critically.

EVER since the accidental discovery of iron blue in 1704 by Diesbach, a Berlin color manufacturer, this bright-colored substance has been in great demand by the industries and the arts. In 1939, 7,437,542 pounds were manufactured in this country (37) and sold for paints, lacquers, printing inks, laundry chalks, and other color uses; this figure does not include an approximate 2,000,000 pounds of iron blue combined with lead chromate in the so-called chrome greens. The continued popularity of this pigment has been due to its low cost, excellent light fastness, deep bright shade, high color strength, and resistance to the action of water, organic media, and acids.

Its outstanding defect has been the high sensitivity to even mild alkalies which destroy the color and form brownish hydrous oxides of iron and soluble complex iron cyanide compounds. This sensitivity has limited the use of iron blue to applications which do not involve exposure to alkaline environments. Attempts have been made, by various modifications in manufacturing procedures, to obtain products of reduced sensitivity (7, 34, 36, 38, 43).
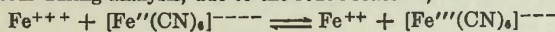
Recently iron blues of improved "alkali resistance" have appeared on the market, and patents have been granted on the use of salts of nickel, as well as of cobalt, to attain this end (34, 36, 38, 43). Iron blues have been formulated (11) as salts of a polynuclear "berlinic acid", $H[Fe''(CN)_6Fe''']$. An interesting problem of chemical structure arises, with the possibility of the formation of nickel and other metallic berlinates with properties differing from those of the ferrous and ferric compounds.

This paper records experimental work directed along these lines, correlated with an extensive literature survey, in an attempt to establish a theoretical basis for the improved alkali resistance of the nickel blues.

CONSTITUTION OF IRON BLUES

A study of the literature of the iron blues discloses considerable controversy and confusion. Although many investigators have attacked the problem during the past fifty years, there is still disagreement, even as to whether the iron blues are to be considered ferrocyanide or ferricyanide compounds. The early identification of Prussian blue as ferric ferrocyanide, $Fe_4[Fe''(CN)_6]_3$, and Turnbull's blue as ferrous ferricyanide, $Fe_2[Fe'''(CN)_6]_2$, was later cast aside in favor of the formulation of both substances as ferrocyanides but alternatively by other investigators as ferricyanides, and was then later generally accepted as ferrocyanides. However, the latest paper on the subject (42) veers back to a ferricyanide formulation for both.

This confusion is not surprising when the experimental difficulties involved in these studies are considered. The conventional analytical methods pursued by a number of investigators have led to erroneous conclusions as to composition, for the following reasons: (a) Considerable change in the original formula may occur during analysis, due to the redox reaction,

$$Fe^{+++} + [Fe''(CN)_6]^{----} \rightleftharpoons Fe^{++} + [Fe'''(CN)_6]^{---}$$

which at equilibrium is displaced largely to the right (2?). (b) The strongly colloidal character of the blues, with accompanying pronounced adsorption effects, results generally in impure gels (1). (c) The failure of most investigators to take adequate account of the pH relations during preparation of the blues results in coprecipitation of the hydrous oxides of iron (39). (d) Hydrolysis may occur during washing of the prepared blues (4, 16). In consequence, the formulas given—for example, $[Fe(CN)_6KH_2]\cdot Fe(OH)_2$ (18) —should be considered merely as a convenient form for statement of the analytical results. Various indirect methods of investigation have been resorted to, in attempts to avoid analytical pitfalls, but much of this work is subject to one or more of the criticisms listed above.

The earliest published attempt at elucidation of the structure of the iron blues (that of Stahl in 1731) offered a simple explanation in line with the then current theory. The substance was said to consist of "phlogiston combined with precipitated iron" (10). The more experimental work of Macquer, Scheele, Berthollet, Berzelius, Gay-Lussac, Williamson, and others gradually led to a better understanding of the composition, and by 1877 the iron blues had been assigned structures which were little altered by later investigators (35, 46).

Hofmann and co-workers published a series of papers between 1904 and 1907 (17–20), reporting extensive investigations on methods of preparation, and assigned structures based on the analytical results and the methods of preparation. However, their conclusions as to structure are largely vitiated by a lack of understanding of the disturbing factors outlined above. Corroborating the earlier conclusions of Skraup (35), Hofmann reported the soluble Prussian and Turnbull's blues to be both ferrocyanides, identical in structure; but he assigned varied, rather complex formulas to the insoluble blues.

Muller and co-workers, in a number of papers from 1908 to 1922 (24–29) pointed out that the formulation of structure on the basis of analysis is improper because of the probable occurrence of a redox reaction upon chemical treatment of the blues. He adopted an indirect method of arriving at the compositions of iron blue precipitates based, not on "strict proof", but on probability. Solutions of the reactants were mixed in various proportions, the compositions of the supernatant liquors were analyzed, and the formulas for these blues were then calculated. By this procedure Muller found, in agreement with Hofmann, that the iron blues, of both the Prussian and Turnbull types, were ferrocyanides. The soluble blues were stated to be identical, $KFe^{+++}[Fe''(CN)_6]$, whereas the insoluble blues were different, Prussian blue being $Fe^{+++}_4[Fe''(CN)_6]_3$ and Turnbull's blue $KFe^{++}Fe^{+++}_3[Fe''(CN)_6]_3$. A series of compounds was listed as forming when varying quantities of Fe^{++} and $[Fe'''(CN)_6]^{---}$ were mixed—e.g., $KFe_2^{++}Fe^{+++}_5[Fe''(CN)_6]_5$, $KFe^{++}Fe^{+++}_3[Fe''(CN)_6]_3$, etc.; they were assumed to form solid solutions.

Papers by Woringer (44, 45) and Eibner and Gerstacker (13), appearing during the same period, disagreed with Muller's conclusions as to the ferrocyanide structure; they preferred a ferricyanide formulation for the iron blues, and a controversy arose over this fundamental point.

Later Weiser (39) pointed out that analysis of a gel, whether by
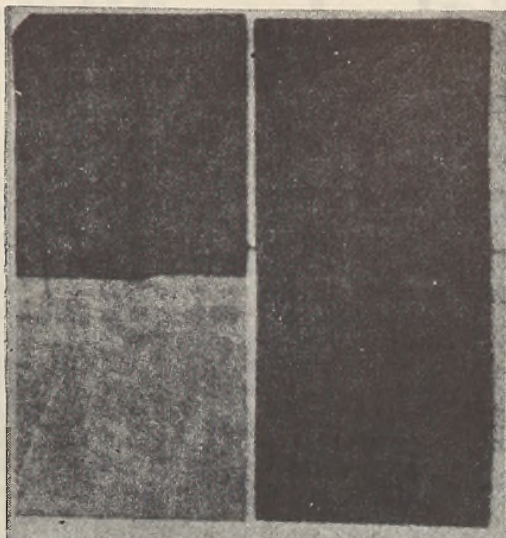
Lithographic Varnish Prints, on Bond Paper of an Ordinary Iron Blue (*left*) and an Alkali-Resistant (Nickel-Type) Blue (*right*), after the Lower Half Had Been Immersed in 1% Aqueous Caustic Soda for One Hour; Left-Hand Print Completely Decolorized in 15 Minutes

direct or indirect methods, does not give sufficient data to establish the existence of definite compounds, when a gel with strong adsorptive capacity is precipitated. The compounds claimed by Muller and others must therefore be regarded sceptically. Prussian blues adsorb ferrocyanide ion even in the presence of metallic cations, and it has been demonstrated that large amounts of the ferrocyanide may be adsorbed—of the order of 0.6 to 0.8 mole per mole of heavy metal ferrocyanide (*40*).

Weiser also directed attention toward the probability of formation of hydrous ferric oxides under the conditions of precipitation (*39*). In this connection, the colloidal studies of Rabinerson (*30*) on the flocculation of negative Prussian blue sols by positive sols of hydrous ferric oxide are of great interest. Rabinerson demonstrated that a surprisingly sharp end point for complete mutual precipitation occurred when a definite ratio was reached (33 millimoles of ferric oxide sol to 67 millimoles of blue sol) in the experiments.

Polynuclear structures for the iron blues have been proposed by several (*8, 11, 14, 31, 33*) as offering better explanations for the color, conductivity, and general reactions of these compounds. While these authors support a polynuclear formulation, they do not agree on the type of structure. This hypothesis appears to be supported by x-ray analysis (*2, 21, 22, 32, 42*) and by the anomalous reactions of other heavy metal ferrocyanides (*14, 31*), although not by magnetic measurements (*12*). The possible coordination structures were outlined by Davidson, who proposed as most probable a three-dimensional supercomplex, formed by coordination of ferric atoms with nitrogens and containing the recurring unit —Fe''—CN—Fe'''—.

In accordance with the polynuclear formulation, soluble blue would be written as $K[Fe''(CN)_6Fe''']$, Prussian blue as $Fe^{+++}-[Fe''(CN)_6Fe''']_3$, and Turnbull's blue as $Fe^{++}[Fe''(CN)_6-Fe''']_2$ or $KFe^{++}[Fe''(CN)_6Fe''']_3$. These compounds might thus be considered as salts of a monobasic acid, $H[Fe''(CN)_6-Fe''']$, named "berlinic acid" by Davidson (*11*), whereby soluble blue would be designated "potassium berlinate".

In recent years the application, by a number of workers, of physical methods to the study of iron blues has led to interesting results. Reference has already been made to x-ray studies which have indicated the identical structure of Prussian and Turnbull's blues. Absorption spectra (*3*) and magnetic susceptibility methods (*5*) have also been used; experimental evidence has shown that the structures of the two blues tend to approach the same composition upon aging. Bhattacharya and Dhar, from a series of adsorption and aging studies (*6*), concluded that the compositions of Prussian and Turnbull's blues both tended to approach the formula $Fe_2(CN)_5$.

The latest papers on the composition of iron blues, by Weiser and co-workers (*41, 42*), apply x-ray diffraction, colloidal, and analytical methods to the problem. Prussian and Turnbull's blues are stated to be chemically identical but are formulated as ferrous ferricyanides, $Fe_3[Fe'''(CN)_6]_2$; thus the ferrocyanide formulations of iron blue are reversed, and the ferrocyanide-ferricyanide controversy is reopened without consideration of the polynuclear theories of structure.

The question as to whether the iron blues are ferrocyanides or ferricyanides becomes meaningless when iron blue is considered, as suggested by Emeleus and Anderson (*14*), to be a resonating system (a hybrid of ferric-ferrocyanide and ferrous-ferricyanide forms) which can be mutually interchanged merely by transfer of electrons within the complex:

$$[Fe''(CN)_6Fe''']^- \longleftrightarrow [Fe'''(CN)_6Fe'']^-$$
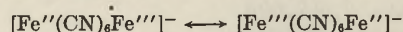
This system would be part of a condensed macromolecular three-dimensional structure. A statistical distribution of resonating forms should result, depending on the relative electron density distribution; differing proportions of each form should be present, as a result of the marked differentiation between the Fe—C and N—Fe coordination bonds in the structure.

The work of Keggin and Miles (*21*) on the x-ray analysis of commercial as well as laboratory preparations of iron blue pigments is of special interest in this connection. These workers found the iron blues to possess a cubic crystalline structure in which iron atoms, not distinguishable as ferrous or ferric, are arranged at the corners of the cubes, while alkali atoms are inserted into the centers of alternate cubes; the chemical composition of the whole is equivalent to a structure $RFeFe(CN)_6$, where R may be an alkali or an ammonium ion.

COMMERCIAL CLASSIFICATION

The commercial iron blue pigments may be classified into a number of diverse types adapted for specific uses and possessing widely varying shades, oil absorptions, textures, etc. Descriptions of these types and general methods for their manufacture have been outlined in the literature (*15, 23*) and will be only briefly discussed here.

The general method of manufacture consists in the aqueous reaction of sodium ferrocyanide with ferrous sulfate in the presence of relatively large amounts of ammonium sulfate, followed by oxidation with sodium chlorate (chloric acid), bichromate, or other oxidizing agents, at various pH values. Variations in physical factors, such as dilution, rate of additions, time of stirring between additions, temperature before and after oxidation, etc., together with alterations in the relative proportions of ingredients, type of oxidizing agent employed, acidity, addition at various stages of other ions, etc., produce an almost limitless number of products which vary in shade and physical properties. As a result of the requirements of the consuming industries, commercial iron blues have become standardized into three main groups, the individual members of which, however, may vary widely: the clean, greenish-blue shade Chinese and Milori blues; the deep, more reddish, so-called Prussian blues; and the toning blues, of very reddish-blue shade, used mainly for toning carbon black inks. There should be included also the soluble blues, used to make laundry bluing and prepared by peptization of insoluble blues with sodium ferrocyanide and oxalic acid.

To tie in with the literature on the constitution of the iron blues, the term "soluble blue" has been used in the earlier part

TABLE I. SOLUBLE BLUES

Blue No.	Type Blue[a]	Method of Preparation	Tests for Uncombined Ions[b]					Remarks
			Fe^{+++}	Fe^{++}	$[Fe''(CN)_6]^{----}$	$[Fe'''(CN)_6]^{---}$	Ni^{++}	
I	P	Fe^{+++} + $K_4[Fe''(CN)_6]$, after 24 hr.	++	....	−		...	4.3% excess $[Fe''(CN)_6]^{----}$ used
		Same, after 1 mo.	++++		−	−		pH 1.7[c]
IX	P	Fe^{+++} + $K_4[Fe''(CN)_6]$, after 5 min.	++	−	−	+++	...	4.3% excess $[Fe''(CN)_6]^{----}$ used
		Same, after 24 hr.	++	−	−	−	....	....
XV	P	Fe^{+++} + $K_4[Fe''(CN)_6]$, after 24 hr.	++	−	−	−	....	No excess used
V	P	I, raised pH 4.3 with NH_4OH	....	....	....	......	...	....
VII	P	I, raised pH 4.9 with NH_4OH	....	....	....	......	...	....
VI	P	I, raised pH 6.9 with NH_4OH	....	....	....	......	...	Redder shade blue than 1
VIII	P	I, raised pH 7.2 with NH_4OH	....	....	....	......	...	Redder shade blue than I
II	P (+Ni)	90 equiv. % Fe^{+++} and 10 equiv. % Ni^{++} + $K_4[Fe''(CN)_6]$	+	....	−	+	−	....
III	P (+Ni)	80 equiv. % Fe^{+++} and 20 equiv. % Ni^{++} + $K_4[Fe''(CN)_6]$	+	....	−	+	−	Slightly greener shade than I
X[d]	O	Fe^{++} + $K_4[Fe''(CN)_6]$, stir 10 min.	−	−	Very marked	Marked	...	Pale greenish-blue ppt.
		Oxidized with H_2O_2	−	−	++++	Marked		Immediate oxidation to sol. blue; pH 2.95
XII	O	X, adjusted to pH 1.7 with H_2SO_4	++	−	−	Marked	...	pH 1.7
XI	O (+Ni)	Fe^{++} + $K_4[Fe''(CN)_6]$, stir 10 min.	−	−	Very marked	Marked	...	Pale greenish-blue ppt.
		Added Ni^{++}, equiv. to K^+ in $K[Fe''(CN)_6Fe''']$, stir 10 min.	−	−	−	−	...	Greenish-blue ppt.
		Oxidized with H_2O_2	−	−	−	−	Marked	Produced insol. blue
XIII	T	Fe^{++} + $K_3[Fe'''(CN)_6]$, after 5 min.	−	−	−	+++	...	....
		Same, after 4 days	+	−	−	+	...	Similar appearance to I
XIV	Ni ferricyanide +Fe^{++}	Ni^{++} + $K_3[Fe''(CN)_6]$						Ni added equiv. to $KNi[Fe'''(CN)_6]$
		Same + Ni^{++}	....	....	....	Very large	+++	Ni added equiv. to $Ni_3[Fe'''(CN)_6]_2$; brownish-yellow gelatinous ppt., slow filtering
		Same + Fe^{++}, equiv. to Ni^{++} used	Marked	Very large	−	−	+++	Olive-green ppt., very slowly changing to turquoise blue on several days' standing

[a] P = Prussian, T = Turnbull's, O = oxidized.
[b] + = very faint test for ion, ++ = faint, +++ = slight, ++++ = small, − = absent. Fe^{+++} tested with KCNS & $[Fe''(CN)_6]^{----}$; Fe^{++} tested with $[Fe'''(CN)_6]^{---}$; $[Fe''(CN)_6]^{----}$ tested with Fe^{+++} (+H^+); $[Fe'''(CN)_6]^{---}$ tested with Fe^{++} (+H^+); Ni^{++} tested with dimethylglyoxime (+NH_4OH).
[c] pH taken with Beckman Model M meter, using glass electrode assembly.
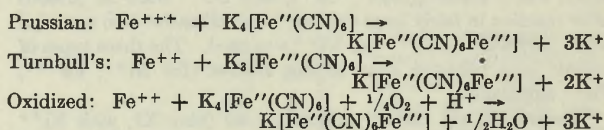[d] This preparation was repeated, with identical results.

of this paper, and will be used hereafter, to designate the substance described in the academic literature—i.e., the "soluble" product of the equimolar reaction of ferric (ferrous) and ferrocyanide (ferricyanide) ions; it thus bears a connotation other than that of the commercial product. Likewise, the term "Prussian blue" is employed here to refer, not to the specific deep-shade commercial type, but to the definite method of preparation from ferric ion.

The commercial products are complex adsorption mixtures which vary widely in composition, depending on the formulation employed. To simplify the experimental systems and thereby facilitate the experimental studies, the general commercial method of preparation (i.e., precipitation of ferrous salt by alkali ferrocyanide followed by oxidation directly to the insoluble blue) was rejected in favor of the procedure outlined below.

The experimental method of study adopted in the present work, therefore, consisted of the preparation by various methods of soluble blues or potassium berlinates; the precipitation or insolubilization of these soluble blues with iron, nickel, and other metallic salts; and testing for alkali resistance by subjecting the washed insoluble blues to the action of alkaline buffers.

PREPARATION OF SOLUBLE BLUES

The three general academic methods of preparation were employed: mixing a ferric salt with a ferrocyanide (Prussian type blue); mixing a ferrous salt with a ferricyanide, (Turnbull's type blue); mixing a ferrous salt with a ferrocyanide, followed by oxidation (oxidized type of blue). In all three cases H^+ (as H_2SO_4) was added, in tenfold molar concentration, in order to prevent the formation of hydrous oxides of iron. The over-all reactions may be represented as follows:

$$\text{Prussian:} \quad Fe^{+++} + K_4[Fe''(CN)_6] \rightarrow K[Fe''(CN)_6Fe'''] + 3K^+$$
$$\text{Turnbull's:} \quad Fe^{++} + K_3[Fe'''(CN)_6] \rightarrow K[Fe''(CN)_6Fe'''] + 2K^+$$
$$\text{Oxidized:} \quad Fe^{++} + K_4[Fe''(CN)_6] + \tfrac{1}{4}O_2 + H^+ \rightarrow K[Fe''(CN)_6Fe'''] + \tfrac{1}{2}H_2O + 3K^+$$

While these equations postulate the formation of the potassium salt of the complex berlinate, it should be pointed out that, owing to the large proportion of ammonium ion introduced with the iron salts, the blue products probably consist of mixtures of the ammonium and potassium derivatives.

The following solutions were prepared from C.P. grade reagents, analyzed for purity by conventional methods:

$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$: 0.005 molar (equivalent to 0.01 molar on basis of one atom of Fe) dissolved in 0.1 molar H_2SO_4.
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$: 0.01 molar, dissolved in 0.1 molar H_2SO_4
$K_4Fe(CN)_6 \cdot 3H_2O$: 0.01 molar
$K_3Fe(CN)_6$: 0.01 molar
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$: 0.01 molar

Equal volumes of reagents were mixed, the ferro- or ferricyanide being added rapidly to iron (or iron plus nickel) solution. The mixture was stirred vigorously for 5 minutes and then allowed to stand for at least 24 hours. The batches were tested qualitatively for ions uncombined, using spot testing technique. The data are given in Table I.

In general, all three types of soluble blue preparations were alike and, apart from the small excesses of reagents found, appeared to obey the stoichiometry demanded by the equations. The "ion excesses" were quantitatively very small, somewhat greater amounts of anions being observed for the oxidized blues (X, XI,

XII, Table I). However, these results were interesting in relation to the modes of preparation followed and are apparently associated with varying adsorption effects, depending on the starting materials employed.

The differences in the observed ion excesses for the oxidized blue of higher pH (X vs. XII) are noteworthy (the higher pH caused by removal of H^+ for the oxidation). On lowering the pH from 2.95 to 1.7, a small excess of ferrocyanide disappeared, while a faint excess of Fe^{+++}, not previously found at the higher pH, was formed. The increased acidity was apparently exerting a solubilizing effect, suggesting the "acid-soluble blues" reported by Chretien (9) and Hofmann (18). On the other hand, the quantitatively small excess of Fe^{+++} obtained for this relatively high acid concentration indicates that the tenfold molar acid concentration, used to inhibit the formation of the hydrous iron oxides, was not too high.

Blue XIV was an attempt to form a Turnbull's blue indirectly; a nickel ferricyanide was precipitated, then treated with equivalent Fe^{++}. Only slight metathesis occurred on long standing, however.

PRECIPITATION OR INSOLUBILIZATION OF BLUES

Aliquots of the soluble blues were treated with various cations in amounts equivalent to the K^+ in $K[Fe''(CN)_6Fe''']$. The batches were stirred vigorously for 5 minutes and then allowed to stand for at least 24 hours, all at room temperature.

The mother liquor was separated by centrifuging. The precipitated blue was washed three times with distilled water (centrifuging after each wash) sufficient to remove $(SO_4)^{--}$ and H^+, and then resuspended in distilled water, preparatory to running alkali resistance tests. Data are recorded in Table II. Precipitation or flocculation was complete unless otherwise noted.

There was no apparent stoichiometry in the reaction of the soluble blues with various cations. While Cu^{++} and Ag^+ reacted in apparently equivalent quantities to the K^+ (in fact, Ag^+ appeared to have displaced a slight amount of Fe^{+++} from the blue), Fe^{+++}, Fe^{++}, Ni^{++}, Co^{++}, and Zn^{++} were all present after reaction in fairly large excess; insolubilization also occurred when only half the Fe^{+++} or Ni^{++} was used. The three types of soluble blue behaved alike in this respect (for Ni^{++}, Fe^{+++}, Fe^{++} additions).

However, in the case of experiment 40 (blue XI, with Ni^{++} added to ferrous-ferrocyanide before oxidation), a smaller excess of Ni^{++} was found; this indicated a larger amount of Ni^{++} reacting to remove the higher anion excess obtained with these oxidized blues. It was found that addition of nickel invariably removed from solution the anions previously present in the soluble blue, in contrast with Fe^{+++} and Fe^{++}.

When 10 and 20% of nickel were used to replace iron during formation of the soluble blue, no excess Ni^{++} was detected, even for subsequent insolubilization with Fe^{+++} (experiments 13 to 16) blues II and III. The nickel must have entered the polynuclear complex, in line with Davidson's "first come, first served" principle (11).

In order to establish whether the incomplete replacement of cation with K^+ might be due to the low pH of the soluble blues, the pH values, both of the soluble blues and of the insoluble slurries, were raised in experiments 10, 11, 12, and 17, 18, 19. No apparent diminution of the Ni^{++} excess was observed up to pH 6.2, whereas the Fe^{+++} gradually decreased and disappeared completely from solution by pH 4.0. (The latter behavior would be anticipated, since iron is completely precipitated as the hydrous oxide by pH 4.) Thus, the nonstoichiometric reaction of nickel was not due to the low pH; a definite statement regarding Fe^{+++} cannot, however, be made.

The large excess of iron (about 30%) found in all cases is in striking variance with the textbook formulas, $Fe^{+++}_4[Fe''(CN)_6]_3$ and $Fe^{++}_3[Fe'''(CN)_6]_2$, or with an iron berlinate formu-

lation, $Fe[Fe''(CN)_6Fe''']_3$. If the low pH is assumed not to prevent, in itself, the reaction of Fe^{+++} with potassium berlinate (probably a safe assumption since, during the formation of soluble blue, iron had reacted almost completely with potassium iron-cyanide), then other possible explanations would be as follows: (a) The formula for insoluble blue is different from what has been represented; (b) the precipitation may consist in coagulation of the sol, involving relatively large amounts of coagulating cation; (c) a combination of (a) and (b).

Bhattacharya and Dhar (6) considered the soluble blues to be merely colloidal precipitates formed by adsorption of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. Furthermore, Weiser (40) stated that the distinction between insoluble and soluble blues is entirely arbitrary, since the former can be brought into colloidal solution by washing. The x-ray work of Keggin and Miles, in which a formula $RFe''Fe'''(CN)_6$ is assigned to the iron blues, appears to provide experimental confirmation for the foregoing theories and is in line with present experimental results. The process of insolubilization would, then, appear to consist not in the replacement of potassium by iron or nickel, but in a salting out of the colloid. There seems to be a definite possibility that soluble blues and insoluble blues possess the same macro-composition.

Indicative of the importance of adsorption effects at insolubilization were the ion excesses, other than those of the added cations, observed for the various preparations (Table II) as well as the peptizations which occurred during washing in experiments 8, 37, 11, 19, 29, 31, 40. At a later stage of the experiments it was observed that a completely soluble, or colloidally dispersed, blue which had been stored in a rather warm location, became completely flocculated; this effect could be accomplished more rapidly by heating to high temperature. An apparent but incomplete redispersion was obtained by thoroughly shaking the flocculated slurry.

The unusually high adsorption and coagulation values for the substances indicated in this work and also reported in the literature (30, etc.) are not surprising, when it is considered that these iron cyanide compounds contain large numbers of nitrogen atoms with active lone pairs. While it appears from the available evidence that these nitrogens are coordinated with iron atoms to form a three-dimensional structure, the precipitated gels undoubtedly contain large numbers of imperfect crystals, with coordinating power incompletely engaged in crystal building; these unsatisfied forces, together with the unbalanced crystal surface fields, would create powerful adsorptive fields.

QUANTITATIVE STUDIES. To test these hypotheses, a series of experiments (Table III) was carried out in which a Prussian soluble blue was insolubilized with iron and nickel cations, individually and jointly; the manner of addition was also varied. In all cases, an equivalent of each cation (equivalent to the K^+ in $K[Fe''(CN)_6Fe''']$) was added so that in experiments 43 and 44 a total of two equivalents was simultaneously used. Ni^{++} was analyzed gravimetrically by the dimethyl glyoxime method. Fe^{+++} was reacted with potassium thiocyanate and analyzed colorimetrically; in order to avoid the disturbing effects on the color formation caused by the presence of other salts and varying pH, the Fe^{+++} standards were so made up as to equal in composition (except for iron) the insoluble blue liquors. Each preparation was aged for a week before the supernatant liquors were sampled for analysis. All operations were conducted at room temperature.

The experimental results may be summarized as follows:

1. Approximately half an equivalent of Ni^{++} was taken up by Prussian soluble blue under the experimental conditions (experiments 2, 41, and 46).
2. On the other hand, a little over 0.7 equivalent of Fe^{+++} was absorbed (experiments 42 and 45).
3. Adding two equivalents, one of each cation, increased the total cation taken up by the blue, but the totals varied, depending on the order of addition; an initial Fe^{+++} addition produced a greater increase in the total and higher Fe^{+++}/Ni^{++} intake (ex-

TABLE II. INSOLUBLE BLUES

Expt. No.	Blue No.	Type[a]	Cation Added	Ions Present after Insolubilization[b]					Other cations	Remarks	Alkali Stability Tests[c]			
				Fe^{+++}	Fe^{++}	[Fe''(CN)$_6$]	[Fe''(CN)$_6$]				Na$_2$CO$_3$–NaHCO$_3$ buffer (pH 9.4)	0.5 N Na$_2$CO$_3$	0.2 N Na$_2$CO$_3$	
7	I	P	Fe^{+++}	Marked	+++					28.6% of added Fe^{+++} unused	D at 7½ min.		
42	XV	P	Fe^{+++}	Marked	+++					Supernatant slightly-colored; slight peptisation at 1st wash; 6% KCl soln. used for 2nd and 3rd washes	D at 3½ min.		
8	I	P	½Fe^{+++}	++	+++						D at 1½ min.		D at 5–6 days
9	I	P	Fe^{++}	+++	Large				Ni^{++} large	42.6% of added Ni^{++} unused	D at 2½ min.	S;	
2	I	P	Ni^{++}	+++					Ni^{++} absent	Marked peptisation at 2nd wash; very strong at 3rd	S	D at 3–4 days	
37	IX	P	½Ni^{++}	(?)							S		
5	I	P	Co^{++}	—	—				Co^{++} present	Used 20% excess Cu^{++}	S after 8 min.		
3	I	P	Cu^{++}	++					Cu^{++} absent		D by 20 hr.		
4	I	P	Zn^{++}	—					Zn^{++} large		D at ½ min.		
6	I	P	Ag^{+}	+++					Ag^{+} absent		S at 1½ min.		
26	IX	P	KCl[c]	++	—	++			Ni^{++} large	Dense rapid-settling ppt.	S		
10	IV	P (pH 1.7)	Ni^{++}	+++	++				Ni^{++} large	pH 1.7	S		
11	V	P (pH 4.3)	Ni^{++}							marked peptisation at 3rd wash	S		
12	VI	P (pH 6.9)	Ni^{++}						Ni^{++} large	pH 4.1; pH 6.1; on centrifuging, lighter-colored (white?) layer settled at bottom	S		
17	VII	P (pH 4.9)	Fe^{+++}	Marked		++				pH 2.2 after mixing (Fe^{+++} soln. with H$^+$ addition)	D at 4½ min.		
18	VIII	P (pH 7.2)	Fe^{+++}	+++		++				pH 2.2 after mixing (Fe^{++} contained H$^+$)	D at 2½ min.		
19	I	P	Fe^{+++}; pH reised to 4	—	—	+				Some peptisation at 2nd wash; very marked at 3rd wash	D at 2 min.		
13	II	P (with 10% Ni)	KCl[c]	Marked	—	+++			Ni^{++} absent		S;	D at 4–5 hr.
14	II	P (with 10% Ni)	Fe^{+++}	—		++++			Ni^{++} absent		S	
15	III	P (with 20% Ni)	KCl[c]	Marked		++			Ni^{++} absent		S	
16	III	P (with 20% Ni)	Fe^{+++}	—		++++			Ni^{++} absent		S up to 20 hr.; D at 3 days	
29	X	O (at pH 2.95)	Ni^{++}	Marked	—	+			Ni^{++} large	Very marked peptisation at 3rd wash	D at 3 days	
30	X	O (at pH 2.95)	Fe^{+++}	Marked	—	++			Ni^{++} large		D at 20 min.	
31	XII	O (at pH 1.7)	Ni^{++}	+++	—	+				Marked peptisation at 3rd wash	S up to 3 days; D at 6 days	
32	XII	O (Ni^{++} before oxidation)	Fe^{+++}	Marked	—	—			Ni^{++} small	Some peptisation at 2nd wash; strong at 3rd wash	D at 15 min.	N;	D at 7–9 days
40		O	No further addition								S		
33	XIII	T	Ni^{++}	+++	++	—			Ni^{++} large	Flocculated blue as fine ppt.; very strong peptisation at 1st wash; 6% KCl for 2nd and 3rd washes	S at ½ min.	N;	D at 2 days
34	XIII	T	Fe^{+++}	Marked		—					D at ½ min.		
36	XIII	T	KCl[c]	—	++	—					D at 1½ min.		
35	XIII	T	Fe^{+++}	++++		++					D at 1¼ min.		
38	IX	P	H$_4$Fe''(CN)$_6$ in ¼ M excess[f]		Very large						D immediately		

[a] See footnote a, Table I.
[b] See footnote b, Table I.
[c] D = decomposed; S = stable.
[d] Half of the slurry from the pH 9.4 test was made up to be 0.2 N in Na$_2$CO$_3$ and 0.0025 N in NaHCO$_3$; also, 0.0000625 M to berlinate (instead of 0.000125 M as in other two tests).
[e] 3 grams of KCl used to salt out 0.0025 mole of berlinate.
[f] Washed with 6% KCl solution to prevent peptisation.
[g] K$_4$Fe(CN)$_6$ was mixed with H$_2$SO$_4$ in excess to form H$_4$Fe(CN)$_6$, and added to the sol. blue aliquot; flocculation occurred.

periments 43 and (44). However, the amount of each metal taken up was decreased by the presence of the other cation, with a greater numerical decrease occurring for the Fe^{+++} intake. Thus, in this competing action the nickel exerted a greater influence, being absorbed to a greater degree than iron in spite of the higher intake of Fe^{+++} over Ni^{++} when the two acted individually.

4. Restoring the H$^+$ concentration of the washed blues released small amounts of Fe^{+++} and Fe^{++} without appearance of anion. Addition, then, of an equivalent of the other cation displaced partly from the blue its original insolubilizing cation in some sort of exchange reaction; however, nonequivalent amounts of the cations were exchanged, a higher Fe^{+++}/Ni^{++} ratio being again in evidence (experiments 45 and 46).

5. Addition to a heat-coagulated soluble blue, which had been redispersed by shaking, of double an equivalent of Ni^{++} produced a lower nickel intake by approximately half (experiment 47). This low intake must have been caused by the change in the physical nature of the blue.

These results again disprove a stoichiometric relation in the change from soluble to insoluble blue, and indicate that the change occurs by a colloidal mechanism.

ALKALI STABILITY

The blues decomposed rapidly when treated with strong alkaline solutions. In milder alkaline buffers the rate of decomposition was found to be dependent upon the pH of the system and the molarity of the blue, increased pH and decreased molarity causing more rapid decomposition. At pH 9.4, in a solution 0.05 normal to sodium bicarbonate and 0.033 normal to sodium carbonate, a marked differentiation was obtained between an iron- and a nickel-treated blue. Whereas the former decomposed completely during about 4 to 9 minutes of stirring, the latter

TABLE III. VARIOUS INSOLUBILIZATIONS WITH Fe^{+++} AND Ni^{++}

Expt. No.	Treatment	% of Cation Unused		% of Cation into Blue		Total Equiv. % of Cation into Blue	Qualitative Tests[a]		Alkali Stability Tests[b]	
		Ni^{++}	Fe^{+++}	Ni^{++}	Fe^{+++}		Fe^{+++}	Fe^{++}	Na_2CO_3–$NaHCO_3$ buffer (pH 9.4)	0.5 N Na_2CO_3
41	Ni^{++} addition	41.2	....	58.8	...	58.8	....	+	S	D, at 20–30 min.
42	Fe^{+++} addition	....	28.6	...	71.4	71.4	....	+ +	D, at 8½ min.	D, at 20–30 min.
43	Ni^{++}, stir 15 min., then Fe^{+++}	59.3	60.0	40.7	40.0	80.7	....	+ + +	S	D, at 2 min.
44	Fe^{+++}, stir 15 min., then Ni^{++}	62.0	52.6	38.0	47.4	85.4	....	+ +	S	D, at 2 min.
45	Fe^{+++}, stand a week Filtered, washed; H+ added to original concn.	....	28.4	...	71.6	71.6	....	+ +	.....	....
	Ni^{++} added	73.6	29.3[c]	26.4	42.3[d]	68.7[e]	+ + + +	+ + +	S[f]	D at 1 min.
46	Ni^{++}, stand a week Filtered, washed, H+ added to original concn.	39.2	...	60.8	...	60.8	....	+	......	......
	Fe^{+++} added	20.3[c]	58.8	40.5[d]	41.2	81.7[e]	+ + + +	+ + +	S	D, at 3 min.
47	Doubled Ni^{++} (on sol. blue flocculated by "warm storage" and then redispersed)	171.2 for 2 equiv.	...	28.8[g]	...	28.8	....	....	S	D, at 3 min.

[a] See footnote b, Table I.
[b] S = stable, D = decomposed.
[c] In expt. 45 addition of Ni^{++} (and H+) released 29.3% of Fe^{+++} in exchange for 26.4% Ni^{++} taken up. In expt. 46 addition of Fe^{+++} (and H+) released 20.3% Ni^{++} in exchange for 41.2% Fe^{+++} taken up.
[d] In expt. 45 percentage of Fe^{+++} remaining in blue equals original content; 71.6% minus that released (29.3%) equals 42.3%. In expt. 46 percentage of Ni^{++} remaining in blue equals original content; 60.8% minus that released (20.3%) equals 40.5%.
[e] Total % consists of percentage of undisplaced cation remaining in the blue plus the percentage of the displacing cation taken up.
[f] After 5 days standing of the alkali-treated slurry, the color became somewhat greener, indicating the beginning of decomposition.
[g] In expt. 47 percentage of Ni^{++} taken up by blue equals 200 equivalent % minus 171.2% unused, leaving 28.8%.

remained indefinitely stable at this pH. All the insolubilized experiments were therefore tested in this buffer mixture. To differentiate further between the more alkali resistant experiments, they were subjected to more stringent conditions (Tables II and III).

The washed insoluble blues, 0.000125 molar with respect to the berlinate complex except where otherwise stated, were mixed into the alkaline solutions. The slurries were stirred vigorously up to 8–10 minutes; those which had not changed up to this point were allowed to stand and set aside for later observation. All of the blues underwent an initial change upon immersion in the alkaline solutions, from greenish to reddish-blue. Some of the preparations did not change further upon stirring or subsequent standing (designated as S); others decomposed at various rates, going through the following series of changes: reddish-blue, greenish suspension (with yellowish supernatant), brownish suspension, reddish-brown color of hydrous iron oxide. They were designated D (decomposed), and the time was noted at which the reddish-brown stage was reached. All tests were carried out at room temperature. The results are given in Tables II and III.

Marked differentiation in stability toward alkaline environments were exhibited by the various "metal salts" of soluble blue. When immersed in a buffer solution of pH 9.4, the different cation-insolubilized Prussian blues fell into six different groups, in order of stability: (a) the Ag^+ treated blue decomposed rapidly; (b) the K^+ salt-out decolorized more slowly, although also comparatively rapidly; with this sample is grouped also the ½ Fe^{+++} experiment; (c) Fe^{++} was better than the two preceding, taking 2.5 minutes for complete decomposition; (d) Fe^{+++} was poor, decomposing in 4 to 9 minutes; (e) the Zn^{++} experiment was much more stable, changing only over a day's standing; (f) however, Ni^{++}, Co^{++}, and Cu^{++} were very stable at this pH. There was no relation between these varied rates of decomposition and the completeness of removal of cation by the soluble blue, since Ag^+ (the most completely reacted) decomposed most rapidly, while Cu^{++} (the next in order) ranked with the most stable.

The method of preparation of the soluble blue affected the rate of decomposition to some extent; Turnbull's blues decomposed more rapidly and the oxidized blues less rapidly, than the Prussian blues. These results are in line with Hofmann's work (18) on the ammonia stability of a number of his blue preparations. These differences were exhibited with the iron-treated experiments, but also with the nickel experiments at higher pH of testing. In the case of Turnbull's blues, Fe^{++} produced slightly higher stability than Fe^{+++}, a reversal of the results for the Prussian blues.

Nickel ion, added at any point in the history of the blue, produced a marked improvement in the resistance to alkaline environments (even as low as ⅛ equivalent, in an unrecorded experiment, gave a large differentiation from iron); at pH 9.4 the nickel experiments were stable up to three to four months, the time limit of observation in this work. This stable state differed, however, from the original condition of the blues, as shown by the change to a more reddish blue. Co-treatments of nickel plus iron (Table III) decreased the stability when tested under more stringent conditions; in these experiments there was no direct proportion between the times required for decomposition and the nickel content of the blues, although the order of listing was similar.

The most stable blue (experiment 16) was obtained by replacing part (20%) of the iron by nickel at formation of the soluble blue; this was stable up to about 4–5 hours in 0.5 N sodium carbonate.

It is difficult to offer a chemical explanation for the beneficial action of nickel salt; an answer might be more easily found from the colloidal approach. The whole question of stability to alkaline environments is one of relative rates of reaction, since increased pH or long standing at a particular pH level may eventually break down the blue. The action of alkalies must involve, first, a peptization of the insoluble blue, followed by decomposition of the polynuclear complex with end-product formation of alkali ferro- and ferricyanides plus hydrous ferric oxides. The mode of peptization would undoubtedly involve the preliminary formation of alkali iron cyanide, which would be adsorbed to exert its usual solubilizing effect.

It would be expected, therefore, that gels containing large quantities of the adsorbed anions would be more readily acted upon; for example, experiment 38, Table II (precipitation by ferrocyanic acid), decomposed rapidly in the alkali stability test, probably because of its high anion content. In practically all cases of nickel addition, it was observed that the anions were removed from solution. The action of the nickel may, then, consist in the precipitation of adsorbed and peptizing polyvalent anion. In this connection, the failure of nickel ferricyanide to metathesize to an iron blue (XIV, Table I) is pertinent, as an indication of high insolubility for the former.

An alternative or adjunctive hypothesis is that the barrier toward peptization and decomposition would be an increase in the particle size of the precipitate by the use of nickel salt; additions of the latter produced a greening of the blue shade, as compared with iron salt additions, and a more rapid settling of the precipitate, factors usually associated with increased particle size in commercial pigment work.

An interesting item in Thomasset's patent on the use of nickel (*36*) is the statement of the requirement of low oil absorption of the blue for maximum alkali stability. This would be indicative of a decreased total surface for the pigment particles, which would be accompanied by decreased powers of adsorption.

To conclude, the constitution of the iron blues is still in doubt. Most of the early work was carried on and interpreted from a single viewpoint only. Because of the complexity of the systems involved, simultaneous attacks on the problem from different angles are required, such as have been initiated recently by Weiser and others. Aging studies under suitable conditions, accompanied by chemical, colloidal, x-ray work, etc., would aid in resolving the controversies over this subject.

The nickel and alkali stability problems are tied up with the general problem of constitution, and further elucidation of the latter will aid in explaining the facts associated with the former.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Abegg, R. W. H., Handbuch der anorg. Chemie, Band 4, Abt. 3, Teil 2B, p. 561, Leipzig, S. Hirzel, 1935.
(2) Bever, A. K. van, *Rec. trav. chim.*, 57, 1259 (1938).
(3) Bhattacharya, A. K., *J. Indian Chem. Soc.*, 12, 143 (1935).
(4) *Ibid.*, 18, 81 (1941).
(5) *Ibid.*, 18, 85 (1941).
(6) Bhattacharya, A. K., and Dhar, N. R. Z., *Z. anorg. allgem. Chem.*, 283, 240 (1933).
(7) Brown, T. P. (to Interchemical Corp.), U. S. Patent 2,269,516 (Jan. 13, 1942).
(8) Cambi, L., and Clerici, A., *Gazz. chim. ital.*, 58, 61 (1928).
(9) Chretien, P., *Compt. rend.*, 137, 191 (1903).
(10) Coleby, L. J. M., *Ann. Sci.*, 4, 207 (1939).
(11) Davidson, D., *J. Chem. Education*, 14, 277 (1937).
(12) Davidson, D., and Welo, L. A., *J. Phys. Chem.*, 32, 1191 (1928).
(13) Eibner, A., and Gerstacker, L., *Chem.-Ztg.*, 37, 137 (1913).
(14) Emeleus, H. J., and Anderson, J. S., "Modern Aspects of Inorganic Chemistry", p. 139, London, G. Routledge & Sons, 1938.
(15) Harrison, A. W. C., "Manufacture of Lakes & Precipitated Pigments", Chap. IX, London, Leonard Hill, 1930.
(16) Hazel, F., and Sorum, C. H., *J. Am. Chem. Soc.*, 52, 1337 (1930).
(17) Hofmann, K. A., Arnoldi, H., and Heindlmaier, H., *Ann.*, 352, 54 (1907).
(18) Hofmann, K. A., Heine, O., and Hochtlen, F., *Ibid.*, 337, 1 (1904).
(19) Hofmann, K. A., and Resenscheck, F., *Ibid.*, 340, 267 (1905).
(20) *Ibid.*, 342, 364 (1905).
(21) Keggin, J. F., and Miles, F. D., *Nature*, 137, 577 (1936).
(22) Levi, G. R., *Giorn. chim. ind. applicata*, 7, 410 (1925).
(23) Mattiello, J., "Protective and Decorative Coatings", Vol. II, p. 263, New York, John Wiley & Sons, 1942.
(24) Muller, E., *J. prakt. Chem.*, 84, 353 (1911).
(25) *Ibid.*, 90, 115 (1914).
(26) Muller, E., and Lauterbach, H., *Ibid.*, 104, 241 (1922).
(27) Muller, E., and Stannisch, T., *Ibid.*, 79, 81 (1909).
(28) *Ibid.*, 80, 153 (1909).
(29) Muller, E., and Treadwell, W., *Ibid.*, 80, 170 (1909).
(30) Rabinerson, A., *Kolloid-Z.*, 39, 112 (1926).
(31) Reihlen, H., and Zimmerman, W., *Ann.*, 451, 75 (1927).
(32) Rigamonti, R., *Gazz. chim. ital.*, 68, 803 (1938).
(33) Rollier, M. A., and Arreghini, E., *Ibid.*, 69, 499 (1939).
(34) Shack, I., and Wilson, E. A. (to Interchemical Corp.), U. S. Patent 2,342,429 (Feb. 23, 1944).
(35) Skraup, H., *Ann.*, 186, 371 (1877).
(36) Thomasset, P. A. (to Ansbacher-Siegle Corp.), U. S. Patents 2,275,929 (March 10, 1942); 2,329,364 (Oct. 14, 1943).
(37) U. S. Dept. of Commerce, Census of Manufactures, 1939. Colors and Pigments, p. 2 (1940).
(38) Van Wirt, A. C., and Jones, G. F. (to Imperial Paper & Color Corp.), U. S. Patent 2,357,296 (Sept. 5, 1944).
(39) Weiser, H. B., "Colloidal Salts", p. 249, New York, McGraw-Hill Book Co., 1928.
(40) Weiser, H. B., "Inorganic Colloid Chemistry", Vol. III, pp. 307, 343, New York, John Wiley & Sons, 1938.
(41) Weiser, H. B., Milligan, W. O., and Bates, J. B., *J. Phys. Chem.*, 45, 701 (1941).
(42) *Ibid.*, 46, 99 (1942).
(43) Wilson, E. A., and Schack, I. (to Interchemical Corp.), U. S. Patent 2,288,309 (June 30, 1942).
(44) Woringer, P., *Chem.-Ztg.*, 36, 78 (1912).
(45) Woringer, P., *J. prakt. Chem.*, 89, 51 (1912).
(46) Wyrouboff, M., *Ann. chim. phys.*, [5] 8, 444 (1876).

PEANUT PROTEIN HYDRATES

Preparation and Properties

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CERTAIN peanut and soybean protein-water interrelations have been observed which not only have significant theoretical aspects but, more important, open new fields of application for isolated peanut, soybean, and other vegetable proteins. The purpose of this paper is to describe some of these protein-water relations and, in subsequent communications, to discuss their practical applications. The water relations of peanut protein have been successfully applied in developing new adhesives for gumming purposes, and in making flexible glues for the setup paper box manufacturer and the bookbinder.

Protein-water relations involving hydration (bound water), swelling, and related phenomena are complicated and, in some respects, controversial. Lloyd (*12*) states that "whatever may be felt to be the limits of 'bound water' in protein, it is generally agreed that water is held with varying degrees of force". Astbury (*1*) says: "The water that proteins can take up seems to fall roughly into two kinds, the loosely and tightly bound." It is also generally agreed that tightly bound water is bound to protein hydrophilic groups by hydrogen bonds, and that it is possible to estimate the quantity of such bound water from a knowledge of the amino acid content of a protein (*14*).

Concerning the mechanism of the second type of water binding, Phillips (*13*) points out that the polar groups of the protein "may not only associate with water molecules by coordination, but may also cause other water molecules to orient themselves and provide an outer sphere of less firmly bound water molecules". Additional references and excellent summaries relative to more recent concepts of protein-water relations are given by Bull (*3*), Greenberg (*10*), and Compton (*7*).

The homogeneous, translucent, hydrated, peanut protein sols are disintegrated by the presence of unbound water, as indicated by the appearance of a second phase; the phenomenon is somewhat analogous to phase reversal of emulsions. This is apparent if these protein hydrates are considered as solutions of water in
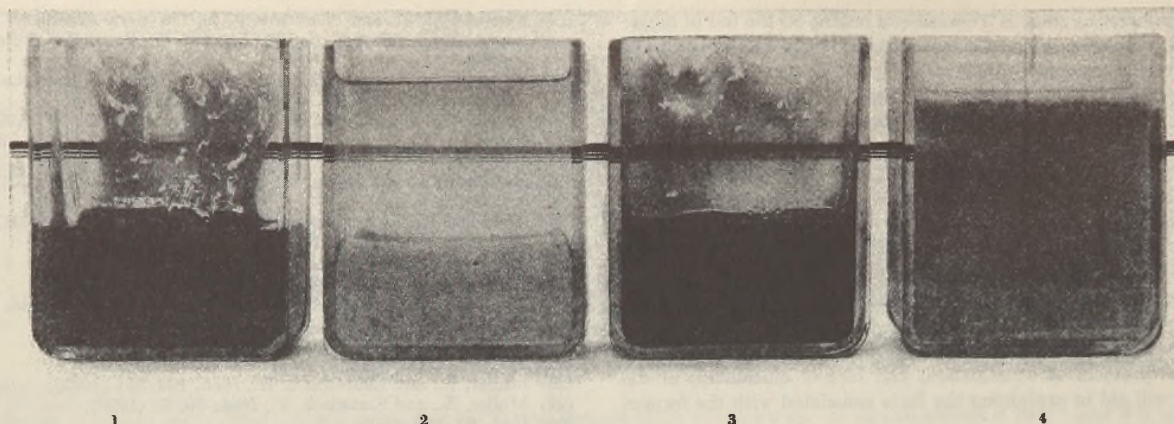
Figure 1.   Peanut Protein Hydrates

Cell 1.   Protein hydrate, pH 5.0, 38% water.   Back of cell smeared with hydrate to show translucency.
Cell 2.   Two phases obtained by adding excess water (80% water, 20% protein) to hydrate in cell 1.   Solid curdlike protein phase has settled
            to bottom of cell.
Cell 3.   Protein hydrate, pH 6.85, 55% water.   Back of cell smeared with hydrate to show translucency.
Cell 4.   Two phases obtained by adding excess water (80% water, 20% protein) to hydrate in cell 3.   Solid phase is a fine colloidal suspension

protein. Addition of water which the protein can no longer dissolve (or bind) results in reversion to a suspension of protein (more or less hydrated) in water. Although at pH values in or near the isoelectric range the protein suspension settles rapidly, relatively stable suspensions result when the pH is raised.

Greenberg (9) points out that there are few criteria by which the hydration of proteins may be defined, and Bull (4) states that "bound water is defined in terms of the experimental technique by which it is measured". In the present paper all the water which a peanut protein will absorb at pH values between 4.5 and 9.0, without disintegration of the sol, to produce a second phase, is considered to be bound to the protein molecules. Such one-phase systems are called "hydrates". The exact manner by which water is retained by the protein micelle may be debatable, but that point is not important for present purposes.

Such views are not offered as supporting evidence for or against any particular theory of protein behavior. They are presented in order to describe various phenomena which occur with solutions of peanut protein; to differentiate solutions of water in protein (hydrates) from dispersions of protein (more or less hydrated) in water which can be prepared in the pH range 4.5 to 9.0; and to stimulate interest in the water relationships of vegetable globulins.

The peanut protein used in this investigation was a mixture of several incompletely characterized proteins in undetermined proportions. For the present purposes the mixtures are referred to as peanut protein, and the conditions under which each product was prepared will be given. Although soybean protein forms similar hydrates, the present paper is limited to peanut protein.

PREPARATION OF PROTEINS

The peanut proteins were prepared from solvent-extracted peanut meal. To extract the protein from the meal, one part of meal was mixed with ten parts of dilute sodium hydroxide solution at 25° C. and at the pH values shown in Table I. The extract was separated from the insoluble fraction of the meal

by a centrifuge equipped with a solid basket, and the centrifuged dispersion was clarified by filtration. The protein was then precipitated from the clarified filtrate at 25° C. by adding sulfurous acid in an amount required to attain the pH value shown in Table I. The protein curds obtained were allowed to settle overnight and were then separated from the supernatant liquor and dried at 50° C. All three proteins shown in Table I were prepared under relatively mild conditions; that is, they were extracted at nearly neutral pH values to avoid contact with alkali, and the opportunity for heat denaturation during drying was minimized.

The same mild conditions must be employed to isolate soybean protein if it is to be suitable for preparing neutral sol hydrates. All commercial soybean proteins examined by the author form gels at the high concentration required to produce a hydrate of the type under consideration. This behavior is probably due to greater alteration in the structure or composition of the protein during its manufacture than occurs under mild extraction and drying conditions.

HYDRATES WITHIN OR NEAR ISOELECTRIC RANGE

Peanut protein has an isoelectric range between pH 4.0 and 5.0 (8), and the same amount of protein can be recovered by precipitation with sulfur dioxide at any pH within this range (5).

When peanut protein curds, prepared by precipitation at pH 4.5 (method 1, Table I), are dried at 50° C., a point is reached at which the interior of shell-dried lumps of curd becomes a translucent, tacky sol which cools to a viscous plastic mass. Results of numerous moisture determinations made on this plastic material indicate that the water content is 38 ± 1.0% at the point where the curds first fuse to form a sol.

When water is added to dried peanut protein 1 to raise the final mixture to approximately 38% water content, the dry protein quickly ab-

Peanut protein hydrates are described which are capable of binding increasing amounts of water, from 38 to about 70% by weight of the sol, as the pH value of the system is increased from 4.5 to 9.0. The presence of water in excess of that bound by the protein results in disintegration of the protein-water system. The protein hydrates are tacky and, at pH values near neutrality, have viscosity characteristics which make them suitable for use as adhesives, provided the protein used is isolated from the meal with a minimum of alteration by heat or alkali. Precipitated and filtered peanut protein curds are dewatered by warming until the curd particles coalesce and exclude unbound water. This reduction of the water content from 70–80 to about 40% greatly reduces drying costs in preparing isolated peanut protein. Similar hydrates can be prepared from isolated soybean protein.
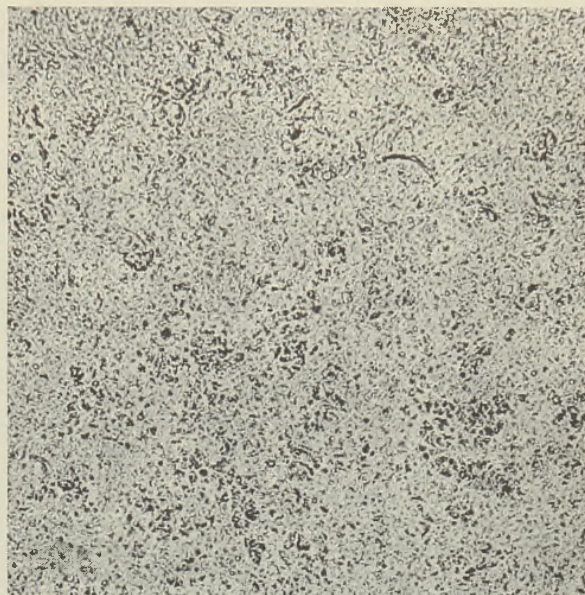
sorbs the small amount of water added. After about 30 minutes the slightly swollen protein particles can be kneaded with the fingers into a homogeneous mass that is translucent when pressed into a thin film. The mass is not tacky at room temperature, but on warming it becomes extremely tacky, and has characteristics identical with those exhibited by the fused curds just described. When water is added to dry (6 to 8%

filtration. The excess water which remains is then eliminated by warming and kneading the curds. This causes the curd particles to coalesce and exclude water which is present in excess of that required to form the protein hydrate.

The curds obtained by precipitation at pH 5.0 differ from those obtained at pH 4.5 in that the former can be reduced readily by heating at 40–50° C. from a water content of 50 to 70% to one
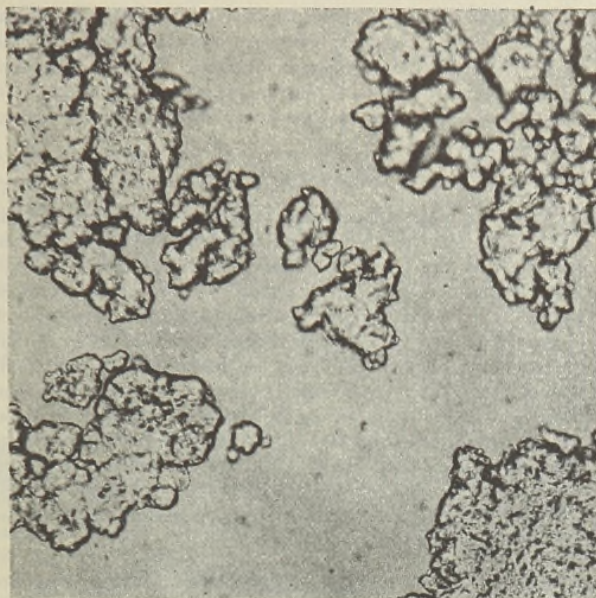
Large solid particles in cell 2   Small solid particles in cell 4

Figure 2. Photomicrographs of Coagulated Proteins (× 250)

moisture) protein 1, in excess of that required to raise the final mixture to 38% water content, the protein particles become opaque after a short time and exhibit little tendency to coalesce. This maximum water content of 38% at which a homogeneous, coherent system can be obtained is close to the 35% water reported to be bound to (isoelectric) proteins (2, 11).

If a portion of the hydrated (38% water) protein with a pH value in the isoelectric range is allowed to stand in excess water, the surface of the hydrate becomes opaque, the substance loses its cohesiveness, and the system disintegrates. The disintegration proceeds rapidly if the hydrated protein mass is broken up by a glass rod. Van Der Dussen and Maaskant (15) state: "One speaks of loss of cohesion when protein gels or similar systems disintegrate."

In contrast to protein 1 (Table I), protein 2, which was precipitated from solution at pH 5.0 and then dried, yields a plastic sol that is tacky at room temperature when the water content is brought to 38%. The hydrate prepared from this protein, which has a pH at the upper end of the isoelectric range, will bind additional water up to about 42% before the system breaks down.

Protein hydrates can also be prepared directly from precipitated protein curds by removing part of the excess water by

corresponding to the bound water capacity of the protein. The filtered curds coalesce as they are warmed, exclude unbound water on kneading, and finally become an extremely coherent mass which can be pulled like taffy, even at room temperatures. The bound water remaining with the protein amounts to about 42.5%. Filtered protein curds precipitated at pH 4.5 can be dewatered only with difficulty by warming and kneading. The forces within the individual hydrated particles appear to be too strong to permit easy coalescence with surrounding particles in the presence of, and to the exclusion of, unbound water. The dewatered curd is "short" at room temperature and breaks when pulled. It can be dewatered, however, to a water content of 38%. This dewatering of the curds can reduce drying costs in the manufacture of isolated protein, as will be emphasized in another paper of this series.

A fair yield of protein can also be obtained by precipitation at pH 6.0 (method 3, Table I). When the protein dispersion is acidified by the slow addition of a saturated aqueous solution of sulfur dioxide, the protein-curd particles, which separate by gravity on standing, coalesce at room temperature; a sol is produced instead of a precipitate of small particles of jelly (curds), similar to that formed by precipitation at pH 4.5 and 5.0 (methods 1 and 2, Table I). The viscous sol obtained after the supernatant liquor is decanted has a water content of about 56%. It is not translucent and appears to be a protein hydrate which is contaminated with finely divided curds.

Although the protein fractions precipitated at pH 4.5, 5.0, and 6.0 may differ with respect to relative contents of the several protein components, it is probable that the marked differences in physical properties of the dewatered protein curds (hydrates) are due primarily to the pH of the curds and not to differences in

TABLE I. PREPARATION OF PROTEINS FROM SOLVENT-EXTRACTED PEANUT MEAL

Protein or Method No.	pH of Extraction	pH of Precipitation	Method of Precipitation
1	7.5	4.5	SO_2 gas
2	7.5	5.0	SO_2 gas
3	7.0	6.0	Water satd. with SO_2 added slowly

protein composition. These dewatered curds have physical characteristics identical with those exhibited by sols which are prepared from dried protein precipitated at pH 4.5 by adding water, or dilute alkali and water, to obtain the equivalent pH and water content of the dewatered curds. In each case the consistency of the hydrate decreases as the pH and water content increase. Further evidence that the pH of the curds exerts a greater influence on the physical properties of the dewatered curds than do the relative contents of protein components is indicated by the following experiment: A protein fraction prepared by precipitation at pH 6.0 and subsequently dried can be redissolved at pH 8.0 and reprecipitated at pH 4.5. The protein obtained has the same physical characteristics as protein precipitated directly from a peanut meal extract at pH 4.5.

EFFECT OF ADDED ALKALI ON HYDRATE SYSTEMS

The effect of alkali on the hydrate system was determined by the addition of varying amounts of water and dilute sodium hydroxide to dry protein 1. It was found that as the pH of the system is raised, increasing amounts of water can be added to the homogeneous, translucent, hydrate system before disintegration takes place. Other changes accompany this increased hydration. In the isoelectric range the cohesiveness, viscosity, and tackiness of the hydrates are at a maximum, and the amount of bound water is at a minimum. As the pH of the hydrate is raised to 6.0, additional amounts of water can be added before disintegration occurs, and less force is required to disintegrate the hydrates, which indicates a decrease in cohesiveness. The force considered responsible for the disintegration of the protein micelles at pH values above the isoelectric point is the osmotic pressure which is brought about by an excess of diffusible ion resulting from the Donnan distribution. Although a gelatin gel is elastic and equilibrium is eventually established on swelling, the micelles of the peanut protein sols are not elastic, and the cohesive forces are so weak that the protein micelles are easily ruptured. The effect of pH on the swelling of peanut protein is difficult to evaluate by the techniques employed for gelatin, because at pH values above the isoelectric range the water-soaked protein particles disintegrate.

At pH values of 6.0 and below, the coagulated protein particles are large enough to settle out in the excess water, and although they appear to consist of white amorphous particles, microscopic observation reveals that they consist of transluscent hydrated jellylike particles. At pH values between pH 6.5 and 9.0, the coagulum obtained upon the addition of excess water is a fine colloidal suspension, which becomes increasingly finer as the pH increases. At pH values above 9.0 the addition of water does not produce a second phase.

Figure 1 is a photograph of peanut protein hydrates prepared at pH 5.0 and 6.85, together with the effect of excess water on the system. Photomicrographs of the coagulated proteins (Figure 2) show the effect of pH on particle size.

The point at which the hydrates disintegrate is not sharp, especially at the higher pH values. In general, within the pH range 4.5 to 6.0 the hydrates can be brought to a water content of 38 to 50% before the system disintegrates; within the pH range 6.0 to 7.0 the limit is 50 to 60%; and between pH 7.0 and 9.0 the limit is 60 to 70%. At pH 9.0 and above, proteins prepared by methods 1, 2, and 3 can be dispersed to give a sol or gel, irrespective of the amount of water present. There is no justification for considering these approximations as more than qualitative evidence of the presence of unbound water.

More important is the ability of the protein to bind more water as the pH increases. This makes it possible to prepare sols from the proteins in Table I that have sufficiently low viscosities between pH values 6.0 and 9.0 to permit their practical use as adhesives. Furthermore, the sols are tacky if excess water is absent, as indicated by the presence of only one phase. In the less viscous hydrates, tackiness becomes apparent where a thin film of sol is applied to the surface to be glued. At pH values above 9.0 the tackiness of peanut protein sols becomes too slight to be of practical value, and the more concentrated mixtures undergo gelation.

INFLUENCE OF SALTS

Obviously, salts influence the properties of colloidal systems of the type described. When isoelectric peanut proteins are leached with excess water to remove salts and other nonprotein material, the consistency of the protein-water systems increases materially. In all unleached protein preparations, the products contained at least part of the natural salts of the meal, as well as a portion of the salts formed during the preparation of the protein and remaining in the dewatered curds. Therefore, duplicate batches of both dewatered curds and dried proteins from dewatered curds, prepared at a given pH value, will contain approximately the same salts, generally in uniform minimum amounts. The effect of salts on the viscosity of peanut protein solutions prepared at lower concentrations and higher pH values has already been discussed (6).

LITERATURE CITED

(1) Astbury, W. T., Trans. Faraday Soc., 36, 871–80 (1940).
(2) Bull, H. B., "Physical Biochemistry", p. 233, New York, John Wiley & Sons, 1943.
(3) Ibid., Chaps. XII and XVIII.
(4) Ibid., p. 235.
(5) Burnett, R. S., and Fontaine, T. D., IND. ENG. CHEM., 36, 284–8 (1944).
(6) Burnett, R. S., Roberts, E. J., and Parker, E. D., Ibid., 37, 276–81 (1945).
(7) Compton, E. D., J. Am. Leather Chem. Assoc., 39, 74–90 (1944).
(8) Fontaine, T. D., and Burnett, R. S., IND. ENG. CHEM., 36, 164–7 (1944).
(9) Greenberg, D. M., in Schmidt's "Chemistry of Amino Acids and Proteins", 2nd ed., p. 481, Springfield, Ill., C. C. Thomas, 1944.
(10) Ibid., Section VII, pp. 1139–44.
(11) Ibid., p. 1139.
(12) Lloyd, D. J., and Shore, Agnes, "Chemistry of Proteins", 2nd ed., p. 476, London, J. A. Churchill Ltd., 1938.
(13) Phillips, Henry, J. Intern. Soc. Leather Trades Chem., 18, 165–74 (1934).
(14) Sponsler, O. L., Bath, J. D., and Ellis, J. W., J. Phys. Chem., 44, 996–1006 (1940).
(15) Van Der Dussen, A. A., and Maaskant, L., in Schmidt's "Chemistry of Amino Acids and Proteins", 2nd ed., p. 450, Springfield, Ill., C. C. Thomas, 1944.
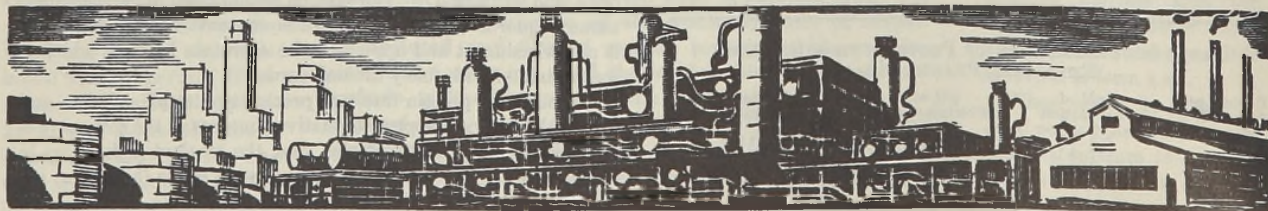
RECOVERY of 2,3-BUTYLENE GLYCOL from FERMENTATION LIQUORS

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A possible industrial source of butadiene is 2,3-butylene glycol, produced by the fermentation of cereal grains. The recovery of butylene glycol from a fermentation liquor is difficult because of its comparatively high boiling point and the presence in the liquor of 2 parts of nonvolatile solids to 1 part of glycol. A recovery process is described in which a concentrated liquor is steam-stripped in a packed column at an elevated pressure. Experimental work underlying this step of the process is described.

SACCHARIFIED wheat or corn mashes have been fermented with a strain of *Aerobacter aerogenes* to produce a beer containing 3.5 to 4.0% *meso-dextro*-2,3-butylene glycol (5) boiling at 183° C., 0.1 to 0.2% acetylmethylcarbinol boiling at 143° C., 0.3 to 0.5% ethanol boiling at 78.32° C., and 6 to 8% nonvolatile solids. Acetylmethylcarbinol and water form an azeotrope (3) which boils at 99.5° C., and the alcohol-water azeotrope boils at 78.15° C. The principal problem of recovery, therefore, is the separation of the highest-boiling volatile compound, glycol, from the nonvolatile solids, present in the approximate ratio of 2 parts of solids to 1 part of glycol. Several methods for accomplishing this step have been studied by various investigators, but few of their results have been published. These methods include solvent extraction, spray drying, kerosene distillation, alcohol precipitation, and drum drying. In the recovery process developed at this laboratory the beer is concentrated and the glycol is removed from the concentrate or sirup by countercurrent steam stripping.

Preliminary consideration of the stripping process led to the conclusion that the operation should be conducted under pressure for purposes of steam economy and greater equipment capacity. Liquid-vapor equilibrium data for the butylene glycol–water system show that the glycol content of vapor from a given liquid increases at a rapid rate as the pressure on the system is increased (1). For example, a water solution containing 10% butylene glycol by weight is in equilibrium with vapor containing 0.33% glycol by weight when the solution is boiled under an absolute pressure of 2.45 pounds per square inch. When the pressure is atmospheric, the vapor contains 1.0% butylene glycol; and at 55 pounds per square inch gage it contains 2.5%. Theoretically 30, 10, and 4 pounds of steam, respectively, would be required to remove the glycol from 1 pound of such a solution by countercurrent stripping. The advantage of stripping at elevated pressures is obvious.

PRELIMINARY EXPERIMENTS

A stripping column 13 feet high was constructed of 6-inch jacketed pipe and packed with 2.5-inch ceramic spheres to a height of 11.5 feet. The arrangement of packing created a con-

tinuous center opening which was plugged with a piece of capped 0.5-inch pipe. Figure 1 is a diagram of the column and auxiliary equipment.

Sirup was prepared in an evaporator by concentrating the beer, made by the fermentation of malted corn mash. The concentrate contained 13.8% glycol and approximately 30% solids. It was pumped at a constant rate through a preheater and into the top of the stripping column. Steam was introduced at the base of the column and vapor issued from the top through a flow-control valve. The pressure in the column was 110 pounds per square inch gage. The vapor was condensed and the condensate weighed. Stripped sirup was discharged from the base of the column through a throttled valve.

For purposes of calculation, the effective steam rate, P, to the base of the column was assumed equal to the rate at which con-
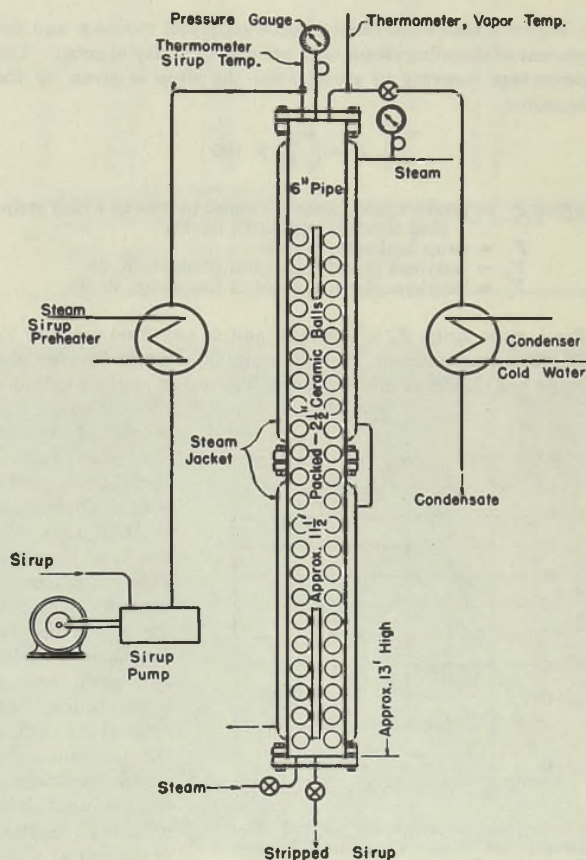

Figure 1. Butylene Glycol Stripping Column

densate was formed. This is true only if the column is operated adiabatically and if there is no difference in the latent heats of vaporization of glycol and water. Since the glycol content of the condensate was small, the effect of the difference in latent heats was insignificant. However, because of heat losses there was some condensation of vapor within the column. In order to obtain applicable values of the steam rate, the assumption was thus made without serious error.

The column was operated until the butylene glycol content of the condensed vapors, as measured by refractive index, became constant. When a steady rate was attained, a sample of the condensate was taken for chemical analysis. Data in Table I show that 95% of the glycol in the sirup was vaporized by the use of 6.08 parts of stripping steam to 1 part of sirup.

TABLE I. VAPORIZATION OF BUTYLENE GLYCOL BY COUNTER-CURRENT STEAM STRIPPING OF GLYCOL EVAPORATOR SIRUP AT 110 POUNDS PER SQUARE INCH GAGE PRESSURE

Run No.	F, Sirup Feed Rate, Lb./Hr.	X_f, Glycol in Sirup, %	Condensate Rate P, Lb./Hr.	Y_p, Glycol in Condensate, %	Product-Feed Ratio P/F, Lb./Lb.	R, Glycol Stripped from Sirup, %
1	25.8	13.8	5.5	4.18	0.21	6.5
2	24.6	13.8	6.2	4.44	0.25	8.1
3	23.3	13.8	17.6	4.52	0.76	24.8
4	23.3	13.8	29.4	4.41	1.26	40.2
5	25.6	12.25	50.0	2.83	1.95	45.1
6	23.4	12.25	62.4	2.32	2.67	50.6
7	23.3	12.25	80.6	2.39	3.46	67.4
8	27.6	12.25	94.6	2.33	3.43	65.2
9	27.6	12.25	115.7	2.44	4.19	83.4
10	27.0	12.25	138.8	2.09	5.14	87.8
11	27.4	12.25	166.7	1.93	6.08	95.8

Figure 2 shows the relation between glycol recovery and the amount of stripping steam used per unit quantity of sirup. The percentage recovery of glycol from the sirup is given by the equation:

$$R = \frac{PY_p}{FX_f} \times 100$$

where P = product rate (assumed equal to rate at which stripping steam is supplied), lb./hr.
F = sirup feed rate, lb./hr.
Y_p = butylene glycol content of product, lb./lb.
X_f = butylene glycol content of feed sirup, lb./lb.

For a given sirup, X_f is constant, and at any fixed pressure Y_p also becomes constant if equilibrium is attained between the liquid and the vapor in the column. Therefore, under conditions of equilibrium, if R is plotted against the ratio P/F a straight line results with a slope equal to $100(Y_p/X_f)$. The broken line of Figure 2 illustrates these ideal operating conditions extrapolated to 100% recovery and a corresponding P/F ratio of 3.1. That the column was grossly inefficient— i.e., contained an insufficient number of theoretical plates —is indicated by the rapid deviation of
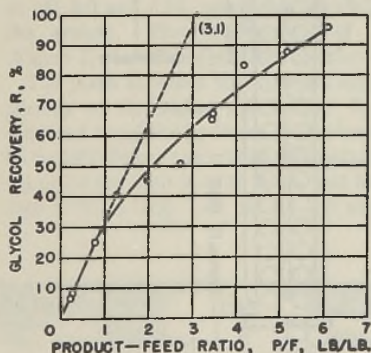

Figure 2. Change in Glycol Recovery in Vapors from 13-Foot Stripping Column with Change in Steam-Sirup Ratio at a Pressure of 110 Pounds per Square Inch Gage

the experimental curve from the ideal line. Actually, a recovery of 95.8% required a P/F ratio of 6.08.

SLUDGE FORMATION. The fermented beer contains both dissolved and suspended solids, and after evaporation 55 to 60% of the total solids in the resulting sirup are insoluble. Approximately 25% of the total solids is ash, composed principally of calcium sulfate and carbonate. Several runs were made to determine whether the insoluble solids of the feed sirup were flowing through the packing, since their accumulation would eventually plug the column. The stripping column was operated until steady-state conditions were established, and the stripped sirup was then collected for a 30-minute period. The following results show that a large part of the solids in the sirup was being deposited in the column:

Run No.	Solids, Lb./Hr. In feed	In stripped sirup	Solids Accounted for, %
12	7.34	4.58	62.2
13	6.81	4.97	73.1
14	6.91	3.93	56.9
15	2.85	1.55	54.3

Since the column was flushed with water between experiments and the runs did not last long, the amount of solids deposited in the column was not enough to cause noticeable flooding. However, when the column was opened after the experiments were completed, the spaces between the pieces of packing were found to be almost completely filled with sludge. This substance was insoluble in water, but its appearance was entirely different from the insoluble solids of the sirup. A chemical analysis of the sludge gave inconclusive results concerning its composition. It is believed that the deposit is a decomposition product of both soluble and insoluble constituents of the sirup, and that its formation is a function of the temperature of stripping. It was recognized that removal of the insoluble solids by filtration of the beer before concentration to sirup would probably lessen the amount of sludge formed during stripping. However, the various methods of filtering and clarifying were found to be impractical because of low operating rates and the high retention of glycol in the separated solids.

PILOT PLANT EXPERIMENTS

The results of the preliminary experiments showed that it was possible to obtain good recoveries of glycol from sirup by the steam stripping process. However, if the process is to be practicable, a method of operation is required which will provide for the removal of the deposited sludge. The column used in the preliminary experiments was lengthened to 27.5 feet to increase the number of theoretical plates. Experiments were conducted to determine a satisfactory type of packing and the maximum operating pressure which could be used without excessive formation of sludge. The amount of sludge deposited was indirectly estimated by the pressure drop across the column. Although sludge was formed at a pressure of 55 pounds per square inch gage, it had a soft texture and could be flushed or washed off the packing by the action of water and steam. The sludges formed at higher operating pressures were harder and more resistant to removal by washing. It was determined that the packing must be large and open in type to minimize the tendency of the sludge to bridge the voids and thus plug the column. For example, iron Raschig rings, 1.9 × 1.9 inches, were found to be a more satisfactory packing than large unglazed ceramic spheres. However, they also plugged or fouled rapidly when packed in a random manner, and were difficult to clean by the countercurrent washing procedure which will be described. An extended experiment proved that by arranging the iron rings in an orderly manner and incorporating a water washing cycle in the operation of the stripping column, prolonged operation was possible.

The column was packed with Raschig rings made by cutting 1.9-inch pieces from standard 1.5-inch pipe. These rings were stacked vertically in circles around a capped 1.5-inch pipe which
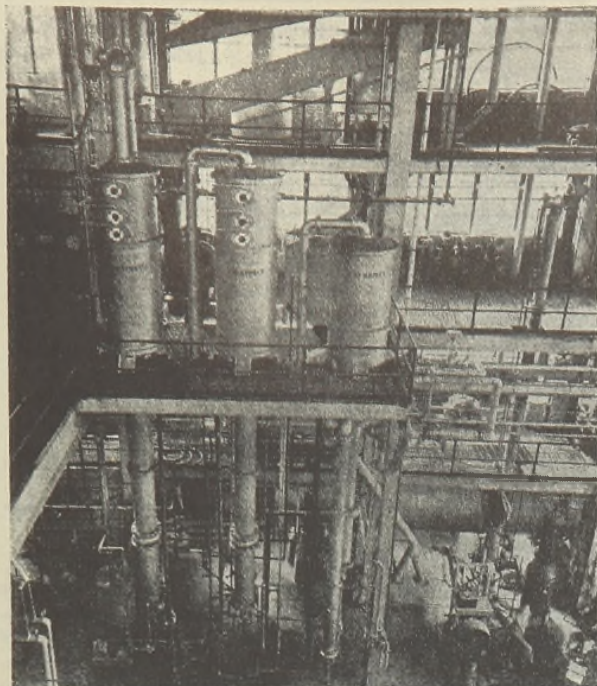
Figure 3. View of Pilot Plant Showing Triple-Effect Evaporator and Stripping Column

plugged the central opening. Each layer of rings was rotated one-half ring in reference to the adjacent layers. The total height of packing was 23 feet. A circular disk, 4 inches in diameter, on which the entering sirup fell, was fixed in the column at approximately 18 inches above the top of the packing.

A duplex proportioning pump was used to feed sirup at approximately 80° F. into the top of the tower at a constant rate from a sirup storage tank which was set on scales to allow frequent checking of the feed rate. Steam at a pressure of 120 pounds per square inch gage was passed through a pressure-regulating valve into the base of the column. The valve controlled the pressure in the base of the column at 55 pounds per square inch gage. The glycol-laden vapors from the top of the column passed into the jacket surrounding the column and were taken from the jacket at the base of the column through a flow control valve. Thus, condensation inside the column was kept at a minimum. The setting of the flow control valve regulated the rate at which steam flowed through the column. The vapors at atmospheric pressure were totally condensed in a multitube single-pass condenser. Stripped sirup from the base of the column was collected in a receiving tank under pressure and discharged to the sewer at intervals. A differential pressure recorder was connected across the column. Figure 3 shows the stripping column and evaporator used to concentrate butylene glycol beer; Figure 4 pictures the sirup weigh tank, feed pump, condenser, and base of the stripping column.

The glycol evaporator sirup used in this experiment was made from fermented, acid-hydrolyzed wheat mash. It was prepared in the pilot plant of Joseph E. Seagram & Sons, Inc., and shipped to this laboratory. Calcium hydroxide to the extent of 1.25% was added to the sirup before

stripping, because previous results had indicated that the sludge from an alkaline sirup was softer and more amenable to removal by water washing than that from an acid sirup. Samples of feed sirup and stripped sirup were taken regularly during the run. All of the condensate was collected, mixed, and sampled at the end of the experiment.

During preliminary runs the amount of condensation within the column was measured. When this was added to the condensate of 210 pounds per hour which was collected as product, the total steam used under the operating conditions was equivalent to a superficial vapor velocity of approximately 2 feet per second. Throughout most of the run the sirup feed rate was 42 pounds per hour; hence, the ratio of steam to sirup, P/F, was 5. These rates were maintained except for the first 24 hours of the experiment, when a slightly lower sirup feed rate was used.

The experiment was conducted for 7 days without interrupting the flow of steam through the column. During the first 24 hours the differential pressure across the column increased from 0 to 1.5 inches of mercury. The sirup feed was stopped, and the column was allowed to drain for 15 minutes. The pressure drop, attributed to retention of thickened sirup or sludge, was then 0.9 inch of mercury. Water, preheated to approximately 240° F., was

TABLE II. OPERATING-WASHING CYCLE OF STRIPPING COLUMN

	Operating Cycle, Hr.		End of stripping cycle[b]	After sirup draining[c]	After water washing and draining[c]	After caustic washing and draining[c]
Wash No.	Stripping	Cleaning[a]				
1	24.25	1.5	1.5	0.9	0.45	...
2	4.25	1.0	1.5	0.9	0.5	...
3	7.25	1.0	1.65	0.95	0.55	...
4	6.5	1.25	1.7	1.05	0.5	...
5	2.5	3.0	1.45	0.9	0.6	0.4[d]
6	11.5	1.25	1.65	0.85	0.6	...
7	12.0	4.0	1.85	1.1	0.6	0.25[e]
8	10.25	1.25	1.4	0.7	0.3	...
9	9.75	1.25	1.6	0.85	0.35	...
10	10.75	1.25	1.6	0.85	0.3	...
11	10.5	1.25	1.5	0.9	0.35	...
12	11.0	1.25	1.5	0.85	0.4	...
13	10.5	1.25	1.55	0.9	0.45	...
14	16.5	1.25	1.8	1.1	0.6	...

Differential Pressure across Tower, In. Hg

[a] Includes time allowed for draining.
[b] Differential readings made with sirup and steam flowing through column.
[c] Differential readings made with steam but no liquid flowing through column.
[d] Caustic solution used contained 5% NaOH.
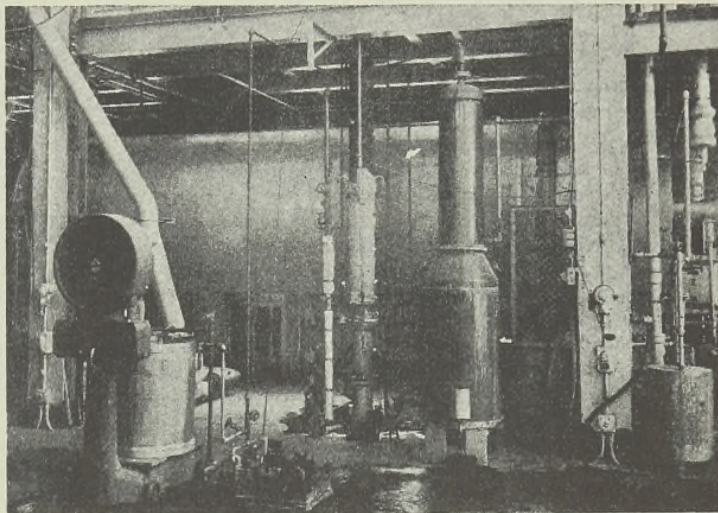[e] Caustic solution used contained 10% NaOH.

Figure 4. Base of Stripping Column with Weigh Tank, Feed Pump, and Condenser

then pumped into the top of the column at a rate of 60 to 120 gallons per hour for 45 minutes. After a short drainage period the pressure drop across the column was 0.45 inch of mercury. This differential indicated some retention of sludge. Subsequent washings were carried out in the same manner. Table II gives results of all cleaning operations.

In addition to the water wash, a solution of sodium hydroxide was pumped into the column at a rate of 60 gallons per hour as part of washes 5 and 7 (Table II) to determine its effect on the sludge which remained on the packing after the water wash. The chemical action of the caustic solution on the sludge apparently caused foaming, and the packing became partially plugged. This was indicated by the rapid rise of the differential pressure during the caustic wash and by entrainment of solids in the condensate. It was eventually determined that these difficulties could be prevented by pumping the solution at the rate of 8 to 10 gallons per hour. The caustic solution dissolved rather than loosened some of the solids, since the liquid which drained from the column during the caustic treatment was thin in consistency but dark in color. After pumping caustic solution at the slow rate for 1 hour, it was possible to increase the rate gradually to 60 gallons per hour without causing an excessive increase in differential pressure.

It is evident from the differential pressure readings that the caustic treatment removes some of the sludge which normally remains after the water wash. Obviously, such a treatment can be included every several days as part of a regular cleaning procedure.
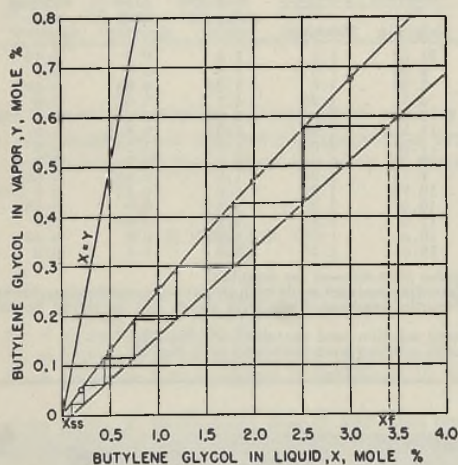

Figure 5. Diagram for Determining Number of Theoretical Plates in Glycol Stripping Column, Operating at 55 Pounds per Square Inch Gage

Six cycles, each lasting approximately 12 hours, were made with good results after wash No. 7. The slow rate at which the final differential pressure increased indicated that only a small amount of permanent deposit was being produced during each cycle. The last stripping cycle lasted 16.5 hours, which was evidently too long as the final pressure drop increased from 0.45 to 0.60 inch of mercury.

The column was opened at the end of the experiment and found to be very dirty, although it had been washed with water in the usual manner. The majority of the rings were open, but most of the spaces between the rings and the walls were plugged, and the rings were partially coated with a firm layer of material $1/16$ to $1/8$ inch thick. This material requires treatment with caustic soda solution for removal. The wall effects were undoubtedly responsible for most of the final differential pressure after washing. It is assumed that these same effects would be negligible in a large column.

TABLE III. PILOT PLANT OPERATING AND RECOVERY DATA

	First Day	Next 6 Days
Duration of run (stripping), hr.	24.5	123.25
Base pressure in column, lb./sq. in. gage	55	55
Sirup feed rate, lb./hr.	31.9	42.3
Condensate rate, lb./hr.	194	210
Steam/sirup ratio, lb./lb.	6.08	4.97
Sirup stripped, lb.	781	5214
Condensate produced, lb.	4750	28,450[a]
pH of feed sirup	8.4–9.1	8.4–9.1
pH of condensate	7.8–8.4	8.0–9.1
pH of stripped sirup	5.6–6.1	6.0–7.2
Butylene glycol content, %		
Feed sirup	6.47	5.31
Condensate	0.89	0.88
Stripped sirup	0.58	0.60
Solids content, %		
Feed sirup	26.5	19.4
Stripped sirup	14.1	12.8
Glycol recovery (based on butylene glycol in condensate), %	83.5	90.4[b]
Ratio of butylene glycol in feed sirup to solids in feed sirup, lb./lb.	0.244	0.274
Ratio of butylene glycol in stripped sirup to solids in stripped sirup, lb./lb.	0.0411	0.047
Glycol recovery (based on above ratios), %	83.2	82.9[b]

[a] Includes some condensate collected during washing.
[b] Average recovery, assuming feed sirup to contain 5.71% butylene glycol, is 84.1%.

Table III gives the operating and recovery results of the experiment. The recovery during the first 24 hours of operation was low in relation to the P/F ratio for that period and is attributed to operating difficulties experienced at the beginning of the experiment. The recovery for the 6-day period was reasonably good, considering the height of the stripping column and the size and the arrangement of packing.

The results indicate that the stripping of butylene glycol from evaporator sirup in a packed column is a practical operation to the extent that a stripping-cleaning cycle has been developed which makes the process semicontinuous. This conclusion, of course, is based on the use of relatively small-sized equipment for only a limited time; the stripping operation should be conducted in a column with a diameter of at least 18 inches to establish firmly the validity of the conclusions before full-scale plant installations are made. Moreover, the packing should be examined visually to ascertain whether sludges that are insoluble even in caustic are likely to accumulate during prolonged operation.

CALCULATION OF THEORETICAL PLATES AND H.E.T.P.

The number of theoretical plates required for stripping glycol from evaporator sirup can be calculated graphically. With the usual simplifying assumptions, the equation of the operating line, obtained by making a glycol balance around the base of the column, is

$$Y_m = r(X_{m+1} - X_{ss})$$

where	Y_m	= butylene glycol in vapor from section m, mole %
	X_{m+1}	= butylene glycol in liquid from section $m + 1$, mole %
	X_{ss}	= butylene glycol in stripped sirup, mole %
	r	= ratio, moles feed/mole vapor/hour

The equation is that of a straight line with a slope of r and an intercept on the X axis of X_{ss}.

Before making the graphical analysis, it was necessary to establish a basis for calculating the glycol concentrations in the feed and in the stripped sirup. In particular, it was necessary to know whether the mole fraction of glycol should be calculated on the basis of the glycol and water, or whether the solids in the sirup should also be included. An experiment was performed, similar to the one previously described, to determine the actual glycol content of the vapors in equilibrium with sirup at a pressure of 30 pounds per square inch gage. A sirup containing 8% by weight of butylene glycol and approximately 25% solids was fed to the 27-foot stripping column, and the glycol content of the vapors was determined for several runs using varying ratios of steam to sirup. The recovery was plotted against the ratio of

Figure 6. Flow Diagram of Butylene Glycol Recovery Process

steam to sirup, and the line going through the origin and those points lying in a straight line was extrapolated to the 100% recovery intercept. The value of the intercept was 5.1. Thus, the glycol content of vapor in equilibrium with sirup was 8.0/5.1 = 1.57% by weight or 0.32 mole %. If it is assumed that the sirup is equivalent to a water-glycol solution (i.e., the solids are considered as though they are water), the sirup would then contain 1.71 mole % butylene glycol (8.0% by weight). The equilibrium glycol content of vapor from a glycol-water solution containing 1.71 mole % glycol at 30 pounds per square inch gage is reported to be 0.34 mole % (1). Since these values are in close agreement, it appears that, in calculating the mole fraction of glycol in a sirup, the solids should not be neglected but should be included with the water.

Assume that it is desired to strip 97% of the glycol from a sirup which contains 15 weight % glycol by the use of 5 pounds of steam per pound of sirup when the operation is conducted at a pressure of 55 pounds per square inch gage. Figure 5 shows the graphical determination of the required number of theoretical plates. The points on the equilibrium curve were taken from liquid-vapor equilibrium data determined by the authors (1). The stripped sirup will contain 0.10 mole % glycol if the column is assumed to operate adiabatically; hence, the operating line intersects the x-axis at $X_{ss} = 0.1$. Its slope, calculated from the steam and feed rates, is $r = 0.176$, and the composition of the feed is $X_f = 3.41$. It is evident that seven theoretical plates are required under the specified operating conditions.

The data for the 6-day experiment (Table III) were subjected to graphical analysis to determine the number of theoretical plates in the stripping column under the conditions of the experiment. The ratio of sirup to condensate was used to calculate the slope of the operating line, and the glycol content of the stripped sirup was corrected for the dilution which resulted from condensation in the column. Analysis indicated that the column contained approximately three theoretical plates. As the length of the packed section of the column was 23 feet, the H.E.T.P. was approximately 8 feet. These calculations are not precise,

since the enrichment of the vapors with glycol as they flow up the column is not a process of distillation; i.e., all the liquid in the column is not at its boiling point. The temperature gradient in the column is small; hence, liquid-vapor equilibrium data at the temperature prevailing at the bottom of the column are applicable. However, since the difference between the boiling points of water and glycol-water solutions of low concentrations is slight, it is believed that the equilibrium data used approximate closely the actual liquid-vapor conditions which exist in the stripping column.

RECOVERY PROCESS

Figure 6 is a flow sheet of the proposed process. By means of multiple-effect evaporation, butylene glycol beer is concentrated to a sirup containing 20 to 25% solids and as much as 15% glycol. In order to retain all of the glycol in the evaporator sirup, the vapors from each effect are rectified. This operation, in conjunction with multiple-effect evaporation, is feasible and is provided for by scrubbing columns in the vapor lines from the effects. Somewhat similar methods were suggested by Chute (2) and by Reich (4). Most of the alcohol is vaporized in the feed effect of the evaporator and is present in the condensate pumped from the steam chest of the third effect. This condensate is fed to a fractionating column (not shown), and the alcohol is recovered as a salable product. Acetylmethylcarbinol is distributed between the various condensates and the evaporator sirup. No practical method has been devised for the recovery of this compound from these dilute solutions. However, the carbinol does not contaminate either the glycol or the alcohol products, since it is separated without difficulty during subsequent distillations.

The evaporator sirup containing all of the glycol is fed to the top of a packed stripping column, which is operated at a pressure of 55 pounds per square inch gage. Steam is passed up the column, in the ratio of 5 pounds of steam per pound of sirup, and absorbs or strips the glycol from the sirup during the countercurrent passage. After every 11 hours of operation the sirup fed to the stripping column is diverted to a storage tank (not shown) and water is pumped through the column for 1 hour to remove the deposited sludge. Steam flow is not interrupted during the washing cycle; hence, the continuity of the operation as a whole is not disturbed. The stripped sirup, which is discharged from the base of the stripping column, is similar to distillers' evaporator sirup and is drum-dried for the production of poultry and cattle feed. The vapor from the top of the column contains butylene glycol, water, and an insignificant amount of impurities. It is led to the base of a bubble-cap scrubbing column, which is also operated under pressure, and is washed free of glycol by a stream of water introduced at the top of the column. A reflux ratio (overflow to vapor) of approximately 0.286 is used in this operation. The vapor from the top of the scrubbing column has a pressure of approximately 50 pounds per square inch gage and is divided into two streams; one stream is used for process work in other parts of the plant, and the other stream is compressed to a pressure of 55 pounds per square inch gage by a thermocompressor with steam at a pressure of 250 pounds per square inch gage. The compressed vapor is re-used for stripping. Steam withdrawn from the system for process use is approximately

equal to that required for compression; hence, the steam required for stripping is practically only that which is condensed because of heat losses in the system. The glycol-water product from the scrubbing column contains approximately 8% butylene glycol and is easily rectified to make a product containing 99% butylene glycol.

ACKNOWLEDGMENT

The cooperation of Joseph E. Seagram & Sons, Inc., in furnishing some of the evaporator sirup used in this investigation is

gratefully acknowledged. The steam cycle of the stripping and scrubbing columns was suggested by E. R. Gilliland.

LITERATURE CITED

(1) Blom, R. H., Mustakas, G. C., Efron, Aaron, and Reed, D. L., IND. ENG. CHEM., 37, 870 (1945).
(2) Chute, H. O., U. S. Patent 963,275 (July 5, 1910).
(3) Northern Regional Research Lab., unpub. data.
(4) Reich, G. T., Chem. & Met. Eng., 49 (5), 129 (1942).
(5) Ward, G. E., Pettijohn, O. G., Lockwood, L. B., and Coghill R. D., J. Am. Chem. Soc., 66, 541 (1944).

LIQUID-VAPOR EQUILIBRIUM in MIXTURES of 2,3-BUTYLENE GLYCOL and WATER

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Liquid-vapor equilibrium measurements have been made for meso-2,3-butylene glycol–water system at pressures and concentrations covering the ranges to be encountered in the recovery of glycol from fermentation liquors. From these data a chart has been prepared which shows vapor composition as a function of pressure for certain arbitrarily chosen liquid concentrations. The chart has an accuracy sufficient for engineering design calculations.

THE process described in the preceding paper for recovering meso-2,3-butylene glycol from fermentation liquors (1) involves concentration of beer at reduced pressures, followed by steam stripping and vapor scrubbing at elevated pressures. The design of equipment necessary to carry out these operations and other concentration and rectification steps by which a 99% butylene glycol product is produced is based largely on the liquid-vapor equilibrium of the butylene glycol–water system.

Liquid-vapor equilibrium data for the meso-2,3-butylene glycol–water system have been determined at 2.45 pounds per square inch absolute (approximately 25 inches of mercury vacuum) and at atmospheric pressures for concentrations of 0 to 100 mole % glycol in the liquid. Data for pressures of 30 and 65 pounds per square inch gage have been determined for concentrations of glycol in the liquid of 0 to 35 mole %. The graph obtained by cross plotting these data can be used to interpolate equilibrium values for the intermediate pressures and concentrations expected in the various steps of the glycol recovery process.

METHOD FOR EQUILIBRIUM DATA

Technical grade meso-2,3-butylene glycol, recovered from an *Aerobacter aerogenes* fermentation of acid-hydrolyzed wheat mash, was purified by distillation of a 50% solution of the glycol which had been autoclaved in the presence of lime. The water fraction was removed at atmospheric pressure, and the glycol was then distilled under vacuum. The purified material was colorless and had only a slight odor. While *A. aerogenes* produces butylene glycol in which the meso variety predominates (5), some dextro-glycol is also formed. The latter sterio-isomer has a boil-

ing point approximately 5° C. below that of meso-glycol and undoubtedly influences liquid-vapor equilibrium results. However, since the amount of dextrorotatory glycol present is small, it is assumed that the effect on the results is negligible, particularly for engineering calculations.

The dynamic method, as described by Othmer (3), was used to obtain equilibrium data. The equipment consisted of two Othmer equilibrium stills (3) constructed of Pyrex and one pressure equilibrium still constructed of stainless steel. One of the glass stills was heated by a gas flame which impinged on the thermal circulation leg of the boiler; the other contained an internal electric-resistance heater. These stills were vented to a glass manifold to which were connected a vacuum ballast tank, a mercury manometer, a source of vacuum, and an atmospheric vent.
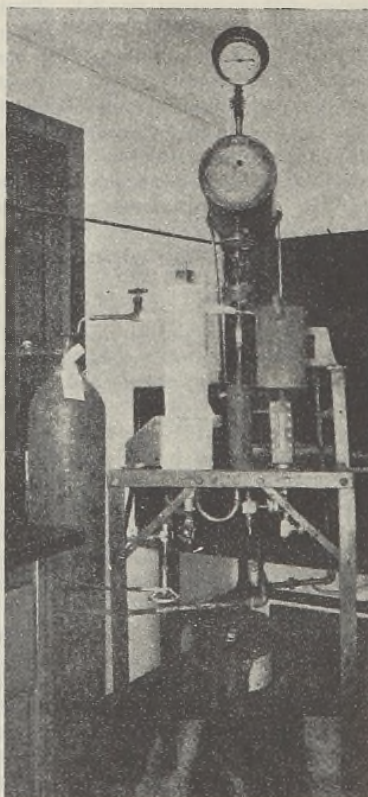

Figure 1. Equilibrium Still for Use at Elevated Pressures

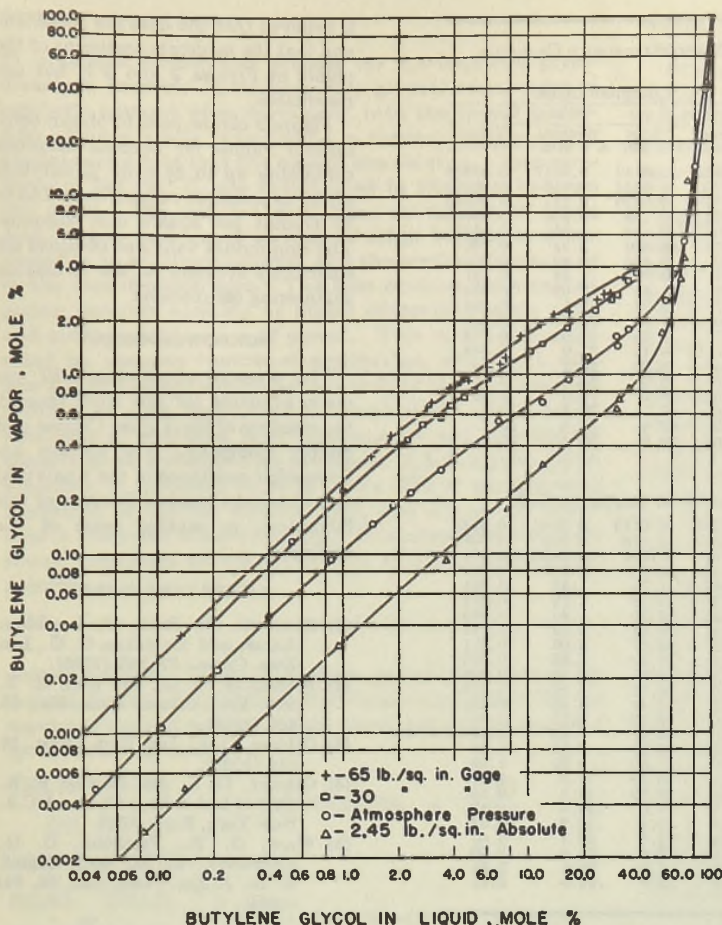[1] Present address, Puget Sound Pulp and Timber Company, Bellingham, Wash.

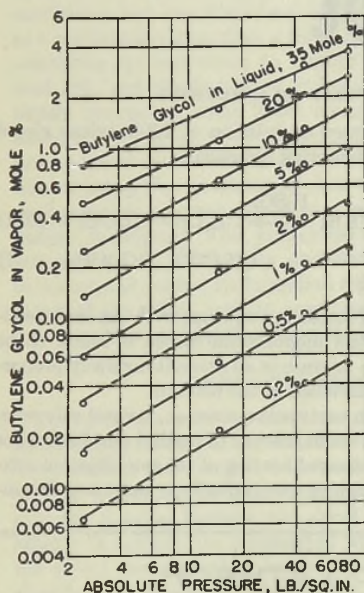**Figure 2. Liquid-Vapor Equilibrium of Butylene Glycol–Water Mixtures at Various Pressures**

Figure 3. Effect of Pressure on Equilibrium Composition

hour. As the volume of the distillate receiver and return tube was about 30 cc., a distillation rate of 6²/₃ cycles per hour was achieved. The distillation was conducted for 1.5 to 3 hours, depending on the glycol content of the liquids; then samples of the liquid in both the boiler and distillate receiver were taken for analysis.

The pressure still (Figure 1) is a large-scale adaptation of the glass stills, and consists of a boiler, condenser, distillate receiver, and pressure-equalizing chamber. It is constructed of stainless steel, is equipped with needle valves and a ballast tank, and has an allowable working pressure of 100 pounds per square inch gage. A more detailed description of the still was given by Othmer (4). The liquid in the boiler was heated by a flame which impinged on the thermal circulation leg. To prevent partial condensation of the vapors, the upper portion of the boiler was wound with resistance wire and electrically heated. Superheating of the vapors was avoided by careful control of the heat input. The entire boiler was insulated by an asbestos jacket. Pressure was indicated by a calibrated Bourdon-type gage, and an iron-constantan thermocouple was used to determine the temperature of the vapor. The equipment was evacuated, and then 800 cc. of liquid were drawn into the still. The entire system was filled with nitrogen and again evacuated to remove any remaining oxygen. Nitrogen was then introduced until the desired operating pressure was reached and heating of the liquid commenced. When the liquid reached its boiling point, the pressure in the still was again adjusted by either adding or venting nitrogen. The rate of evaporation was approximately 420 cc. of liquid per hour. The capacity of the distillate receiver and return tubes was adjusted to approximately 60 cc. by the insertion of a metal block in the receiver. Thus a distillation rate of 7 cycles per hour was achieved. The distillations were conducted for 2 to 3 hours, depending on the glycol content of the mixture charged to the boiler. Samples were taken at the end of the distillation period and analyzed for their glycol content.

The butylene glycol content of samples containing less than 5 weight % of glycol was determined chemically by a periodic acid-oxidation method. This method, based on the formation of 2 moles of acetaldehyde by the oxidation of 1 mole of 2,3-butylene glycol with periodic acid, will be described in a future publication. Samples containing between 5% and 94 weight % of glycol were analyzed by refractive index. Samples containing more than 94% glycol were analyzed for their water content by the method of Karl Fischer (2).

DISCUSSION OF RESULTS

Table I presents results of the equilibrium determinations. Temperatures are reported for only a few points, since the accuracy of measurement was not sufficient to detect consistently the small differences in temperature between many of the points. The equilibrium data were plotted and the resulting diagram is given in Figure 2. Logarithmic coordinates were used in order to avoid crowding the points at the lower concentrations. Figure 3 is a logarithmic cross plot of vapor composition against absolute pressure at a few arbitrarily chosen liquid concentrations. Straight lines were drawn to average the four points although some curvature is indicated at the higher pressures. However, in view of the experimental error and the fact that the equilibrium values were not all determined in the same apparatus, it

The glass stills could, then, be operated under either vacuum or atmospheric pressure. A centigrade thermometer with 1° graduations was used to measure the vapor temperature. After approximately 300 cc. of glycol-water mixture was charged to the boiler of a still, the vacuum was adjusted or the still was vented to the atmosphere, and heating of the liquid commenced. The rate of evaporation averaged approximately 200 cc. of liquid per

TABLE I. LIQUID-VAPOR EQUILIBRIUM DATA FOR MESO-BUTYLENE GLYCOL–WATER MIXTURE

Temp., °C.	Butylene Glycol Weight % in:		Mole % in:		Temp., °C.	Butylene Glycol Weight % in:		Mole % in:	
	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
	Pressure = 750 ± 5 Mm.					Pressure = 127 ± 5 Mm.			
100.0	0.231	0.0244	0.0462	0.00486	58.4	0.423	0.0142	0.0847	0.00280
	0.530	0.0535	0.106	0.0107		0.700	0.0244	0.141	0.00486
	1.06	0.112	0.214	0.0224	58.5	1.34	0.0430	0.271	0.00859
	2.00	0.226	0.406	0.0453		4.58	0.153	0.950	0.0307
	4.28	0.470	0.886	0.0944		5.05	0.160	1.05	0.0321
	6.90	0.733	1.46	0.147		14.7	0.500	3.33	0.100
	8.84	0.920	1.90	0.185	59.0	15.8	0.460	3.62	0.0924
100.5	10.8	1.09	2.36	0.220		30.1	0.900	7.93	0.181
	15.2	1.45	3.46	0.293	60.4	40.6	1.60	12.02	0.324
101.0	27.6	2.68	7.08	0.548		58.7	2.92	22.1	0.598
101.8	40.7	3.40	12.1	0.699	63.0	69.0	3.16	30.8	0.648
	50.7	4.57	17.1	0.948		69.7	3.56	31.5	0.733
103.0	58.2	5.95	21.8	1.25	64.0	73.7	4.10	35.9	0.848
	69.4	7.66	31.2	1.63	71.0	85.5	8.20	54.1	1.76
105.0	70.0	7.00	31.8	1.48	74.0	91.6	15.2	68.6	3.46
106.0	73.7	8.40	35.9	1.80	81.0	93.3	19.0	73.6	4.48
109.3	87.6	11.8	58.6	2.61	92.0	93.6	40.9	74.5	12.2
113.4	90.3	16.8	65.1	3.88	106.2	96.2	63.4	83.5	25.7
117.0	92.9	22.5	72.4	5.49	118.0	98.6	79.3	93.4	43.4
134.8	95.7	45.7	81.7	14.4					
158.5	98.8	76.1	94.3	38.9					
	Pressure = 30 Lb./Sq. In. Gage					Pressure = 65 Lb./Sq. In. Gage			
130.0	1.46	0.308	0.295	0.0617	154.5	0.291	0.0715	0.0583	0.0143
	2.66	0.585	0.543	0.117		0.670	0.176	0.135	0.0352
	5.05	1.10	1.10	0.222		2.67	0.692	0.545	0.139
	10.50	2.19	2.28	0.446		4.10	1.03	0.847	0.208
	12.3	2.60	2.73	0.531		6.87	1.73	1.45	0.351
	15.1	2.82	3.43	0.577		8.37	2.03	1.79	0.412
	16.9	3.26	3.89	0.669		8.58	2.21	1.84	0.449
	19.5	3.62	4.61	0.745	156.0	13.5	3.44	3.03	0.707
	21.4	4.01	5.16	0.828		13.5	3.27	3.08	0.671
136.0	24.8	4.61	6.19	0.957		16.8	3.90	3.88	0.805
	37.5	6.40	10.7	1.35		19.1	4.34	4.51	0.899
	40.2	7.20	11.9	1.53		19.3	4.57	4.56	0.948
	41.0	7.10	12.2	1.51	156.5	20.2	4.49	4.82	0.931
	50.0	8.60	16.7	1.85		25.0	5.28	6.25	1.10
138.0	61.1	10.6	23.9	2.32		27.8	5.47	7.15	1.14
139.5	66.2	11.9	28.1	2.63		29.7	5.95	7.82	1.24
149.7	68.5	12.8	30.3	2.85		33.9	7.80	9.30	1.66
151.6	73.5	14.6	35.7	3.31		40.4	8.90	11.9	1.92
155.0	76.7	16.2	39.7	3.72		44.7	9.70	13.9	2.10
					157.5	44.9	10.0	14.0	2.17
						50.3	10.4	16.8	2.27
					159.6	60.8	11.8	23.7	2.61
					160.2	64.0	12.6	26.2	2.80
					170.5	66.3	12.9	28.2	2.88
					172.2	72.0	15.0	34.0	3.41

is believed that the data are consistent and that the moderate scattering of the points in Figures 2 and 3 is not unreasonable.

Figure 3 can be used to obtain equilibrium values for aqueous solutions containing up to 35 mole % butylene glycol at pressures varying from 2.45 to 80 pounds per square inch absolute. The equilibrium values so obtained are sufficiently accurate for use in making engineering calculations.
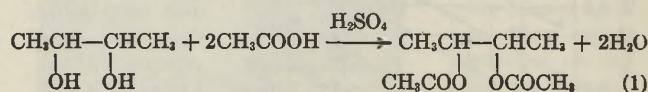
ACKNOWLEDGMENT

LITERATURE CITED

(1) Blom, R. H., Reed, D. L., Efron. Aaron, and Mustakas; G. C., IND. ENG. CHEM., 37, 865 (1945).
(2) McKinney, C. D., and Hall, R. T., IND. ENG. CHEM., ANAL. ED., 15, 460 (1943).
(3) Othmer, D. F., IND. ENG. CHEM., 35, 614 (1943).
(4) Othmer, D. F., and Morley, F. R., Div. of Ind. & Eng. Chem., A.C.S., New York, Sept., 1944.
(5) Ward, G. E., Pettijohn, O. G., Lockwood, L. B., and Coghill. R. D., J. Am. Chem. Soc., 66, 541 (1944).

CONTINUOUS PROCESS for ACETYLATION of 2,3-BUTYLENE GLYCOL

THE development of a commercially feasible process for the production of 1,3-butadiene from 2,3-butylene glycol depended largely on the adaptation of each step to continuous operation. It has been shown (4) that the pyrolysis of the glycol diacetate is a more efficient route to butadiene than the direct catalytic dehydration of the glycol. The pyrolysis operation, the separation and purification of the butadiene, and the recovery and rectification of the acetic acid and by-products (6) were all readily adaptable to continuous processing equipment. The conversion of the glycol to its diacetate by continuous methods, however, required a more detailed investigation. Continuous esterification processes now in commercial operation are confined almost wholly to the manufacture of esters which can be removed from the reaction mixture by distillation. Since 2,3-butylene glycol diacetate has a boiling point of 193° C. and its water azeotrope (boiling point, 99.5° C.) is not readily separable from acetic acid, its manufacture was not adaptable to these systems (3).

ESTERIFICATION REACTIONS

The mineral-acid-catalyzed acetylation of 2,3-butylene glycol may be illustrated by the following equation:

$$CH_3CH\!-\!CHCH_3 + 2CH_3COOH \xrightarrow{H_2SO_4} CH_3CH\!-\!CHCH_3 + 2H_2O$$
$$\underset{OH\ \ \ OH}{} \qquad\qquad \underset{CH_3COO\ \ \ OCOCH_3}{} \quad (1)$$

This reaction probably proceeds in two steps with the intermediate formation of the glycol monoacetate which is found to be present in the acetylation mixture in an amount inversely proportional to the degree of completion of the reaction.
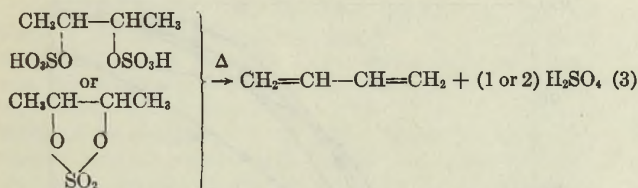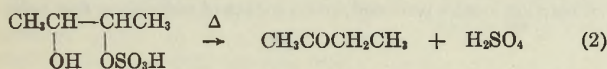
In addition to the main acetylation reaction, several side reactions may also occur. A small amount of methyl ethyl ketone is always produced, and prolonged heating of the esterification mixture results in the formation of some butadiene and tarry decom-

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A practical continuous process for 2,3-butylene glycol diacetate consists in feeding the glycol, along with a catalytic amount of sulfuric acid, into the top of a reaction column while introducing a continuous stream of glacial acetic acid into the base of the column. Temperatures of 140-150° C. are maintained in the zone between the feeds. The column distillate, consisting of acetic acid, water, and traces of methyl ethyl ketone, is dehydrated in an auxiliary column, and the acetic acid returned to the esterification feed. The base product from the reaction column consists of glycol diacetate, acetic acid, and sulfuric acid esters of glycol. This mixture is separated by vacuum fractional distillation, the acetic acid and sulfuric acid esters being returned to the esterification column as feed and catalyst, respectively. The glycol diacetate so produced is of high quality and suitable for conversion to butadiene by pyrolysis. 2,3-Butylene glycol diacetate is produced in 97% yield; 3% of the glycol is converted to methyl ethyl ketone, and the excess acetic acid is recovered quantitatively. This procedure has been found applicable to the production of other high-boiling acetates.

position products. These by-products probably result from the thermal decomposition of the sulfuric acid esters, formed by the reaction of the acid catalyst and the glycol, and may be explained by the following equations:

$$\underset{\underset{OH}{|}\;\;\underset{OSO_3H}{|}}{CH_3CH-CHCH_3} \xrightarrow{\Delta} CH_3COCH_2CH_3 + H_2SO_4 \qquad (2)$$

$$\left.\begin{array}{c}\underset{\underset{HO_3SO}{|}\;\;\underset{OSO_3H}{|}}{CH_3CH-CHCH_3}\\ \text{or}\\ \underset{\underset{O}{|}\;\underset{O}{|}}{\underset{\diagdown\!\!\!/}{CH_3CH-CHCH_3}}\\ \underset{SO_2}{}\end{array}\right\} \xrightarrow{\Delta} CH_2=CH-CH=CH_2 + (1 \text{ or } 2)\ H_2SO_4 \quad (3)$$

Both of these side reactions occur to a certain extent under all conditions, but are minimized by conducting the esterification as a continuous rather than a batch operation. Under controlled conditions the conversion to methyl ethyl ketone does not exceed 3%, and the formation of butadiene can be almost completely prevented. The latter occurs only when the reaction mixture is subjected to prolonged heating or when the temperature is raised to 170° C. or above. This reaction is always accompanied by the formation of charred and tarry decomposition products and does not represent a satisfactory method of producing butadiene. The production of butadiene during the esterification is particularly undesirable because it is difficult to collect and purify, its formation represents an inefficient utilization of the glycol, and the accompanying decomposition products complicate the purification of the esterification products.

BATCH INVESTIGATIONS

The acetylation of 2,3-butylene glycol by batch processing methods was studied on both the laboratory and pilot-plant scale. The results of these studies were later used as a guide in developing the continuous process. Laboratory investigations showed that the reaction between the glycol and acetic acid proceeded rapidly to equilibrium (established at about 45% conversion to the glycol acetate) when heated in the presence of the usual esterification catalysts. Continuous removal, by an entrainer system, of the water formed during the reaction served to carry the reaction to about 90% completion within 4 to 5 hours. Ef-

fecting the last 7-10% of the reaction required 2 to 3 hours at the temperature of the refluxing reaction mixture.

Of the various catalysts studied, sulfuric acid and p-toluene sulfonic acid were the most effective in low concentrations. Sulfuric acid was chosen since it gave a satisfactory reaction rate at concentrations of 1-1.5% of the weight of the glycol, whereas 3% of p-toluene sulfonic acid was required. The availability and low cost of the sulfuric acid were also taken into consideration.

While the esterification reaction proceeded slightly faster at high ratios of acetic acid to glycol, completely satisfactory results were obtained on a batch scale by operating at a ratio of 2.5 moles of acetic acid to 1 mole of glycol.

Entrainers were evaluated on the basis of their water-carrying capacity and on their efficiency, in so far as loss of acetic acid in the removed water was concerned. Benzene and toluene removed water satisfactorily, but their use entailed some loss of acetic acid since both also form azeotropes with the acid. Isopropyl ether and petroleum ether were eliminated on the basis of their low-water carrying capacities. Isopropyl acetate, n-propyl acetate, and n-butyl acetate gave the most promising results. Of these, isopropyl acetate was selected for the batch investigations. Its azeotrope carries sufficient water to balance the rate of water formation and its separation from acetic acid is readily accomplished. n-Butyl acetate was not satisfactory for batch work since the rate of water production during the latter stages of the reaction was not sufficiently high to maintain the azeotropic composition with a fixed amount of entrainer. As a result, acetic acid became the lowest-boiling component of the system and was removed as distillate to a considerable extent. n-Propyl acetate was not available in sufficient quantity for this work. Preliminary investigations indicated, however, that it would be satisfactory.

LABORATORY PROCEDURE. The reaction flask was charged with 1 molar part of glycol, 2.5 molar parts of acetic acid, 0.016 molar part of sulfuric acid, and 0.5 part by weight of isopropyl acetate per part of glycol. The flask was equipped with a thermometer well and a packed fractionating column. The top of the column was connected to a condenser and decanter system. The decanter was adjusted so that the top, or entrainer layer, was continuously returned to the column as reflux, and the bottom, or water layer, was collected in a graduated receiver. The reaction mixture was heated to a vigorous boil, and the progress of the reaction was followed by noting the rate of water production. In the laboratory studies 6 to 8 hours were required to complete the reaction of a 10-gram-molar charge, as indicated by the cessation of water production. In every case the reaction was about 90% complete in the first 4 to 5 hours, and the remaining 2 to 3 hours were required to complete the reaction. During this latter period some darkening of the reaction mixture and some butadiene formation were noted. The temperature of the reaction mixture gradually increased during the course of the run from about 110° to 140° C.

At the end of a run the sulfuric acid catalyst was neutralized by the addition of an equivalent amount of crystalline sodium acetate. The precipitated sodium sulfate was removed by filtration, and the filtrate was fractionally distilled. The isopropyl acetate-acetic acid mixtures were analyzed and re-
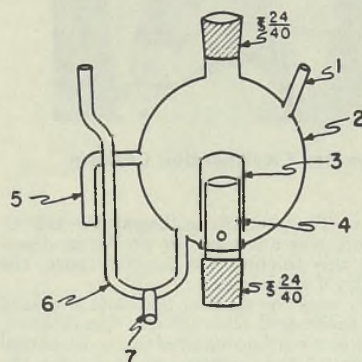

Figure 1. Unit or Plate of Laboratory Continuous Esterification Column

1. 10-mm. tube for thermometer insert
2. 250-ml. Pyrex flask
3. Cap sealed to outside of vapor inlet, having 3 vapor outlet holes near base
4. Vapor inlet from plate below
5. 10-mm. tube drain line
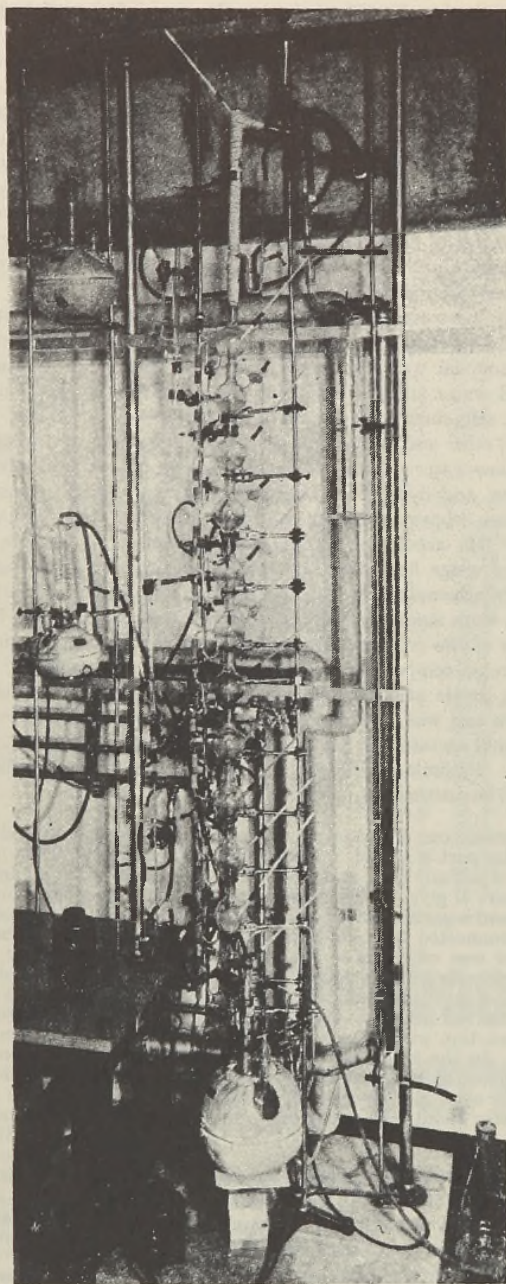6. 10-mm. tube liquid inlet line
7. Capillary sampling tube

Figure 2. Laboratory Esterification Column

pound-moles of glycol were esterified in this equipment. The rate of heat transfer in the kettle was quite slow, and 24 to 30 hours were required to complete the reaction. Even after water production ceased, the reaction mixture still contained the equivalent of 4 to 5% of glycol monoacetate. In order to produce a diacetate of satisfactory quality for pilot-plant pyrolysis, it was necessary to complete the reaction with acetic anhydride. This was done after the catalyst had been neutralized and the charge filtered. The filtered charge was analyzed and the percentage of monoacetate calculated. Acetic anhydride, sufficient to react with all of the monoacetate and any water present, was added to the charge in a 50-gallon enamel-lined batch still. The charge was heated to 140° C. for an hour and then fractionally distilled under reduced pressure. The diacetate was collected after the acetic acid content of the distillate was less than 1%. The distilled diacetate produced by this method had a purity of 99.5–100%. All foreshots were charged back into subsequent charges or refractionated. Approximately 1500 pounds of high-quality diacetate was produced by this procedure, and yields of 96–97% were obtained consistently. Acetic acid recoveries were again quantitative, but the breakdown of isopropyl acetate exceeded expectations. The long time required for the pilot-plant runs and the lack of facilities for restripping the water produced resulted in considerable hydrolysis of the entrainer.

CONTINUOUS PROCESS STUDIES

During the batch investigations it was shown that the reaction proceeded to the extent of about 90% at a reasonably rapid rate, but complete esterification, as measured by water removal, required a disproportionate length of time. It seemed probable, therefore, that a study of time and temperature factors might result in the establishment of more favorable reaction conditions which would be applicable to continuous processing methods.

APPARATUS. A bubble-cap column, or an interconnected series of reaction vessels provided with a means of controlling flow rates
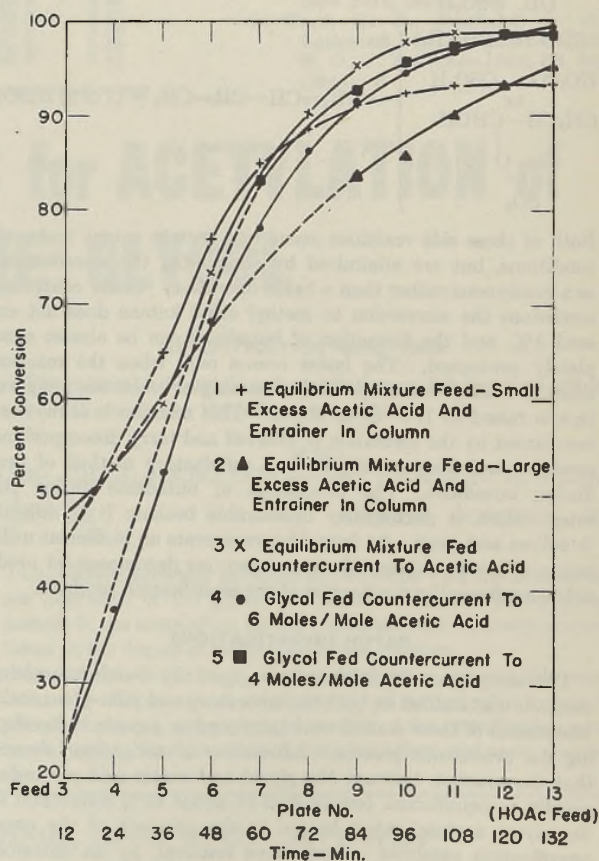
used in subsequent charges. The fraction distilling at 190–193° C. under atmospheric pressure was analyzed for purity as diacetate. In most instances this fraction was 98–99% pure, the other 1 to 2% being the glycol monoacetate.

In a series of laboratory runs the yield of diacetate averaged 97% of theoretical; the acetic acid recovery was quantitative, but some isopropyl acetate loss was encountered due to its partial hydrolysis and the removal of the isopropyl alcohol, with the water, from the system.

PILOT-PLANT PROCEDURE. On the basis of conditions developed in the laboratory studies, diacetate, for use in pilot-plant pyrolysis studies, was produced in a 150-gallon enamel-lined jacketed kettle equipped with a circulating-oil heating system. The column used on this kettle was constructed of copper and packed with stoneware Raschig rings. The vapors from this column were condensed and run to a glass decanter from which the entrainer was returned to the column, and the water was collected in a container mounted on a scale. Charges of 1.5 to 2.0

Figure 3. Conversion-Time Data for Continuous Esterification of 2,3-Butylene Glycol

and temperatures during the various stages of the reaction, appeared to be the most desirable types of apparatus for these studies. A column of heat-resistant glass was constructed of an interconnected series of units or plates as illustrated in Figure 1. These plates were joined through ⊤ 24/40 joints, and the drain and inlet lines were connected via short lengths of glass and rubber tubing. Each plate was equipped with a sampling line attached to the liquid-inlet line so that samples could be withdrawn during operation and the contents of each plate drained for analysis at the end of a run. Each plate was heated by a small ring burner fitted around the vapor inlet connection from the plate below. The column, made up of twelve such plates, is shown in Figure 2. Under operating conditions each of these plates held 100 cc. of liquid. By using ten plates in the reaction zone, the liquid-holding capacity was 1000 cc., and the flow rate and residence time were readily calculated. In all cases two or three plates were installed above the glycol feed plate to effect some fractionation of distilling vapors. The base of the column was connected to either a large boiling flask (Figure 2), containing a catalyst neutralizing agent, or to a small flask equipped with a continuous drain line.

TABLE I. ESTERIFICATION DATA

Sample Source	Average Temp. of Boiling Liquid, °C.	Composition, %							% Complete
		H₂O	Estimated H₂SO₄	Free HOAc	Combined HOAc	Glycol monoacetate	Glycol diacetate		

Sample Source	Average Temp. of Boiling Liquid, °C.	H₂O	Estimated H₂SO₄	Free HOAc	Combined HOAc	Glycol monoacetate	Glycol diacetate	% Complete
Acetic Acid–Glycol Molar Ratio, 6 to 1								
Distillate	107	19.55	0.00	78.22	0.56	...	0.81	..
Plate 1[a]	108.5	8.36	0.00	90.53	0.44	...	0.64	..
Plate 2	....	8.16	0.00	89.93	0.24	...	0.35	..
Plate 3 (glyco feed)	116.5	8.00	0.75	62.72	8.04	17.69	(14.74 glycol)	22.50
Plate 4	...	5.46	0.75	72.67	7.87	17.32	(3.8 glycol)	37.83
Plate 5	124	4.03	0.75	71.39	11.20	26.95	1.53	52.23
Plate 6	....	2.25	0.75	55.00	23.32	23.99	18.01	68.14
Plate 7	146	1.43	0.75	36.91	36.70	22.53	38.37	78.19
Plate 8	....	0.69	0.75	24.15	47.43	16.50	57.91	86.35
Plate 9	152	0.38	0.75	19.02	52.60	10.44	69.41	91.73
Plate 10	151.5	0.33	0.75	20.65	52.40	6.65	71.62	94.55
Plate 11	150	0.23	0.75	22.93	51.55	3.87	72.22	96.70
Plate 12 (HOAc feed)	135	0.13	0.75	34.48	44.23	1.44	63.20	98.54
Product (pot)	162	0.00	0.77	12.08	60.35	1.14	86.78	99.15
Acetic Acid–Glycol Molar Ratio, 4 to 1								
Distillate	101	27.29	...	67.96	2.00	...	2.90	(1.85 MEK)
Plate 1[a]	103	Not sampled						
Plate 3 (glycol feed)	116							
Plate 5	130							
Plate 7	145	0.62	1.15	16.94	50.71	22.70	58.58	83.10
Plate 8	....	0.41	1.15	17.67	52.81	12.28	68.49	90.44
Plate 9	147	0.40	1.15	18.94	52.66	8.92	70.50	92.85
Plate 10	147	0.30	1.15	20.35	52.69	5.21	72.99	95.69
Plate 11	148	0.16	1.15	21.36	52.53	3.35	73.98	97.18
Plate 12 (HOAc feed)	133	Not sampled						
Plate 13	....	0.18	1.15	42.24	38.65	1.10	55.33	98.68
Product (pot)	153	0.00	0.73	23.09	52.19	1.47	74.72	98.74
Vacuum dist. of product	115 (20 mm.)	0.00	0.00	26.35	50.78	0.00	73.65	100.00

[a] Plates numbered from top down (Figure 2).

ENTRAINER SYSTEM. For the initial experimental work the plates in the reaction zone were charged with an amount of acetic acid equal to the molar excess used in batch operations. After this acetic acid had been brought to a boil, isopropyl acetate was charged to the top sections of the column. A feed, consisting of the stoichiometric amounts of glycol and acetic acid together with the sulfuric acid catalyst, was heated for about one hour to establish equilibrium, and then introduced near the top of the column. The feed rate was regulated to give a definite residence time in the column, usually 2 or 3 hours. Boiling was maintained in each plate and the distillate, consisting of the water–isopropyl acetate azeotrope, was condensed and run to a decanter, and the entrainer was returned to the top of the column. The water from the decanter was collected in a graduate to serve as an estimation of the reaction rate. The mixture obtained from the base of the column was either removed continuously or collected in a base receiver containing sufficient sodium acetate to neutralize the sulfuric acid catalyst. Feed rates, temperatures, and rate of water production were checked at regular intervals, and samples were periodically drawn from the various plates of the column to determine the course of the reaction. After standardizing the operating procedure by a series of trial runs, several longer runs were conducted in which the feed rate was varied to determine the residence time necessary for maximum conversion.

In all cases in which an entrainer was used in the system, the conversion to diacetate did not exceed 94% (Figure 3, curves 1 and 2). Residence times of 2 and 3 hours gave almost identical results. During these runs the temperatures of the boiling liquids in the center plates of the column were only a few degrees above the boiling point of acetic acid. Only the bottom plates were at a higher temperature. Analyses showed that these plates had lost acetic acid by fractionation. Attempts were then made to maintain a higher percentage of acetic acid in the column, but again the fractionation which occurred and the high reflux ratio resulting from the recycled entrainer kept the column temperatures too low for rapid reaction.

COUNTERCURRENT REACTOR SYSTEM. Atwood (1) had shown that a high degree of conversion was possible by continuously distilling a mixture of water and acetic acid from the reaction mixture while adding glacial acetic acid to the reaction vessel. From these data it appeared that a continuous system could be developed in which an excess of acetic acid was used to remove the water from the zone of reaction and at the same time provide the additional driving force to carry the acetylation to completion.

To test this procedure the column was converted to a countercurrent reactor in which a distillate of dilute acetic acid was removed at the top, and a continuous stream of glacial acetic acid was introduced near the base. The glycol-catalyst mixture was fed to the third plate from the top, the two plates above serving to fractionate the acetic acid–water mixture partially. By feeding a glycol–acetic acid equilibrium mixture countercurrently to acetic acid and by maintaining a ratio of 6 moles of acetic acid per mole of glycol, it was possible to raise the temperatures in the lower half of the zone between the feeds to 140–145° C. This resulted in a 98% conversion of glycol to diacetate, at a residence time of 2 hours. On further experimentation it was found that a feed of glycol and sulfuric acid introduced countercurrently to the acetic acid gave results equally as good as those obtained with the equilibrium mixture (Figure 3, curves 3, 4, and 5). The maintenance of a temperature range of 140–150° C. in the lower two thirds of the reaction zone resulted in 99% completion of the reaction. It was found that the same degree of completion could be attained in a 2-hour residence time with 4 moles of acetic acid per mole of glycol instead of the 6 previously used, provided the temperatures in the reaction zone were held in the 140–150° C. range. The data on several of these runs, showing the degree of reaction in the various plates of the column, are given in Table I and illustrated in Figure 3 (curves 4 and 5).

A material balance on several runs showed excellent yields and recoveries even though some acetic acid was lost due to slight leaks which developed in the apparatus during the operations.
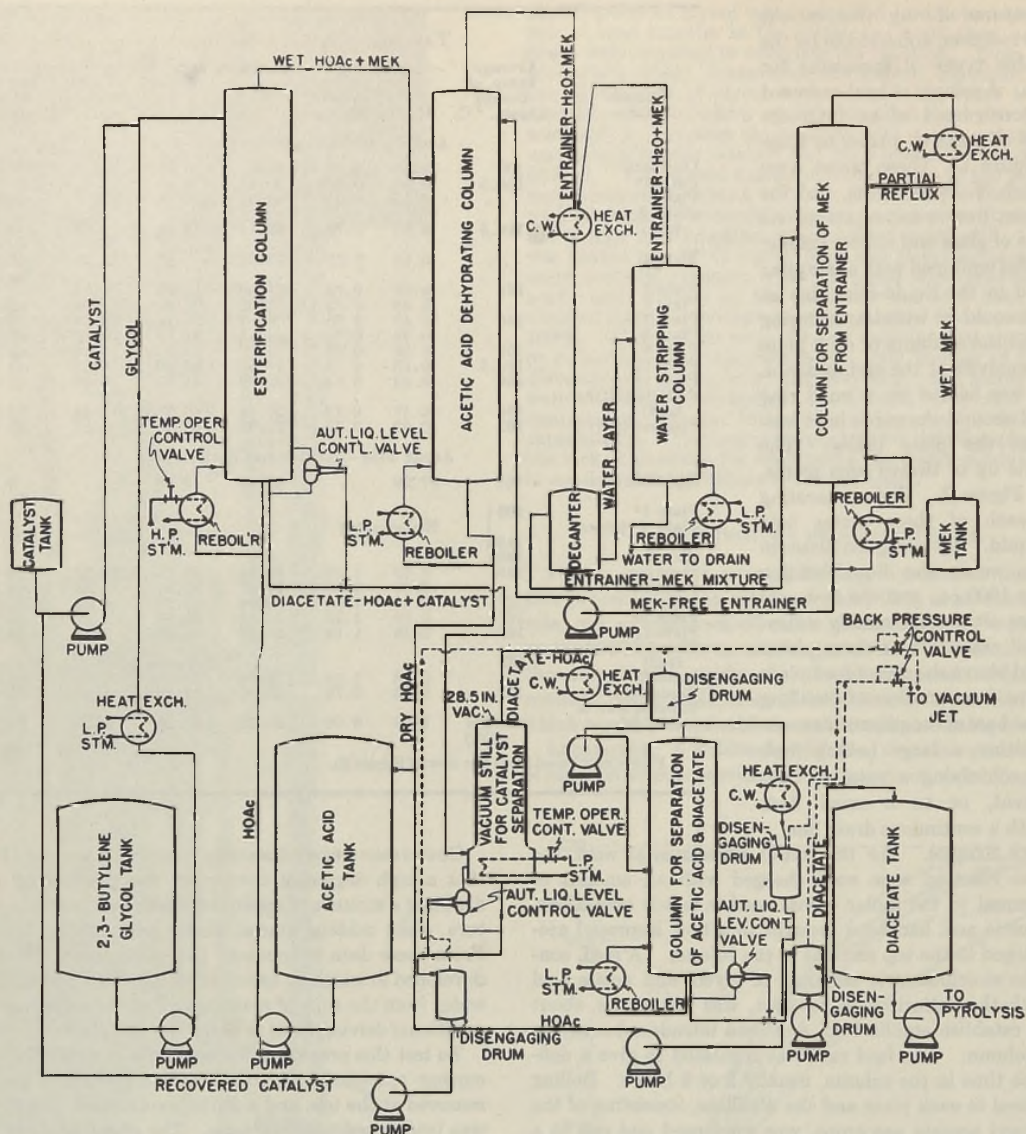
Figure 4. Flow Diagram of Proposed Continuous Process for the Acetylation of 2,3-Butylene Glycol

The average of these results shows 97% conversion of the glycol to acetates and a 3% conversion of glycol to methyl ethyl ketone. The acetate fraction consisted of 99% diacetate and 1% monoacetate. The over-all acetic acid recovery, as free and combined, was 98%. The acetic acid losses were mechanical and could be prevented in plant operation. No butadiene was produced.

RECOVERY OF ACETIC ACID. The acetic acid–water mixture collected as distillate contained 68% acetic acid, 27% water, 2% methyl ethyl ketone, and 3% glycol diacetate. This mixture was dehydrated in a batch still by adding isopropyl acetate and distilling the water-entrainer azeotrope to a continuous decanter which returned the entrainer layer to the packed column. After the water was removed, the anhydrous mixture was distilled. The isopropyl acetate fraction contained the methyl ethyl ketone. The glycol diacetate, which was evidently distilled with the dilute acetic acid from the esterification column as its water azeotrope, remained in the anhydrous acetic acid. Since it was retained in the dehydrated acetic acid from the dehydrating column and returned to the esterification column, no loss was incurred.

Dehydration of the esterification-column distillate by an entrainer system can be readily accomplished by the continuous

methods used in the commercial dehydration of acetic acid (5). The presence of methyl ethyl ketone in this distillate necessitates an additional operation to prevent accumulation of the ketone in the entrainer. Using n-butyl acetate as entrainer, the separation of methyl ethyl ketone is effected by stripping its water azeotrope (boiling point 73.4° C.) from the entrainer layer before the butyl acetate is returned to the dehydration column.

PURIFICATION OF PRODUCT. The mixture which was continuously removed from the bottom of the esterification column consisted of 75% glycol diacetate, 23% acetic acid, 1% glycol monoacetate, and 1% sulfuric acid, combined in the form of glycol esters. Two methods of diacetate isolation were investigated. One involved the neutralization of sulfuric acid with sodium acetate, followed by filtration and fractional distillation. Under these conditions some solids always remained dissolved in the filtrate and accumulated in the still. This would be particularly troublesome in a continuous system. In addition, any glycol monoacetate present in the original mixture or liberated by neutralization of the sulfuric acid esters was left in the diacetate, and its presence was undesirable in the subsequent pyrolysis step (4). A second method consisted in a continuous

vacuum distillation of the unneutralized product. By operating at a sufficiently reduced pressure so that the diacetate boiled at a temperature lower than that at which the sulfuric acid esters decomposed, it was possible to remove practically all of the diacetate–acetic acid mixture by distillation. The residual mixture of diacetate and the sulfuric acid esters can be recycled as the esterification catalyst, since several experiments have shown that this material functions fully as well as fresh sulfuric acid. This method has the following advantages over the neutralization method: It requires no filtration equipment; there are no dissolved solids to foul the distillation equipment; when the esterification is carried to a high degree of completion, the distillate contains practically no glycol monoacetate. Fractionation readily separates the acetic acid from the diacetate, or the mixture may be used directly for pyrolysis (4). Recycling of the catalyst residue also serves to prevent the loss of incompletely acetylated glycol. The distillation method does, however, require a vacuum of at least 28 inches to accomplish the separation of diacetate from the sulfuric acid esters without loss due to charring.

This continuous esterification process was applied to the preparation of ethylene glycol diacetate, methyl Cellosolve acetate, diethylene glycol diacetate, and glycerol triacetate. Excellent results were obtained in every case, and application of the method to the manufacture of a wide variety of industrially important acetates is indicated. A modification of the method has recently been applied to the manufacture of 2,3-butylene glycol diacetate in a column of commercial design by the staff of Joseph E. Seagram & Sons, Inc., who cooperated with this laboratory throughout the butylene glycol–butadiene investigation (2). It was found possible to reach and maintain the desired temperature

in the reaction zone by supplying heat only to the column calandria. When a sufficiently high concentration of diacetate was produced in the reaction zone and when the temperature necessary for rapid esterification was maintained, a glycol to diacetate conversion of 98–99% resulted during a 2-hour residence time in the column.

Figure 4 is a flow diagram of the proposed process for acetylation of 2,3-butylene glycol, developed cooperatively with the Seagram organization.

LITERATURE CITED

(1) Atwood, K., private communication.
(2) Callaham, J. R., *Chem. & Met. Eng.*, 51, 94 (1944).
(3) Keyes, D. B., IND. ENG. CHEM., 24, 1096 (1932).
(4) Morell, S. A., Geller, H. H., and Lathrop, E. C., *Ibid.*, 37, 877 (1945).
(5) Othmer, D. F., *Ibid.*, 27, 250 (1935).
(6) Schniepp, L. E., Dunning, J. W., Geller, H. H., Morell, S. A., and Lathrop, E. C., *Ibid.*, 37, 884 (1945).

CONVERSION of 2,3-BUTYLENE GLYCOL to 1,3-BUTADIENE by PYROLYSIS of DIACETATE

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The conversion of 2,3-butylene glycol to butadiene by pyrolysis of its diacetate has been studied over a wide range of temperatures and contact times. Yields of 82% of butadiene (purity, 99%) were obtained on one-pass pyrolyses in the temperature range 575° to 600° C. An additional 5% was secured by isolation and pyrolysis of the intermediates left in the pyrolysis liquors. Acetic acid recoveries of 99% were obtained under optimum conditions. Methyl vinyl carbinyl and crotyl acetates were identified as the intermediates of the reaction. The main by-products were methyl ethyl ketone, methyl ethyl ketone enol-acetate (2-acetoxy-2-butene), and methyl acetyl acetone.

ONE of the important problems chosen for study at the inception of this laboratory in 1940 was the development of a commercial process for the production of 2,3-butylene glycol by fermentation of carbohydrate materials (21). It was understood that when sufficiently high yields of 2,3-butylene glycol were obtained to make the process of commercial interest and

when the chemical was available, the development of a process for 1,3-butadiene would be undertaken. Work was actively started in January, 1942, at which time the importance of producing butadiene had become a major problem of national defense.
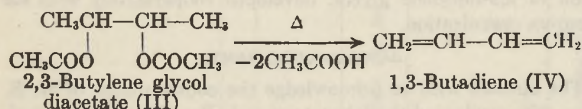
The possibility of direct catalytic dehydration by the methods in commercial use in Germany for converting 1,3-butylene glycol to 1,3-butadiene (5) was given first consideration as the basis of a process. A study of approximately seventy dehydration catalysts under a variety of conditions indicated that this route was impractical. Highest one-pass yields of butadiene reached 20% of theory, the main product in every case being methyl ethyl ketone, which did not yield butadiene under any of the conditions tried. The predominate tendency to form ketones under dehydration conditions is characteristic of compounds having hydroxyl groups on adjacent carbon atoms:

$$CH_3CHOHCHOHCH_3 \xrightarrow[\text{dehydration}]{\text{catalytic}} CH_3CH_2COCH_3$$

2,3-Butylene glycol (I)   Methyl ethyl ketone (II)
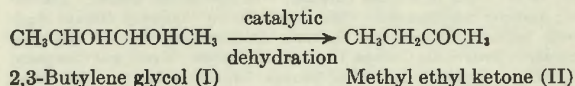
Van Pelt and Wibaut (14) studied the behavior of a number of acetates under pyrolysis conditions and found that the olefins or
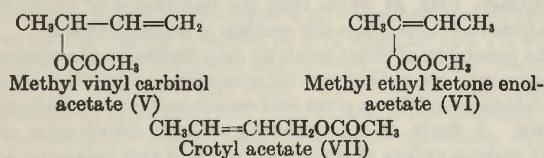
[1] Present address, Pabst Brewing Company, Milwaukee, Wis.

diolefins obtained were those normally expected on dehydration of the original alcohol or diol. Smith et al. (19) also showed that the pyrolysis of esters offers better control of this type of reaction. On the basis of evidence available, the pyrolysis of the esters of 2,3-butylene glycol was undertaken. The diacetate was chosen because of the commercial availability of acetic acid, acetic anhydride, and ketene:

$$
\begin{array}{c}
CH_3CH{-}CH{-}CH_3 \\
| \qquad | \\
CH_3COO \quad OCOCH_3
\end{array}
\xrightarrow[-2CH_3COOH]{\Delta}
CH_2{=}CH{-}CH{=}CH_2
$$

2,3-Butylene glycol   1,3-Butadiene (IV)
diacetate (III)

The production of butadiene by this method was first disclosed in a patent granted in 1938 to Hill and Isaacs (7). In general, their claims have been confirmed. The yields cited by Hill and Isaacs are based upon several recycles of the pyrolysis liquors; the present investigation has shown that this procedure did not lead to optimum results. The accumulation of a nonbutadiene-yielding intermediate, methyl ethyl ketone enol-acetate, was not recognized by Hill and Isaacs, which probably led them to believe that the second stage of the butadiene reaction did not occur so readily as the first. Obviously their yield calculations, based on ester converted, took no account of this intermediate.

By August, 1942[2], laboratory results were sufficiently promising to warrant pilot-plant investigations, which are described in another publication (16). Both laboratory and pilot-plant studies were conducted simultaneously, and the results led to a more complete understanding of the reactions.

The pyrolysis of 2,3-butylene glycol diacetate to butadiene appears to be a noncatalyzed, homogeneous, gas-phase reaction involving two stages: (a) elimination of one molecule of acetic acid to form a mixture of unsaturated acetates (V, VI, and VII), and (b) loss of another molecule of acetic acid from V and VII to form butadiene (IV). The over-all course of the reactions—i.e. conversion to butadiene, composition and yield of unsaturated acetate intermediates, and formation of by-products—is determined essentially by temperature and contact time. The quality of butadiene is exceptionally high, 99+ % pure under all conditions of operation. Optimum butadiene production is obtained under conditions which give a maximum first-pass conversion; this is due to the fact that methyl ethyl ketone enol-acetate (VI), which is formed to a greater or lesser extent under all conditions, does not yield butadiene. The diacetate pyrolysis reaction proceeds essentially through the MVC (methyl vinyl carbinol) acetate intermediate (V); crotyl acetate (VII) probably arises from V by an allylic rearrangement. Both of these intermediates may be pyrolyzed to butadiene in even higher yields than the diacetate:

$$
\begin{array}{c}
CH_3CH{-}CH{=}CH_2 \\
| \\
OCOCH_3
\end{array}
\qquad
\begin{array}{c}
CH_3C{=}CHCH_3 \\
| \\
OCOCH_3
\end{array}
$$

Methyl vinyl carbinol   Methyl ethyl ketone enol-
acetate (V)   acetate (VI)

$$
\begin{array}{c}
CH_3CH{=}CHCH_2OCOCH_3 \\
\end{array}
$$
Crotyl acetate (VII)

The following brief description of the pyrolysis procedure shows the nature and extent of by-product formation, as well as acetic acid recovery: The diacetate was fed at a controlled rate through a heated reaction tube. The exit gases entered a fractionating column where the butadiene and other gases were separated from the condensed liquid (called "pyrolysis liquor") which was continuously collected from the bottom of the column. The gas stream was scrubbed with water and dried, and the butadiene condensed in traps cooled by dry ice. The volume of gas not condensed in the traps (vent gas) was measured by a wet test meter; it comprised only a small fraction (<0.5%) of the diacetate and apparently arose essentially from the pyrolysis of acetic acid. The total acetic acid recovery, determined as the sum of free and combined acetic acid, was about 99%. The main by-products are derivatives of MEK (methyl ethyl ketone) which appear in two forms: as MEK enol-acetate (VI); and as methyl acetyl acetone (VIII). The latter probably arises from VI by the following reaction, since pyrolysis of VI results in about 20% conversion to VIII:

$$
\begin{array}{c}
CH_3C{=}CHCH_3 \\
| \\
OCOCH_3
\end{array}
\longrightarrow
\begin{array}{c}
CH_2COCHCOCH_3 \\
| \\
CH_3
\end{array}
$$

Methyl ethyl ketone   Methyl acetyl acetone
enol-acetate (VI)   (VIII)
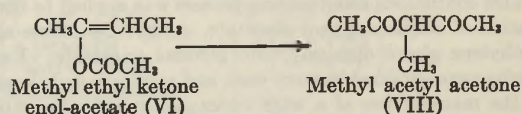
Both VI and VIII are quantitatively converted to free MEK and acetic acid when hydrolyzed with alkali. Other by-products of the pyrolysis reaction are vinylcyclohexene, formed by the dimerization of butadiene, and traces of low- and high-boiling hydrocarbons (tars). Under optimum operating conditions, the diacetate conversions on one pass are approximately as follows:

		Mole %
Butadiene		82
MVC acetate (V) + crotyl acetate (VII)		6
MEK { free	1.5 }	8
{ as MEK enol-acetate (VI)	5.0 }	
{ as methyl acetyl acetone (VIII)	1.5 }	
Other by-products		4

The pyrolysis liquor is composed mainly of acetic acid (about 85%) and contains the intermediate unsaturated acetates (V, VI, and VII), MEK (II), methyl acetyl acetone (VIII), unreacted diacetate (III), some dissolved butadiene, and the other by-products. A number of methods have been studied in connection with the re-use of the pyrolysis liquor.

The pyrolysis reaction was studied over a wide range of conditions. At about 400° C., 15 to 25% of the diacetate, depending on feed rate, undergoes reaction, as evidenced by the formation of acetic acid. Butadiene formation increases progressively with temperature, reaching a maximum at 575° to 600° C. Experiments on low-temperature pyrolysis showed that the formation of MEK and MEK enol-acetate could not be prevented under any conditions. Based upon the amount of diacetate reacted, conversion to total MEK was approximately constant under all conditions. No advantage could therefore be derived from multiple pyrolysis at the lower temperatures. Since the other side reactions are minimized by pyrolysis at short contact times, optimum operating conditions are those giving maximum one-pass conversions of diacetate to butadiene.

2,3-Butylene glycol may occur in dextro, levo, and meso forms. Two of these stereoisomers had been made here by different fermentation processes. It was, therefore, useful to determine whether both of these products would be suitable intermediates for butadiene production. One of the processes yielded meso-glycol containing a small percentage of dextrorotatory form; the other produced the levorotatory form exclusively (22). No differences could be detected in the yield and quality of the butadiene produced on pyrolysis of the diacetates of these glycols.

The glycols were acetylated by the method of Hill and Isaacs (7) and by the batch method described in another paper (17).
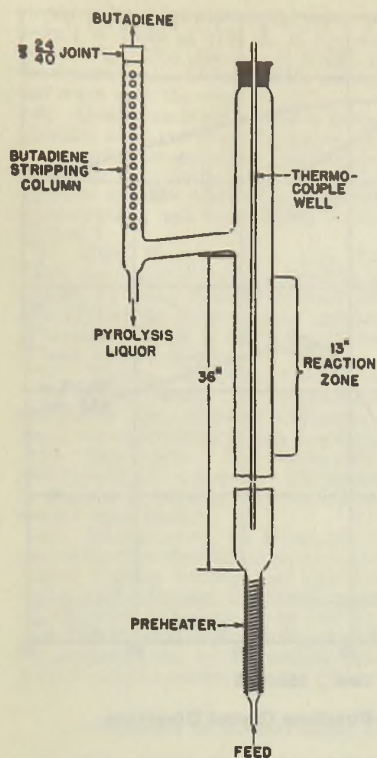
Figure 1. Apparatus B, 2 × 36 Inch Pyrex Pyrolysis Tube

The physical properties and chemical analysis of these compounds, and of some of the pyrolysis intermediates, have been described (12).

PYROLYSIS APPARATUS

In preliminary experiments a filament-type unit was used (23). Although this apparatus was suitable for the laboratory preparation of butadiene in yields of 75 to 80% from the diacetate (13), it was inadequate for a study of the reaction. The following forms of apparatus were then used:

APPARATUS A, ONE-INCH PYREX TUBE. A 48 × 1 inch (122 × 2.5 cm.) Pyrex tube, packed with Raschig rings, was supported vertically in a 36-inch (91-cm.) electrically heated furnace. The diacetate was fed to the top of the tube, and the products were collected at the bottom. This apparatus was used for preliminary experiments on low-temperature pryolysis and served for solving mechanical difficulties.

APPARATUS B, TWO-INCH PYREX TUBE. A 48 × 2 inch (122 × 5 cm.) Pyrex tube (44.9 mm. i.d.) was arranged as an upward-feed pyrolysis unit (Figure 1). It was supported vertically in a 36-inch electrically heated furnace constructed from 2¹/₂-inch (61-cm.) iron pipe. The 12 × 1 inch (30.5 × 2.5 cm.) Vigreux column, sealed to the upper portion of the tube by a 5 × 1 inch (12.7 × 2.5 cm.) side arm, served as the butadiene stripping column. It was connected, by the TS 24/40 joint, to a 400-mm. bulb condenser above which was placed a 400-mm. spiral condenser. This arrangement prevented flooding during rapid butadiene production. The gas stream was then passed through a T-type mercury safety trap, a water scrubber preceded by a trap, a soda-lime drying tower, two tared dry ice traps for the butadiene, and a wet test meter for measuring the volume of vent gas. The bottom of the Vigreux column was connected to a U-tube for collecting the pyrolysis liquor. The bottom of the pyrolysis tube was wound with Nichrome wire and served as a preheater, maintained at 250° C. The pyrolysis tube was packed with stainless steel shavings which served as a convenient heat transfer medium. The thermocouple well, 9-mm. Pyrex tubing, was supported with a rubber stopper. The diacetate was fed by gravity at a controlled rate, 1 to 15 grams per minute. In conducting an experiment it was necessary to operate for definite time intervals under controlled temperature and feed rate conditions. Three-way stopcocks were inserted at both the U-tube and soda-lime tower outlets. When the system was operating smoothly, the time, diacetate volume, and wet test meter readings were recorded; the stopcocks were turned to connect with tared receivers for the collection of butadiene and pyrolysis liquor. This procedure was repeated at the end of the experiment, and good weight recoveries were obtained.

Reaction temperatures up to 550° C. were studied and were automatically controlled by a potentiometer. The temperature gradient in the pyrolysis tube from wall to center did not exceed 5° C. but was considerable from bottom to top. The zone of reaction was arbitrarily defined as that in which the temperature was within 10° of the maximum. Temperature profiles taken during operation showed that this involved a 13-inch (33-cm.) length in the upper section of the tube. The volume

of the reaction zone was calculated at 524 cc. After about 100 hours of operation, some tar formed in this zone.

APPARATUS C, GLASS COIL. Standard 9-mm. Pyrex tubing (8 mm. i.d.) was wound into a coil and immersed in an 8 × 10 inch (20.3 × 25.4 cm.) gas-heated lead bath. The length of coil immersed in the lead bath was 254 cm., which gives a reaction zone volume of 128 cc. The diacetate was fed by a bellows-type pump (1 to 20 grams per minute capacity), and the butadiene and pyrolysis liquor were collected as described in B. A U-tube immersed in an oil bath, maintained at 250° C., served as the preheater. Reaction temperatures up to 600° C., as measured by a thermocouple in the bath, were studied. After about a dozen experiments, crystallization of the glass caused mechanical difficulties.

APPARATUS D, STAINLESS STEEL COIL. A stainless steel coil (6.9 mm. i.d.) was arranged as described in C. An electrically heated copper tube (8 × 1 inch), brazed to the pyrolysis coil and equipped with a thermocouple well, served as the preheater. The outlet of the coil was welded into the side of an 18-inch (45.7-cm.) length of ³/₄-inch (1.9-cm.) stainless steel pipe at a point 3 inches (7.6 cm.) from the bottom. The pipe served as the butadiene stripping column. The bottom of this pipe was brazed to 6-mm. stainless steel tubing, which was connected to a glass U-tube for collection of the pyrolysis liquor; the top was tapered to a TS 24/40 joint and was connected by a glass adapter to a 400-mm. bulb condenser. In other respects the assembly was identical with B. A total length of 340 cm. of coil was immersed in the molten lead, which gives a reaction zone volume of 126 cc.

CONTACT TIME. The feed rates were calculated by the following empirical equation:

$$\text{Contact time (sec.)} = \frac{(\text{vol. of reaction zone, cc.})\ 60}{\left(\dfrac{T}{273}\right)\left(\dfrac{22{,}400}{\text{mol. wt.}}\right)(\text{grams/min. feed})}$$

This made it possible to compare the results of experiments conducted with different types of apparatus.

ANALYTICAL METHODS

1. 2,3-BUTYLENE GLYCOL. The use of periodic acid has been described (3, 4). To 10-ml. aliquots, containing 0.1 to 0.2 gram of sample, in a 200-ml. Erlenmeyer flask are added 25 ml. of 0.1 N periodic acid. After 15 minutes, 4 ml. of 2 N sulfuric acid and 50 ml. of 0.5 M Na₂HPO₄ buffer are added. After thorough mixing, 4 grams of potassium iodide are added, and the iodine liberated is titrated with 0.1 N sodium thiosulfate. Blanks are run under the same conditions. At pH 7 the iodic acid formed does not react with potassium iodide. In the above procedure, the pH is approximately 6.6 before the potassium iodide addition, 7.0 after, and 7.1 at the end of the titration. With pure glycol, the results are approximately 0.5% high.

2. FREE AND COMBINED ACETIC ACID. These components are expressed on a weight per cent basis. "Combined acetic acid" is defined as the number of grams of acetic acid liberated from 100 grams of a sample on saponification. In conducting routine analysis, the use of this term has proved more convenient than the usual "saponification equivalent". Both free and combined acetic acid are determined on the same sample as follows: To a tared 125-ml. stoppered flask containing 10 ml. of water is added approximately 1 gram of sample. Direct titration to a phenolphthalein end point is conducted using 0.3 N sodium hydroxide. To the neutralized solution are added 10 ml. of 2 N sodium hydroxide in 85% methanol. The mixture is heated under reflux on the steam bath for 15 minutes, cooled, and titrated with 0.4 N hydrochloric acid to a phenolphthalein end point. Blanks are included. This method has given uniformly good results, duplicate samples usually agreeing to ±0.15%. With pure substances the results were quantitative. In connection with studies on esterification, some difficulty was encountered with samples containing acetic anhydride, which caused bleaching of the indicator. The use of thymol blue avoided this difficulty, the anhydride being completely titrated during the free acetic acid determination.

3. 2,3-BUTYLENE GLYCOL DIACETATE. The purity of the diacetate was determined by two methods from which the percentage of diacetate could be calculated: (a) By saponification and (b) by glycol analysis on a saponified sample by the following procedure: To a weighed sample in a 125-ml. flask is added 25 ml. of 2 N sodium hydroxide in 85% methanol. The solution is heated under reflux on a steam bath for 15 minutes, cooled, and exactly neutralized with 0.4 N hydrochloric acid. After dilution

to 100 ml. with water, 10-ml. aliquots are analyzed for free glycol as described in method 1. With samples containing unsaturated components, which absorb some of the iodine liberated at the end point, an empirical correction is applied by titrating an aliquot with 0.1 N iodine solution.

4. 2,3-BUTYLENE GLYCOL MONOACETATE. This compound is usually encountered as part of a mixture, but in the absence of other acetates it may be determined by saponification.

5. MIXTURES OF 2,3-BUTYLENE GLYCOL DIACETATE, MONOACETATE, AND ACETIC ACID. It is frequently necessary, especially in connection with the determination of diacetate purity, to analyze this three-component mixture. The difference in the theoretical percentage of combined acetic acid for the diacetate (68.95%) and for the monoacetate (45.44%) makes it possible to analyze such a mixture by method 2. By means of simultaneous equations, the following are derived:

$$\% \text{ diacetate} = 4.253 \,(\% \text{ combined acetic}) + 1.933 \,(\% \text{ free acetic}) - 193.258$$

$$\% \text{ monoacetate} = 100 - (\% \text{ diacetate} + \% \text{ free acetic})$$

Errors in the combined acetic acid determination are magnified in the calculation of per cent diacetate. A variation of 0.15% in combined acetic acid results in a variation of 0.64% for a diacetate sample of about 99% purity. This method compares favorably, however, with an independent analysis for free hydroxyl groups, by the pyridine–acetic anhydride procedure.

6. UNSATURATED ACETATES. These are usually obtained as a mixture, along with acetic acid and free MEK, from the distillation of the pyrolysis liquor (method 13). The amount of unsaturated acetates is determined by saponification. The MEK enol-acetate component is determined independently (method 8), and the MVC and crotyl acetates are determined by difference. No attempt has been made to distinguish the two latter analytically, since both yield butadiene on pyrolysis.

7. FREE MEK. The 2,4-dinitrophenylhydrazone method described by Iddles and Jackson (9) was modified as follows: Solutions containing not over 40 mg. of MEK are weighed in stoppered 50-ml. Erlenmeyer flasks containing 10 ml. of water.
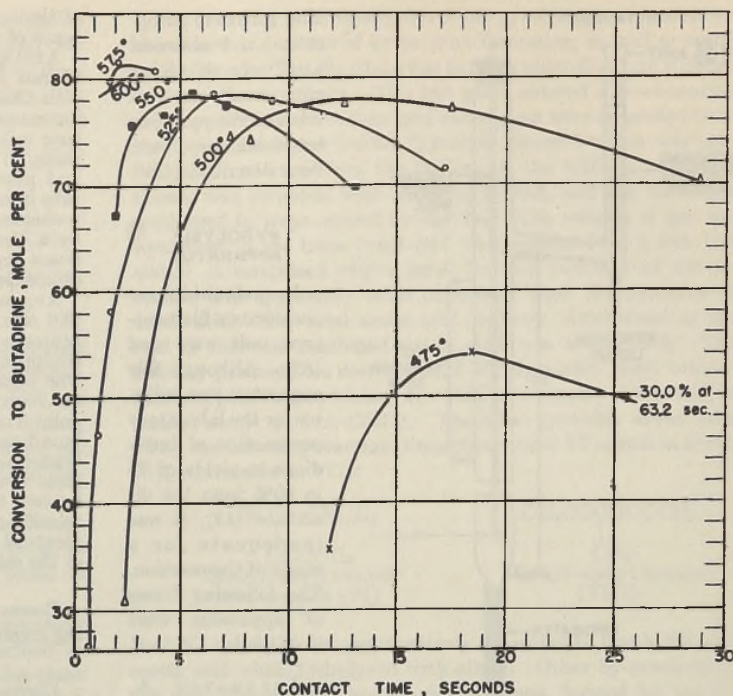

Figure 2. Pyrolysis of 2,3-Butylene Glycol Diacetate

After the samples are cooled to 5° C., 25 ml. of the hydrazine reagent (4.2 grams of 2,4-dinitrophenylhydrazine per liter of 2 N hydrochloric acid) are added slowly with shaking, the mixtures are cooled for one hour in the refrigerator, and the precipitate is filtered, washed with three 10-ml. portions of water, and dried in vacuo over sulfuric acid to constant weight. Recoveries of pure MEK were 95 ±1%, so that this factor was applied empirically in all analyses. A comparison of this method with one based

TABLE I. PYROLYSIS OF 2,3-BUTYLENE GLYCOL DIACETATE

| | Conditions | | | | Products | | | | | | | Mole % Conversion of Diacetate to: | | | | | | |
Expt. No.	Temp., ° C.	Apparatus	Contact time, sec.	Diacetate pyrolyzed, grams	Pyrolysis liquor, grams	Butadiene, grams	Vent gas, ml./ mole diacetate[a]	Recovery, % — Acetic acid — Free	Combined	Total	Total wt.	MVC + crotyl acetates	MEK enolacetate	MEK	Methyl acetyl acetone[b]	Unreacted diacetate	Other by-products[c]	Butadiene
150	475	B	11.9	947.5	826.0	104.8	156	51.7	...	...	98.5	..	...	...	...	..	..	35.6
157	475	B	14.8	3029.0	2503.2	472.7	237	67.2	...	...	98.0	..	...	...	...	..	..	50.3
151	475	B	18.4	1075.5	895.7	167.2	227	71.8	...	...	99.0	..	...	...	...	..	..	54.2
145	475	A	63.2	497.5	431.7	46.3	50	64.2	...	...	96.1	..	...	...	...	..	..	30.0
53	500	C	2.4	267.2	227.8	25.4	182	47.1	46.1	93.2	94.8	25.1	4.6	0.3	...	32.1	7.3	30.6
172	500	B	7.2	371.9	283.3	86.0	281	88.2	10.8	99.0	99.5	7.8	5.9	1.3	4.1	0.8	5.7	74.4
171	500	B	8.1	354.1	267.1	81.6	289	86.0	11.7	97.7	98.7	9.2	5.8	1.3	4.7	1.0	6.3	74.1
170	500	B	12.5	415.2	309.8	100.3	293	90.8	7.4	98.2	99.0	9.2	1.3	2.9	2.1	0.4	6.4	77.7
169	500	B	17.4	387.0	289.6	92.7	360	91.5	7.0	98.5	99.0	4.7	4.8	1.6	1.7	0.3	9.9	77.0
173	500	B	28.8	332.1	252.8	72.4	417	92.7	4.9	97.6	98.2	3.4	3.6	2.9	1.6	0.3	18.1	70.1
70	525	D	0.7	369.4	339.0	30.3	165	46.0	53.3	99.3	100.1	30.3	5.0	1.0	...	35.5	1.8	26.4
69	525	D	1.1	351.2	291.8	50.7	268	64.0	28.0	92.0	97.7	20.1	5.8	1.4	...	16.9	9.4	46.4
68	525	D	1.7	330.9	261.0	60.0	405	72.9	22.8	95.7	97.3	21.0	5.3	1.7	...	9.4	4.3	58.3
71	525	D	6.4	283.4	207.1	69.2	491	91.2	5.5	96.7	97.8	5.2	0.3	2.3	2.4	0.5	10.8	78.5
176	525	B	9.1	380.3	284.3	92.1	320	91.1	5.6	96.7	99.2	5.9	2.2	3.1	2.1	0.4	8.4	77.9
175	525	B	11.5	307.3	223.9	83.2	454	89.8	4.9	94.7	97.0	4.0	3.5	2.6	2.0	0.5	10.8	76.6
174	525	B	17.1	372.3	280.3	82.7	491	91.7	4.1	95.8	97.8	2.0	3.1	3.1	1.9	0.6	17.9	71.4
67	550	C	1.9	895.6	687.7	186.5	274	83.9	12.5	96.4	97.8	11.5	5.7	1.8	7.4	1.4	5.2	67.0
65	550	C	2.7	217.5	158.3	51.0	456	87.4	8.3	95.7	96.6	4.5	5.7	1.3	3.4	0.7	9.0	75.4
54	550	C	4.1	279.0	201.5	66.4	723	91.9	4.0	95.9	96.3	0.6	4.7	1.6	2.0	0.4	14.2	76.5
199	550	B	5.4	360.0	268.7	87.8	1360	93.7	3.8	97.5	99.9	2.6	2.6	3.7	1.8	0.4	10.5	78.4
64	550	C	5.5	211.5	153.2	51.6	740	91.5	5.7	97.2	97.7	1.0	4.4	1.9	3.0	0.6	10.6	78.5
198	550	B	7.0	335.0	244.3	80.6	1270	91.4	3.5	94.9	97.9	3.2	1.5	3.7	1.6	-0.3	12.3	77.4
197	550	B	13.0	255.0	194.1	55.4	2180	92.9	2.1	95.0	99.3	7.6	2.0	3.8	1.6	0.3	14.8	69.9
59	575	C	1.6	271.2	192.6	67.1	693	88.8	7.2	96.0	96.2	4.4	5.3	1.4	2.5	0.5	6.3	79.6
106	575	D	2.0	297.9	219.3	75.3	934	93.2	5.3	98.5	99.3	4.6	2.7	2.5	1.0	1.1	6.6	81.5
58	575	C	2.3	272.0	193.0	68.7	684	91.2	4.8	96.0	96.7	0.7	4.7	1.8	2.1	0.4	9.1	81.2
57	575	C	3.7	252.0	181.9	63.2	1036	93.3	4.1	97.4	98.0	0.0	4.0	2.2	2.4	0.5	10.2	80.7
61	600	C	1.7	267.1	189.1	65.5	1205	90.6	3.9	94.5	96.2	1.7	3.9	2.4	2.8	0.6	9.7	78.9
60	600	C	2.2	228.7	162.0	56.7	1674	91.6	2.6	94.2	96.8	1.6	2.4	2.9	2.7	0.6	10.1	79.7

[a] Average gas density equals 1.16 grams per liter at 25° C. and 745 mm.
[b] Where no analysis was conducted for methyl acetyl acetone it was included in the calculation of unreacted diacetate.
[c] Calculated by difference from 100%.

on the ultraviolet absorption spectrum of MEK (ϵ[mole/liter, 1 cm.] = 16.22 at 2775 Å. in cyclohexane) showed agreement within 2%. The presence of MEK enol-acetate does not affect the determination of free MEK; methyl acetyl acetone, however, will react with the reagent.

8. COMBINED MEK. This is defined as the number of grams of MEK liberated from 100 grams of sample on saponification. The samples are saponified as described in method 2, using aqueous rather than alcoholic 2 N sodium hydroxide. The saponified solutions are then acidified with hydrochloric acid to a 2 normal concentration, and total MEK is determined as described in method 7.

9. MEK ENOL-ACETATE AND METHYL ACETYL ACETONE. These two materials are separated by distillation of the pyrolysis liquors, VI being obtained in the fraction boiling below 145° C. and VIII in the higher-boiling fraction. From a determination of combined MEK in the respective fractions, the concentration of each may be calculated.

10. WATER. The Karl Fischer method (18) was used.

11. VENT GASES. An Orsat apparatus was employed. The gas density (approximately 1.16 grams per liter at 25° C. and 745 mm.) was determined by the Regnault method.

12. BUTADIENE. The maleic anhydride method of Tropsch and Mattox (20) was used. The apparatus was slightly modified in that the absorption chamber was immersed in an electrically heated water jacket.

13. DISTILLATION OF PYROLYSIS LIQUOR. Three fractions are obtained by distillation of the pyrolysis liquor through a 12 × 1 inch Vigreux column: (a) Dissolved butadiene, by heating under total reflux for 10 minutes, is stripped out and condensed; (b) the fraction boiling up to 145° C. contains acetic acid, the intermediate unsaturated acetates, MEK, and the lower-boiling by-products; and (c) the residue contains unreacted diacetate, methyl acetyl acetone, and the higher boiling by-products.

PYROLYSIS OF 2,3-BUTYLENE GLYCOL DIACETATE

Table I presents the results of one-pass pyrolyses of the diacetate in the temperature range 475° to 600° C. The diacetate analyzed 99 to 100% pure by analytical method 5. The effects of temperature and contact time on butadiene conversions are illustrated in Figure 2. An example of the method of calculation is shown in the following detailed experiment.

EXPERIMENT 106. Diacetate (297.9 grams, 1.712 moles) was pyrolyzed in apparatus D at 575 ± 3° C. and a feed rate of 9.61 grams per minute. The contact time was calculated as 2.0 seconds. The following products were obtained:

	Grams
Pyrolysis liquor	219.3
Butadiene	75.3
Vent gas	1.1 (934 ml. at 25° C., 745 mm.)
Total recovered	295.7 (99.3%)

The butadiene was found to be 99+ % pure. Table II shows the analysis of this pyrolysis liquor from which the mole per cent conversions and recoveries are readily calculated (experiment 106, Table I).

Samples of the vent gases were collected for analysis during a number of experiments. The percentage composition of a typical sample was as follows: carbon dioxide, 18.6; illuminants, 9.3; hydrogen, 3.2; carbon monoxide, 37.5; ethane, 2.0; methane, 26.6; unaccounted, 2.8. This composition agrees well with that reported (8) for the pyrolysis of acetic acid. Correlation of the total acetic acid recovery with the weight of vent gas, as well as with an over-all oxygen balance, indicated that approximately 75% of the vent gas arose from the decomposi-

TABLE II. ANALYSIS OF PYROLYSIS LIQUOR FOR EXPERIMENT 106

Component	Analytical Method No.	Weight %	Grams	Moles
Dissolved butadiene	12, 13	0.1	0.2	0.004
Free acetic acid	2	87.4	191.6	3.190
Combined acetic acid	2	5.0	10.9	0.181
MVC + crotyl acetates	6, 13	4.1	9.0	0.079
MEK	7, 13	1.4	3.1	0.042
MEK enol-acetate	9, 13	2.4	5.2	0.046
Unreacted diacetate	3, 13	1.5	3.2	0.018
Methyl acetyl acetone	9, 13	0.9	1.9	0.017
Other by-products[a]	...	2.2	4.8	[b]

[a] By difference. The figures for combined acetic acid are not included in calculating the difference from 100%, since they represent the total combined acetic acid observed in the pyrolysis liquor, approximately 98–99% of which is accounted for as the sum of the various acetates individually analyzed.

[b] The mole per cent conversion of diacetate to other by-products, appearing in Table I, is calculated by difference from 100%.

tion of acetic acid. The remainder may arise from the MEK enol-acetate, as shown later.

It was necessary to determine the effect of certain substances on the pyrolysis of the diacetate (Table III). When pyrolyses were conducted under optimum conditions, acetic acid exerted a favorable effect, the butadiene conversion being over 85%. Acetic anhydride caused a slight decrease in butadiene conversion. The presence of water had no apparent effect. When diacetate was mixed with the intermediate acetates and by-products and separated from the pyrolysis liquor, the butadiene conversion was that expected from the sum of the diacetate and the MVC plus crotyl acetate intermediates present in the mixture. Pyrolysis of a mixture of diacetate and MVC acetate also resulted in the butadiene conversion expected from both ingredients.

ISOLATION AND IDENTIFICATION OF INTERMEDIATES AND BY-PRODUCTS

By adding water to the pyrolysis liquor and distilling, an oil was obtained which comprised a mixture of the intermediate acetates (V, VI, and VII), the low-boiling by-products, and some acetic acid. The acetic acid was removed by washing with water. The oil was dried by distillation of its water azeotrope to a gravity separator which continuously removed the water, and the dried oil was carefully fractionated through a 48 × ³/₄ inch column packed with glass helices.

MEK. The fraction (boiling range 79–80° C.) was identified as MEK by means of its 2,4-dinitrophenylhydrazone (melting point 115° C.); a mixed melting point with an authentic sample showed no depression.

MVC ACETATE. The fraction (boiling range 111–112° C.) was identified as MVC acetate by saponification and isolation of the carbinol as described in a previous communication (12).

MEK ENOL-ACETATE. The fraction (boiling range 118–120° C.) was found to be a mixture of 90% MEK enol-acetate and 10% crotyl acetate, as determined by analytical methods 2 and 8.

TABLE III. EFFECT OF VARIOUS SUBSTANCES ON THE PYROLYSIS OF 2,3-BUTYLENE GLYCOL DIACETATE

Expt. No.	Temp., °C.	Apparatus	Compn. of Mixt., Wt. % Diacetate	Compn. of Mixt., Wt. % Other component[a]	Rate of Feed G./Min.	Mixture Pyrolyzed, Grams	Vent Gas, Ml.	Butadiene, Grams	Weight Recovery, %	Conversion to Butadiene, Mole %
23	500	B	74.4	25.6 AA	10.0	322.5	700	54.2	96.0	72.6
24	500	B	59.2	40.8 AA	9.3	373.6	900	52.0	93.5	75.9
41	500	B	20.0	80.0 AA	6.5	351.4	200	17.0	98.5	78.3
31	500	B	80.0	20.0 MVC acetate	6.2	192.2	550	51.9	97.2	79.3
93A	575	D	20.0	80.0 AA	7.8	318.6	350	16.9	97.7	85.3
93B	575	D	20.0	80.0 AA	4.0	261.5	190	13.2	96.5	81.2
103	575	D	99.0	1.0 AAn	9.3	298.8	1035	72.8	98.2	79.1
104	575	D	94.5	5.5 AAn	10.1	304.0	1200	70.7	97.5	79.1
105	575	D	99.5	0.5 AAn	9.2	295.5	1000	73.4	98.4	80.3
169	575	D	97.7	2.3 H₂O	9.5	305.0	1100	74.4	97.5	80.5
125	575	D	95.7	4.3 SO[b]	10.0	299.4	2300	72.7	98.8	79.8
127	575	D	90.0	10.0 SO[c]	9.9	592.0	6300	138.1	97.8	80.7

[a] AA = acetic acid; AAn = acetic anhydride; SO = stripped oil.
[b] Contains 39.1% MVC plus crotyl acetates.
[c] Contains 20.4% MVC plus crotyl acetates.

TABLE IV. PYROLYSIS OF METHYL VINYL CARBINOL ACETATE

Expt. No.	Temp., °C.	Contact Time, Sec.	Acetate Pyrolyzed, Grams	Vent Gas, Ml./Mole Acetate	Pyrolysis Liquor, Grams	Butadiene, Grams	Conversion to Butadiene, Mole %
164	475	17.0	132.9	172	78.1	45.8	72.8
187	475	28.5	149.7	685	85.1	54.9	77.5
195	500	7.5	158.5	288	89.0	65.6	87.3
191	500	9.2	129.3	616	66.7	54.2	88.3
196	500	11.2	131.5	520	73.8	52.0	83.5
194	500	21.5	118.3	1639	65.5	44.1	78.4
192	525	8.9	129.5	1939	67.9	53.2	86.7

Further purification by fractionation was not successful. On hydrogenation over Raney nickel at 130° C. and 1600 pounds per square inch, one mole of hydrogen was consumed per mole of acetate and the main product was *sec*-butyl acetate (boiling range 111–112° C.). The *sec*-butanol formed on saponification was identified as its 3,5-dinitrobenzoate (melting point 75–76° C.); a mixed melting point with an authentic sample showed no depression. Only one reference to this enol-acetate was found in the literature, Gwynn and Degering (6) reported it as a probable component in a mixture of butenol acetates (boiling range 118–120° C.) formed from MEK by reaction with ketene.

CROTYL ACETATE. The fraction (boiling range 129–131° C.) was identified as crotyl acetate. On saponification it yielded crotyl alcohol (boiling range 121–121.5° C., n_D^{26} 1.4242, d_{26} 0.8433). The p-nitrobenzoate melted at 49° C.; a mixed melting point with an authentic sample showed no depression.

1-VINYL-3-CYCLOHEXENE (BUTADIENE DIMER). The wet oil from distillation of the pyrolysis liquor with water was redistilled, and the mixture of water azeotropes collected. Saponification of the oil layer of this distillate, followed by exhaustive extraction with water, drying, and distilling, yielded a fraction with a boiling range of 128–129° C. and n_D^{26} of 1.4625. These constants, as well as analyses for carbon and hydrogen, are in agreement with those reported for 1-vinyl-3-cyclohexene (1).

METHYL ACETYL ACETONE. The fraction of the pyrolysis liquor boiling above 145° C. (method 13) was cooled to −40° C., and the white crystals were separated by filtration. During distillation a fraction of boiling range 170.5–171.5° C. was obtained (n_D^{26} 1.4413, d_{27} 0.9728). These constants are in agreement with those reported for methyl acetyl acetone (2). By alkaline hydrolysis acetic acid and MEK were formed quantitatively. The formation of acids and ketones by alkali cleavage is reported to be a general reaction for 1,3-diketones (11). On hydrogenation over Raney nickel at 130° C. and 1600 pounds per square inch, two moles of hydrogen were consumed and the main product was identified as 3-methyl-2,4-pentanediol (boiling range 205–207° C., n_D^{26} 1.4418). The diketone was also characterized as its semicarbazide, melting at 149° C. (15). As the result of treatment with 2,4-dinitrophenylhydrazine in alcohol containing 2% hydrochloric acid, two products were obtained—a bright yellow compound melting at 155° C. and an orange compound melting at 250° C. By analysis, the former is apparently 1-(2,4-dinitrophenyl)-3,4,5-trimethylpyrazole, formed by reaction with one mole of the hydrazine, and the latter is the di-2,4-dinitrophenylhydrazone of methyl acetyl acetone.

PYROLYSIS OF INTERMEDIATES AND BY-PRODUCTS

The following experiments were conducted in apparatus *D* except that apparatus *B* was used for MVC acetate:

MVC ACETATE. The acetate (boiling range 112–113° C.) was prepared as described by Ingold and Ingold (10) from MVC and acetic anhydride. The pyrolysis data are presented in Table IV. In all cases the resultant butadiene analyzed 99+%.

CROTYL ACETATE. The ester (boiling range 132–133° C.) was prepared from crotyl alcohol as described for MVC acetate (10). It was pyrolyzed at 575° C. at a contact time of 1.86 seconds, with

the following results: conversion to butadiene, 87.6%; weight recovery, 96.1%; vent gas, 910 ml. per mole of acetate. The butadiene obtained analyzed 99+%.

MEK ENOL-ACETATE. The mixture of MEK enol-acetate (90%) and crotyl acetate (10%), with a boiling range of 118° to 120° C., obtained as described above, was pyrolyzed at 575° C. at a contact time of 1.69 seconds. Based upon total acetate fed, the conversion to butadiene was only 7.5%, apparently derived entirely from the crotyl acetate. Vent gas to the extent of 12.2 liters per mole of acetate was produced, an indication that MEK enol-acetate had undergone extensive decomposition. Analysis of the pyrolysis liquor showed that MEK enol-acetate had been converted approximately as follows: to methyl acetyl acetone, 20%; to MEK and acetic acid, 25%; unchanged, 40%; unaccounted, including vent gas, 15%. The butadiene was only 72% pure, and was contaminated with the decomposition products from MEK enol-acetate. Pyrolysis at lower temperatures resulted in less decomposition; at 500° C. practically all the MEK enol-acetate was recovered.

MEK. A sample of freshly distilled MEK (boiling range 79–80° C.) was pyrolyzed at 575° C. at a feed rate of 5.6 grams per minute. A quantitative weight recovery as liquor was obtained, no gaseous products being formed. The liquor analyzed 91% MEK. A 1:4 mixture of MEK and acetic acid was pyrolyzed at 595° C. at a feed rate of 6.7 grams per minute. A recovery of 99% by weight as liquor was obtained, the acetic acid content being the same as in the mixture fed. This showed that MEK and acetic acid do not combine under the pyrolysis conditions employed.

METHYL ACETYL ACETONE. A sample of methyl acetyl acetone (95% purity), obtained from diacetate pyrolysis liquor, was mixed with 4 parts of acetic acid and pyrolyzed at 575° C. at a feed rate of 8.1 grams per minute. The results were similar to those achieved with the isomeric MEK enol-acetate; no butadiene was formed, and decomposition to vent gases was extensive.

OILS SEPARATED FROM DIACETATE-PYROLYSIS LIQUORS. The oils separated from the diacetate pyrolysis liquors by "stripping" with water, as described below, were pyrolyzed at 500–600° C. and feed rates of 2 to 12 grams per minute. The composition of these oils was approximately as follows: 30% MVC plus crotyl acetates, 30% MEK enol-acetate, 15% MEK, 10% acetic acid, and 15% other by-products. The results were in agreement with the experiments described above for the pyrolysis of the individual components. At temperatures of 575–600° C., the MVC and crotyl acetate components which had reacted were converted to butadiene in 88% yield, and all but traces of these materials had decomposed on two recycles of the pyrolysis liquors. The resultant butadiene was contaminated (80% purity) with the decomposition products formed from the MEK enol-acetate and other by-products. On pyrolysis at 500° C. the quality of the butadiene was improved (90% pure), but lesser quantities of the MVC and crotyl acetate components reacted per pass. The presence of water had no apparent effect on the pyrolysis of the oils.

BUTYLENE GLYCOL MONOACETATE. Since this compound is an intermediate in the preparation of the diacetate and may be present as an impurity in the latter, it was necessary to study its behavior on pyrolysis. While it was possible, by the method of Winstein and Lucas (24), to prepare small quantities of pure monoacetate, the preparation of larger quantities resulted in mixtures containing about 15% diacetate. When such a mixture was pyrolyzed at a temperature of 575° C. and at a contact time of 2.15 seconds, the yield data indicated that 10% of the monoacetate was converted to butadiene. This was based on the assumption that 81% of the diacetate was converted to butadiene. Approximately 25% of the monoacetate was converted to MEK, and only traces of combined acetic acid were found in the pyrolysis liquor. From these results, it was evident that the presence of the monoglycol acetate, as an impurity in the diacetate, was to be avoided in the pyrolysis reactions.

RE-USE OF PYROLYSIS LIQUOR

Three basic problems were involved in the successful utilization of the diacetate pyrolysis liquor: production of more butadiene from the MVC and crotyl acetate intermediates, recovery of acetic acid for re-esterification, and separation of by-products. The approximate composition of the pyrolysis liquor obtained under optimum one-pass operating conditions is given in Table II.

The percentages of MEK and its derivatives (i.e., the enol-acetate and methyl acetyl acetone) which were formed during the

pyrolysis of the diacetate were surprisingly constant over wide ranges of temperature and contact time. Since these materials were not convertible to butadiene, it was evident that their formation was the chief limiting factor in the over-all yield of butadiene which could be obtained. Because the degree to which these materials were formed could not be reduced to any appreciable extent by altering the pyrolysis conditions, the problem of securing the highest yield of butadiene involved the determination of the best procedure for converting the MVC and crotyl acetates left in the diacetate pyrolysis liquors. The following procedures were investigated in connection with the re-use of these liquors:

1. RECYCLING. Experiments on the recycling of liquors from the diacetate pyrolyses at various temperatures are presented in Table V. Although the MVC and crotyl acetate intermediates are effectively converted to butadiene, a number of objections may be raised to this procedure: It involves recycling of large amounts of acetic acid; the problems of by-product removal and acetic acid recovery from spent liquor are essentially the same as those from the liquor secured from the first pass; successive pyrolysis of MEK enol-acetate and methyl acetyl acetone components lowers the purity of the butadiene as a result of decomposition reactions; and the over-all 84% yield of butadiene so achieved was only slightly higher than the 81–82% yield obtained from one pass at optimum operating conditions (Table I).

2. CRYSTALLIZATION. Although the bulk of the acetic acid may be separated by refrigeration from the pyrolysis liquor as glacial acid, processing difficulties on a commercial scale would be considerable and a simpler method, preferably a distillation procedure, was sought.

3. FRACTIONAL DISTILLATION. Fractionation of the pyrolysis liquor did not affect the desired separations. The only components conveniently separated by this method were free MEK (boiling range 79–80° C.), methyl acetyl acetone (171–172° C.), unreacted diacetate (192–194° C.), and residual tars. Attempts to separate the intermediate acetates (boiling between 111° and 112°, 118° and 120°, and 129° and 131° C. for V, VI, and VII, respectively) from the large amount of acetic acid present (boiling at 118° C.) were unsuccessful. In this connection, an investigation of the binary systems MEK–MVC acetate, MEK–acetic acid, and MVC acetate–acetic acid was conducted with the following results: MEK was separated readily in both cases, the separation of MVC acetate from acetic acid was impractical, and no evidence of azeotropicity was found.

4. RE-USE OF LIQUORS FOR ESTERIFICATION OF GLYCOL. The acetylation of 2,3-butylene glycol with pure acetic acid, described in another paper (17), is readily accomplished with a mineral acid catalyst and a suitable entrainer for continuous azeotropic removal of water. Hill and Isaacs (7) state that the acetic acid produced in the decomposition of the diacetate—i.e., the pyrolysis liquor—can be re-used for esterification by employing sulfuric acid as the catalyst and benzene as the entrainer. They infer that the same procedure found successful for producing the diacetate from pure acetic acid is applicable to the pyrolysis

liquor. It has been found, however, that the diacetate pyrolysis by-products, especially MEK, interfere with the entraining agents used for conducting the esterification; the MEK–water azeotrope (boiling at 73.4° C.) soon prevented the formation of two layers in the gravity separator. This difficulty can be overcome by introducing a lower-boiling entraining agent which does not form an azeotrope with acetic acid. By using isopropyl ether, for example (boiling point of water azeotrope is 62.2° C.), it was possible to conduct the esterification in the usual manner. Although the yield and purity of the diacetate so obtained were identical with that from pure acetic acid, the intermediate acetates and by-products present underwent the following reactions during the course of esterification: The MEK enol-acetate and methyl acetyl acetone components were completely converted to free MEK and acetic acid; the MVC and crotyl acetate intermediates were converted to butadiene to the extent of about 33%; 67% remained as an equilibrium mixture of acetates (80%) and carbinols (20%). From a commercial operating viewpoint, the production of butadiene during the esterification step under nonoptimum conversion conditions, and with the concurrent problems of collection and separation, is obviously undesirable.

5. DISTILLATION WITH WATER (STRIPPING). The addition of water to the pyrolysis liquors, followed by distillation, results in the removal of an oil-water azeotrope containing MEK, the intermediate acetates (V, VI, and VII), and the other low-boiling by-products. On fractional distillation of the residue from this operation, the bulk of the acid may be recovered as glacial acetic acid. This method provides a means of separating the intermediate acetates from the liquors, as well as producing an acetic acid residue which, on distillation, is essentially pure and is suitable for re-use in esterification. The mixed unsaturated acetates obtained in this manner may then be pyrolyzed separately to yield butadiene. Because of these advantages, this method of operation, referred to as stripping, was used in the pilot-plant studies (16).

6. COMBINATION OF METHODS 4 AND 5. Experiments were also conducted on the possibility of combining the esterification and stripping operations—i.e., starting the glycol esterification with the pyrolysis liquor and then stripping with the water so formed. The equilibrium, established at about 45% conversion to glycol diacetate, is rapidly attained in the presence of an excess of acetic acid. At equilibrium a sufficient amount of water is present to bring about stripping.

On mixing the pyrolysis liquor (2 moles of acetic acid) with glycol (1 mole) and sulfuric acid (0.02 mole), and heating for 30 minutes on a steam bath (90–93° C.), the MEK enol-acetate and methyl acetyl acetone components present were completely hydrolyzed. Simultaneously, the MVC and crotyl acetate intermediates were retained as mixtures of approximately 80% acetates and 20% carbinols. Under these conditions, referred to as equilibrium esterification with the pyrolysis liquor, no butadiene was formed. The technique of continuous esterification described in another paper (17) was employed to test this method of re-using the diacetate pyrolysis liquor. A 20 M glycol equilibrium esterification mixture was fed to the esterification column, countercurrently to a stream of glacial acetic acid. The MVC and crotyl acetates and the free MEK were stripped from the system by the vapor stream of wet acetic acid. These components were then separated from the column distillate as their water azeotropes; the fractions boiling at 72–75° C. contained MEK, and those at 75–90°C. contained the equilibrium mixture of MVC and crotyl acetates and carbinols. The following yields and recoveries were obtained: Over-all weight recovery, 99.5%; diacetate yield, 97.2%; purity of distilled diacetate, 99.6%; conversion of MEK enol-acetate and methyl acetyl acetone to free MEK and acetic acid, 100%; conversion of MVC plus crotyl acetates to butadiene, 5.9%; recovery of MVC plus crotyl acetates and carbinols, 86.2%. Tarry components of the original pyrolysis liquors were deposited in the lower plates of the column.

This method of re-using the pyrolysis liquors would appear to offer advantages in that the MEK enol-acetate and methyl acetyl acetone components, both of which decompose on pyrolysis without formation of butadiene, would be completely converted to free MEK and acetic acid during equilibrium esterification; the MEK, which is also formed as a side reaction product during the

TABLE V. BUTADIENE CONVERSIONS FROM 2,3-BUTYLENE GLYCOL DIACETATE BY RECYCLING PYROLYSES

Expt. No.	Temp., °C.	Apparatus	Pass No.	Rate of Feed, G./Min.	Weight Recovery, %	Cumulative Butadiene, Conversion Mole %
151	475	B	1	4.8	99.0	54.2
	475		2	4.7	98.6	71.7
	475		3	5.5	95.5	77.5
75	475	D	1	2.5	97.4	45.8
	475		2	2.3	99.1	60.4
	475		3	6.2	96.1	79.1
76	487	D	1	6.0	98.2	34.3
	487		2	5.2	..	53.2
	487		3	4.9	..	64.6
	487		4	5.2	..	71.9
	487		5	5.2	92.1ᵃ	80.5
186	500	B	1	9.3	97.4	71.6
	500		2	7.6	99.0	83.1
67	550	C	1	10.4	97.6	67.0
	550		2	8.9	99.2	82.1
	550		3	10.0	99.2	83.8
88	585	D	1	11.3	98.4	81.0
	575		2	8.3	96.7	83.7
87	595	D	1	11.4	98.6	78.6
	575		2	8.7	95.8	81.5

ᵃ Cumulative weight recovery

acetylation of 2,3-butylene glycol with glacial acetic acid (17), would be removed at only one point in the over-all process; the MVC and crotyl acetate intermediates would be recovered for re-pyrolysis with diacetate, uncontaminated with the nonbutadiene-yielding MEK enol-acetate; and the distillation of acetic acid in process would be limited to that used as excess during the esterification. The deposition of tars in the esterification column, and the highly complicated mixture of materials undergoing reaction in this column would, however, make it difficult to maintain and control the continuous esterification operation. Although this method could undoubtedly be used for batch esterification, the advantages of the continuous process using purified acetic acid are obvious. Because of these factors, this method was not explored in the pilot-plant studies.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Beilstein, F. K., Handbuch der organische Chemie, 4th ed., Vol. 1, p. 406, Berlin, J. Springer, 1930.
(2) Ibid., Vol. 5, p. 63.
(3) Brockmann, M. C., and Werckmann, C. H., IND. ENG. CHEM., ANAL. ED., 5, 206 (1933).
(4) Clutterbuck, P., and Reuter, F., J. Chem. Soc., 1935, 1467.
(5) Egloff, G., and Hulla, G., Oil Gas J., 41, No. 31, 49 (1942).
(6) Gwynn, B. H., and Degering, E. F., J. Am. Chem. Soc., 64, 2217 (1942).
(7) Hill, R., and Isaacs, E. (to Imperial Chem. Ind.), Brit. Patent 483,989 (April 28, 1938); U. S. Patent 2,224,912 (Dec. 17, (1940).
(8) Hurd, C. D., "Pyrolysis of Carbon Compounds", p. 332, New York, Chemical Catalog Co., 1929.
(9) Iddles, E. A., and Jackson, C. E., IND. ENG. CHEM., ANAL. ED., 6, 454 (1934).
(10) Ingold, E. H., and Ingold, C. K., J. Chem. Soc., 1932, 759.
(11) Karrer, P., "Organic Chemistry" (tr. by Mee, A. J.), p. 234, New York, Nordemann Pub. Co., 1938.
(12) Morell, S. A., and Auernheimer, A. H., J. Am. Chem. Soc., 66, 792 (1944).
(13) Morell, S. A., and Geller, H. H., "Organic Syntheses", New York, John Wiley & Sons, in press.
(14) Pelt, A. J. van, Jr., and Wibaut, J. P., Rec. trav. chim., 60, 55 (1941).
(15) Posner, T., Ber., 34, 3981 (1901).
(16) Schniepp, L. E., Dunning, J. W., Geller, H. H., Morell, S. A., and Lathrop, E. C., IND. ENG. CHEM., 37, 884 (1945).
(17) Schniepp, L. E., Dunning, J. W., and Lathrop, E. C., Ibid., 37, 872 (1945).
(18) Smith, D. M., Bryant, W. M. D., and Mitchell, J., J. Am. Chem. Soc., 61, 2407 (1939).
(19) Smith, L. T., Fisher, C. H., Ratchford, W. P., and Fein, M. L., IND. ENG. CHEM., 34, 474, Table I (1942).
(20) Tropsch, H., and Mattox, W. J., IND. ENG. CHEM., ANAL. ED., 6, 104 (1934).
(21) Ward, G. E., Pettijohn, O. G., and Coghill, R. D., J. Am. Chem. Soc., in press.
(22) Ward, G. E., Pettijohn, O. G., Lockwood, L. B., and Coghill, R. D., Ibid., 66, 541 (1944).
(23) Williams, J. W., and Hurd, C. D., J. Org. Chem., 5, 122 (1940).
(24) Winstein, S., and Lucas, H. J., J. Am. Chem. Soc., 61, 1581 (1939).

PILOT-PLANT CONVERSION of 2,3-BUTYLENE GLYCOL DIACETATE to 1,3-BUTADIENE

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LABORATORY investigations (2) on a process for the manufacture of 1,3-butadiene from 2,3-butylene glycol by pyrolysis of the diacetate resulted in development of a small-scale pilot-plant pyrolysis unit; in this apparatus the effects of various factors, such as time, temperature, and pressure could be investigated, and optimum conditions for the highest yields and by-product recoveries could be determined. Because of critical material shortages, the design was the simplest possible which would serve to determine data for larger-scale design. The findings of this research were used as a basis for operation in the 2000-pound-per-day pilot plant of Joseph E. Seagram & Sons, Inc.

The pilot-plant pyrolysis unit (Figure 1) consisted of a gas-heated lead bath in which interchangeable pyrolysis coils, having production capacities of 20 to 100 pounds of butadiene per day, could be immersed. The glycol diacetate to be pyrolyzed was pumped from a weigh tank by a proportioning pump to a vaporizer which was connected to the inlet of the pyrolysis coil in the lead bath. The outlet of the pyrolysis coil was connected through a 3-foot section of 1/2-inch I.P.S. (iron pipe size) pipe to the base of a jacketed column where the butadiene was separated from

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condensed acetic acid and other liquid pyrolysis products. These pyrolysis liquors passed through a U-trap at the base of the column, and were collected in a tared receiver mounted on a scale. The butadiene and small amounts of other gaseous products from the head of the butadiene separating column were washed with water in a small scrubbing tower to remove traces of entrained acetic acid. The gases then passed through a tower packed with calcium chloride to remove moisture. The dry gases were picked up by a compressor, through a pressure control valve, and the butadiene, compressed to 38–40 pounds per square inch, was condensed and collected in a weigh tank. The gaseous by-products, not condensable at room temperature under 38–40 pounds per square inch, were vented from the compressor system by a pressure control valve at the top of a refrigerated reflux condenser which was connected into the line carrying butadiene to the weigh tank. The weigh tank was vented to this condenser to prevent trapping of noncondensable gases in the tank. The volume of noncondensable gases was measured by a wet test meter. Samples of the vent gases, butadiene, pyrolysis liquors, and glycol diacetate feed were taken for analyses during each run. All parts of this unit which came into contact with liquid, or gaseous, acetic acid were constructed of stainless steel.

Pilot-plant studies of the process for producing 1,3-butadiene from 2,3-butylene glycol diacetate by pyrolysis have shown that an 88% yield can be obtained. The process consists in pyrolyzing the diacetate at 595° C. to obtain an 83% conversion to 99+% pure butadiene. The intermediate butenol acetates are separated from the acetic acid of the pyrolysis liquors and repyrolyzed to obtain the additional 5% of butadiene. Approximately 8% of useful by-products are obtained. These consist of methyl ethyl ketone, methyl ethyl ketone enol-acetate (2-acetoxy-2-butene), and methyl acetyl acetone, the latter two being hydrolyzable to methyl ethyl ketone and acetic acid. The over-all acetic acid recovery is 99%, and 0.8% of the initial diacetate is converted to vent gases. A proposed continuous process for production of butadiene from 2,3-butylene glycol is described briefly. The over-all yield and recoveries of by-products follow: butadiene yield (from glycol), 85.4%; conversion of glycol to methyl ethyl ketone, 11.2%; acetic acid recovery, 99.5%, and conversion of glycol to butadiene polymers and vent gases, 3.0%.

Thermocouples were inserted in the outlet of the vaporizer, in the lead bath, in the outlet of the pyrolysis coil, in the line connecting this coil to the column, and in the base and head of this column. The thermocouple in the vapor stream at the outlet of the pyrolysis coil was connected to an indicating temperature controller which controlled the lead-bath heating mechanism. This arrangement served to control the outlet pyrolysis vapor temperatures within ±2° C. The pyrolysis temperatures referred to later are those measured by this thermocouple.

Pressure gages were installed at the inlet of the vaporizer, between the vaporizer and the pyrolysis coil, between the pyrolysis coil and the butadiene stripping column, and between the drying tower and the butadiene compressor.

This pilot plant was sufficiently versatile to permit the study of pyrolysis conditions over a wide range: production rates up to 100 pounds of butadiene per day, temperatures up to 700° C., contact times as low as 0.1 second, and pressures between several inches vacuum and 300 pounds per square inch.

The contact times referred to in these studies were calculated in the same manner as those reported in the laboratory work (2), i.e., by the empirical formula:

$$\text{Contact time (sec.)} = \frac{(\text{vol. of tubes in ml.})\ 60}{\left(\dfrac{T}{273}\right)\left(\dfrac{22,400}{\text{mol. wt.}}\right)(\text{g./min. feed})}$$

In the coil-type pyrolysis chamber it was not possible to measure the gas temperatures in the various parts of the coil or to predict the exact volume of the reaction zone. A portion of the coil necessarily served to raise the temperature of the entering vapor to reaction temperature, and obviously the true reaction zone volume was not the total coil volume. Since the total coil volume and the temperature of the gases at the coil outlet were the only definitely determinable factors, all contact time calculations were based on these values. The contact times indicate the residence time in the total coil length, assuming a constant temperature throughout. That these contact time values are relative to each other at each
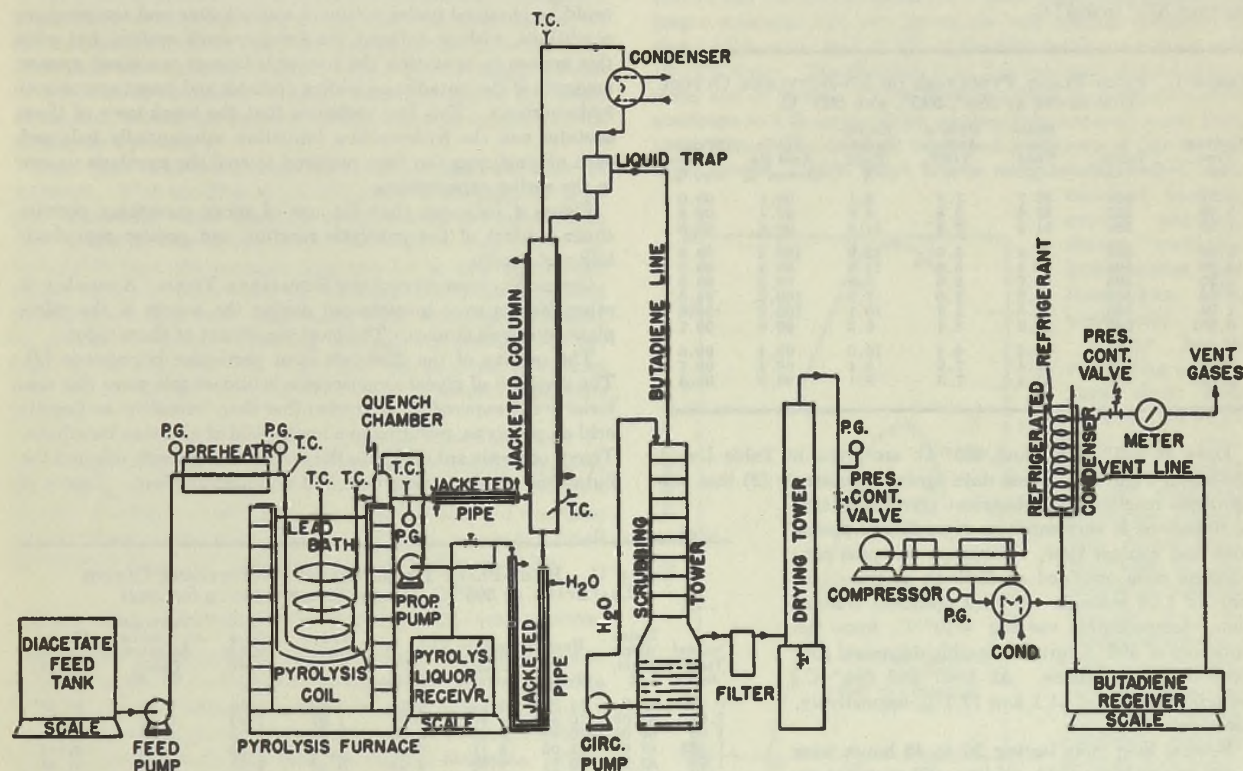

Figure 1. Flow Diagram of Pilot-Plant Pyrolysis Apparatus for Conversion of 2,3-Butylene Glycol Diacetate to Butadiene

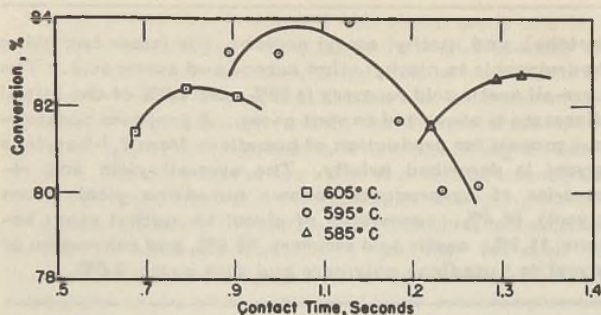P.G. = pressure gage;   T.C. = thermocouple

Figure 2. Effect of Temperature on Conversion–Contact Time Data (Jacketed Pipe Cooling System)

temperature studied is indicated by the uniformity of results obtained in two coils of different lengths constructed of different sizes of pipe. In both of these coils the peaks of the conversion-contact time curves, at a gas outlet temperature of 595° C., were found to be at about the same contact time. This indicates that the portion of the coil required to raise the entering vapors to reaction temperature is proportional to the total coil volume in both cases.

The 2,3-butylene glycol diacetate used in the pilot-plant studies was prepared by large-scale batch esterification of the glycol (3), and was all 99–100% pure.

PYROLYSIS STUDIES

Orienting experiments were conducted in a pyrolysis coil constructed from a 27-foot length of $1/8$-inch I.P.S. stainless steel (18-8-Cb) pipe which had a butadiene production capacity of about 20 pounds per day. A series of relatively short runs served to establish conversion–contact time data at temperatures varying from 575° to 625° C.

TABLE I. PILOT-PLANT PYROLYSES OF 2,3-BUTYLENE GLYCOL DIACETATE AT 585°, 595°, AND 605° C.

Contact Time, Sec.	Temp., °C.	Butadiene Yield, %	Unsatd. Acetate Yield, %	Hydrocarbon Yield, %	Acetic Acid Recovery, %	Weight Recovery, %
1.57	585	82.7	7.1	8.1	98.1	99.0
1.49	585	82.6	6.8	8.6	97.4	98.6
1.33	585	81.5	7.2	11.6	99.6	99.0
1.44	595	80.2	5.0	12.9	100.2	99.9
1.36	595	80.1	5.0	11.9	99.4	99.2
1.25	595	81.7	6.0	9.8	99.3	99.0
1.16	595	83.9	7.0	7.6	100.0	99.9
1.04	595	82.6	5.8	10.1	100.2	99.8
0.891	595	83.2	8.4	6.3	99.9	99.2
0.912	605	82.2	6.1	10.0	99.4	99.6
0.792	605	82.4	7.0	8.4	99.4	99.7
0.681	605	81.4	7.3	9.1	98.9	99.6

Data at 585°, 595°, and 605° C. are given in Table I and plotted in Figure 2. These data again demonstrate (2) that the pyrolysis reaction of 2,3-butylene glycol diacetate to butadiene is very sensitive regarding temperature and contact time. Maximum one-pass conversions were obtained at 595° C. at a contact time of 1.04 seconds. At this optimum contact time, temperatures varying ±10° C. from the optimum of 595° C. give noticeably decreased conversions to butadiene. At 585° and 605° C., butadiene yields of 81.1 and 77.1%, respectively, are obtained.

Several long runs lasting 30 to 48 hours were made to establish yield, quality, and material recovery data. At contact times ranging from 0.97 to 1.02 seconds, these runs gave an average yield of 82.1% of 99% pure butadiene. The over-all weight

recovery averaged 99.8, and acetic acid recovery was also 99.8%. An average of 0.62% of the total weight of glycol diacetate pyrolyzed was converted to noncondensable gases. These runs served to confirm the yields and quality of the butadiene and the high acetic acid and weight recoveries that had been indicated in the shorter runs.

COOLING OF PYROLYSIS VAPORS. For these runs, a water-jacketed $1/2$-inch I.P.S. pipe served to cool the pyrolysis vapors going to the butadiene stripping column. Approximately 0.3 second was required to cool the pyrolysis vapors from 595° to 118° C. During this interval some butadiene dimerized (the rate of this reaction being quite rapid at elevated temperatures), and some of the methyl vinyl carbinol and crotyl acetates in the pyrolysis liquor pyrolyzed to butadiene. This loss of butadiene through dimerization, as well as the pyrolysis of the butadiene-yielding acetates under nonoptimum conditions, was undesirable. To obtain the highest yields of butadiene, the pyrolysis and polymerization reactions should be stopped immediately as the vapors leave the pyrolysis coil. A spray-quench system, shown in Figures 1 and 3, was therefore built into the pyrolysis vapor line, adjacent to the pyrolysis coil outlet. Cooled pyrolysis liquors were pumped by a proportioning pump through the spray housing into the pyrolysis vapor stream.

A larger pyrolysis coil, made from 45 feet of $1/4$-inch I.P.S. high-chrome steel pipe and having a capacity of 100 pounds of butadiene per day, was then installed. Data obtained in this pyrolysis unit at the optimum temperature of 595° C. are given in Table II and are plotted as the lower curve in Figure 4. About 0.5% of glycol diacetate remained unreacted in all runs.

Table II shows a substantial reduction in hydrocarbon formation over the earlier pilot-plant results shown in Table I. The percentage retention of methyl vinyl carbinol and crotyl acetates increased correspondingly. The most striking feature of the results was that approximately the same conversion to butadiene could be obtained under optimum contact time and temperature conditions, with or without the spray-quench system, but with this system in operation the pyrolysis liquors contained greater amounts of the butadiene-yielding acetates and lesser amounts of hydrocarbons. This fact indicates that the breakdown of these acetates and the hydrocarbon formation substantially balanced each other during the time required to cool the pyrolysis vapors in the earlier experiments.

Figure 4 indicates that the use of spray quenching permits closer control of the pyrolysis reaction and greater reproducibility of results.

OTHER FACTORS AFFECTING BUTADIENE YIELD. A number of other factors were investigated during the course of the pilot-plant pyrolysis studies. The most significant of these follow:

The quality of the diacetate is of particular importance (2). The presence of glycol monoacetate is undesirable since this material is decomposed to products other than butadiene and acetic acid on pyrolysis, resulting in a lower yield of glycol to butadiene. Traces of acetic anhydride in the diacetate adversely affected the butadiene yield. Acetic acid had no harmful effect. Traces of

TABLE II. PILOT-PLANT PYROLYSES OF 2,3-BUTYLENE GLYCOL DIACETATE AT 595° C. (USING SPRAY-QUENCH SYSTEM)

Contact Time, Sec.	Butadiene Yield, %	Unsatd. Acetate Yield, %			Hydrocarbon Yield, %	Free MEK Yield, %	Conversion to Noncondensable Gases, Wt. %	Cumulative Yield[a], %
		Total	MEK[a] acetate	MVC acetate				
0.92	75.9	14.23	5.44	8.79	1.28	1.28	0.58	83.37
1.01	81.62	10.46	4.47	5.99	1.97	1.62	0.59	86.72
1.02	82.09	10.72	4.12	6.60	1.44	1.73	0.58	87.70
1.027	82.6	11.05	5.11	5.94	1.22	1.35	0.60	87.65
1.06	82.75	10.31	4.30	6.01	3.12	1.97	0.57	87.86
1.07	82.90	12.37	4.82	7.55	0.22	1.41	0.55	89.32
1.08	82.84	9.79	4.54	5.25	0.36	1.70	0.59	87.31
1.114	81.8	11.00	4.68	6.26	0.63	1.41	0.64	87.12

[a] Approximately 30% methyl acetyl acetone.

Figure 3. Pyrolysis Furnace in Butadiene Pilot Plant, Showing Pre-heater, Gas Heating System, Spray-Quench System, and Butadiene Stripping Column

copper salts dissolved in the diacetate had no harmful effects on the butadiene yield and quality. There were no detectable differences between the results obtained from diacetates prepared from the meso- or levorotatory glycols.

The effect of pressure in the pyrolysis system was investigated. Pressure up to 14 pounds per square inch had no noticeable effect on butadiene yields. At 80 pounds per square inch the butadiene yield was markedly reduced, with a corresponding increase in hydrocarbon formation. Slightly reduced pressures, 5–6 inches of vacuum, showed no measurable differences as compared with atmospheric pressures.

Some data on pressure drops across the pyrolysis coil were determined. With the 27-foot coil of $1/8$-inch I.P.S. pipe, the pressure differential varied from 1.2 to 1.8 pounds per square inch over several months of operation. With the 45-foot coil of $1/4$-inch I.P.S. pipe, the pressure drop was 7.0 to 11.8 pounds per square inch. In both cases, the pressure differential increased slightly over long periods of operation. This was probably caused by gradual deposition of carbon, although its amount was too small to be measured. In either case the pressure differences were not of sufficient magnitude to cause significant variations in yield.

QUALITY OF THE BUTADIENE. The butadiene obtained in all of these pilot-plant pyrolysis runs was of excellent quality, 99 to 100% pure by analysis. Tests by The Goodyear Tire and Rubber Company showed that it was satisfactory for synthetic rubber manufacture after simple distillation to remove small amounts of dimer and antioxidants which had been added.

SEPARATION OF COMPONENTS OF THE PYROLYSIS LIQUORS

Laboratory investigations (2) of the pyrolysis liquors served to establish which of the pyrolytic intermediates and by-products were capable of yielding butadiene on repyrolysis so that, by examination of the analytical data, it was possible to predict the potential yield of butadiene from the original diacetate. Pilot-plant data indicated that the highest cumulative yields were obtained under conditions giving the highest first-pass yields. Examination of numerous pyrolysis data from runs under these conditions showed that the formation of nonbutadiene-yielding by-

products averaged 10 to 12%. Therefore, the indicated maximum butadiene yield was 88 to 90% of theoretical.

The best means of obtaining the additional butadiene, available on repyrolysis of the intermediates in the pyrolysis liquors, was considered from several angles. Since these liquors consisted of about 85% acetic acid, repyrolysis would involve the handling of large volumes of material in order to produce an additional 5 to 6% of butadiene. A pyrolysis chamber nearly equal in size to that used for the initial diacetate pyrolysis would be required if this second stage were to be run separately. Direct recycling of the total liquors to the diacetate feed was not desirable for two reasons: First, the pyrolysis chamber would have to be much larger to accommodate the greater volume of materials handled. Second, pyrolysis of the nonbutadiene-yielding components had shown that these materials gave some breakdown products which were not readily separable from butadiene. For these reasons it seemed desirable to separate the intermediates from the bulk of the acetic acid and then repyrolyze these materials in an auxiliary unit.

BATCH SEPARATION. It had been found (2) that the intermediates, by-products, and acetic acid of the pyrolysis liquors could be separated if some water, not to exceed 25% of their weight, was added to these liquors, and this mixture was distilled. Practically all of the nonacetic acid components boiling below 150° C. could be removed as water azeotropes. Under the conditions of batch operation, in which the water was added to the liquors and distillation carried to a point where the distillate no longer separated into two layers, the still residues consisted of about 85% acetic acid, 3–5% of the high boiling materials, and 10–12% water. The distillate from this operation separated into water and oil layers. The oil layer was dried by distillation of its azeotrope to a decanter which continuously removed water from the system. The dried oil comprised a mixture of free methyl ethyl ketone, methyl ethyl ketone enol-acetate, methyl vinyl carbinol acetate, crotyl acetate, steam volatile hydrocarbons, and less than 10% acetic acid.

Under batch stripping conditions, about 20% of the methyl ethyl ketone enol-acetate present in the original pyrolysis liquors was hydrolyzed. The bulk of the butadiene-yielding acetates was recovered unchanged. This method was used for the recovery of the unsaturated acetates in most of the pilot-plant studies. The acetic acid residue was dehydrated by a batch-operated
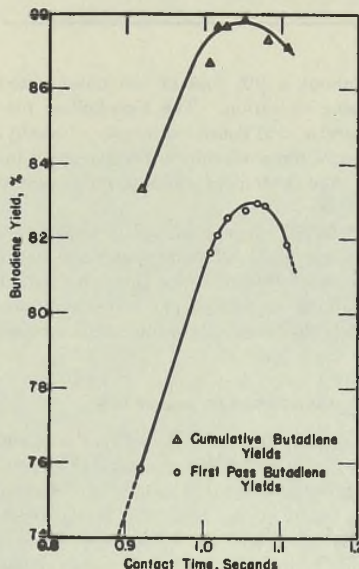

Figure 4. Effect of Contact Time on Butadiene Yield at 595° C.

(Spray-quench cooling system)

entrainer system, and then used for the esterification of glycol by the batch method described in another paper (*3*).

Laboratory distillations of the acetic acid residue from the stripping operation showed that it was readily fractionated into dilute acetic acid, a main cut of 98–100% acetic acid, and a residue of high-boiling materials.

On the basis of these results it appeared that the stripping operation provided a means for both the separation of repyrolyzable acetates from the acetic acid and the production of a readily rectifiable acetic acid. In addition to accomplishing the desired separation of the pyrolysis liquors, the stripping operation was found to be adaptable to continuous operation. This was confirmed in both the laboratory and the pilot plant.

CONTINUOUS SEPARATION. For pilot plant operations a copper column 6 inches in diameter and 5 feet high was constructed. It contained four bubble-cap plates at the top and sixteen perforated screen-covered plates. All plates were spaced about 3 inches apart. The pyrolysis liquors were pumped through a heat exchanger, which raised their temperature to 95–100° C., and were then introduced into the middle plate of the column. The decanter, attached to the condenser drain at the head of the column, was filled with water, and sufficient water was introduced into the column itself to fill the four bubble-cap plates at the top. The column was mounted on a 30-gallon kettle equipped with steam coils. In operation the liquors distilling up the column contacted the water in the upper section where the water-oil azeotropes were fractionated from the acetic acid. The distillate was condensed and run to a decanter which continuously returned the water layer to the top plate of the column and drained the oil layer to a receiver. The stripped acetic acid was removed from the base receiver. Table III shows the results obtained on a typical run in the pilot plant column.

TABLE III. SEPARATION OF ACETATES FROM PYROLYSIS LIQUORS BY AZEOTROPIC STRIPPING

Component	Wt. of Components in Feed and Products, Lb.			
	Pyrolysis liquor feed	Unsatd. acetate fraction	Acetic acid residues	Recovery, %
Acetic acid	36.35	0.33	36.2	100.4
Unsatd. acetates	4.96	4.023	0.80	96.8
Free methyl ethyl ketone	0.499	0.487	0.00	97.6
Diacetate	0.256	0.041	0.215	100.0

These results indicate about a 3% loss of the unsaturated acetates during the stripping operation. The high-boiling material left in the stripped acetic acid consisted largely of methyl acetyl acetone. The material removed during the stripping included essentially all of the butadiene-yielding unsaturated acetates.

The pilot-plant column was not efficient enough to produce an anhydrous acetic acid solution of high-boiling materials as the base product. Fractionation of this material through another column gave a first cut of dilute acetic acid and a main fraction of 98–100% acetic acid. All other materials in this mixture boiled above 150° C.

PYROLYSIS OF UNSATURATED ACETATES

Separation of the butadiene-yielding methyl vinyl carbinol and crotyl acetates from the methyl ethyl ketone enol-acetate by fractional distillation of the mixture separated from the diacetate pyrolysis liquors had been found impractical (*2*). It was desirable, however, to distill the mixed acetates before repyrolysis in order to remove components boiling above 140° C. which caused coke deposition in the pyrolysis chamber.

The pyrolysis of these mixed unsaturated acetates was studied in both the laboratory and pilot plant. In general, the tempera-

ture–contact time relations were found to be less critical than for the diacetate pyrolysis, and a much higher proportion of noncondensable gases was produced. Pyrolyses conducted at 595° C. and a contact time of 0.6 second, followed by two recycles of the liquors, resulted in an 84.4% conversion of the methyl vinyl carbinol–crotyl acetates fraction to butadiene and an 87% acetic acid recovery.

By applying the conversion value of 84.4% to the methyl vinyl carbinol–crotyl acetates, produced in the diacetate pyrolyses shown in Table II, the over-all butadiene yields may be calculated. These cumulative yields (last column) average about 88% for these runs in which the diacetate was pyrolyzed under optimum conditions. The upper curve in Figure 4 illustrates these cumulative yields.

The butadiene produced by pyrolysis of the mixed unsaturated acetates was only 85% pure. Since the effect of these impurities on the polymerization characteristics of the butadiene was not known, the pilot plant pyrolysis of these recovered acetates was conducted as a separate operation. Although the amount of butadiene thus obtained represents only 5–6% of the total from the initial diacetate, it seemed desirable to purify it separately, rather than to contaminate the 99+% pure product from the diacetate pyrolysis. Fractional distillation gave a main cut of over 90% purity so that the purity of the composite butadiene would be reduced by less than 0.5%.

The 13% loss of acetic acid, incurred during the pyrolysis of the recovered acetates, does not seriously affect the acid recovery on the basis of the over-all process. Since only 3% of the total acetic acid is involved in this operation, the loss amounts to 0.4% of that in process.

RECOVERY OF BY-PRODUCTS FROM HIGH-BOILING RESIDUES

The high-boiling residues left on distillation of the stripped acetic acid and those from the rectification of the acetate mixture from the stripping operation consisted mainly of polymeric tars, methyl acetyl acetone, and small amounts of unpyrolyzed glycol diacetate. The methyl acetyl acetone and the diacetate may be separated from the tars by steam stripping the residues, or the greater portion may be recovered by distillation under reduced pressure. The amount of diacetate recoverable from these residues is so small that it is doubtful if a recovery operation is justified. The methyl acetyl acetone is more readily recoverable and may be of value, although its utility has not been established. Both of these materials may be hydrolyzed with alkali and the acetic acid recovered from the hydrolysis mixture on acidification. Under these conditions methyl acetyl acetone yields acetic acid and methyl ethyl ketone. Unless more useful outlets can be found for methyl acetyl acetone, hydrolysis for purposes of acetic acid recovery may be the most economical means of disposal. The small amount of glycol diacetate may be directly recovered and returned to pyrolysis, or it may be hydrolyzed and the acidified hydrolysis residue combined with fermentation beers prior to concentration and glycol recovery.

All of the important steps of the pyrolysis and recovery operations discussed here have been conducted on a semiplant scale in standard equipment by the research and pilot-plant engineering staff of Joseph E. Seagram & Sons, Inc. (*1*). These operations gave satisfactory results, and there is every indication that the yields and recoveries obtained in the small scale plant can be duplicated in plant-size equipment.

PROPOSED CONTINUOUS PROCESS

On the basis of the results presented in this and the paper on esterification (*3*), the over-all process for butadiene from 2,3-butylene glycol may be summarized as follows:

The glycol is acetylated in a column which functions as a continuous countercurrent reactor. The bulk of the excess of the acetic acid used, of the water formed, and of the methyl ethyl ketone produced during this operation pass as vapors to a de-

TABLE IV. MATERIALS BALANCE FOR CONVERSION OF 2,3-BUTYLENE GLYCOL TO 1,3-BUTADIENE

	Pounds	Mol. Wt.	Moles	Moles per Mole	Parts per Part	% Yield Based on Glycol	% Recovered as Such
Materials charged							
2,3-Butylene glycol	195.16	90.1	2.166	1.00	1.00	...	...
Acetic acid	519.84	60.0	8.664	4.00	2.665	...	...
Sulfuric acid	3.46	98.1	0.0358	0.0163	0.0077	...	...
Products and recoveries							
1,3-Butadiene	100.0	54.08	1.849	0.854	0.512	85.40	...
Acetic acid	517.39	60.00	8.623	3.98	2.651	...	99.5
Methyl ethyl ketone	17.54	72.1	0.244	0.1124	0.0898	11.24	...
Hydrocarbons and tars	2.20	(54.1)$_x$	0.0407	0.0188	0.0113	1.88	...
2,3-Butylene glycol (as diacetate)	1.83	174.1	0.0105	0.005	0.005	...	0.50
Noncondensable gases	2.87	...	...	...	0.0078^a	...	...

^{a} Parts by weight of noncondensable gases per part of glycol diacetate pyrolyzed. These gases arise from both glycol and acetic acid, and yield percentages are not easily expressed.

hydration column in which the water and methyl ethyl ketone are removed by an entrainer system. The methyl ethyl ketone is recovered from the entrainer by fractionation. The anhydrous acetic acid is recycled to the esterification column. The mixture of diacetate, acetic acid, and sulfuric acid esters from the base of the esterification column is vacuum-distilled and the sulfuric acid esters, left as residue, are recycled as acetylation catalyst. The vacuum distillate is fractionated, the acetic acid is returned to the esterification column, and the glycol diacetate is run to the pyrolysis unit. The yield of diacetate is 97%, the conversion of glycol to methyl ethyl ketone is 3%, and the acetic acid recovery is quantitative.

The glycol diacetate is pyrolyzed at 595° C. at a contact time of 1.06 seconds. The butadiene is separated from the pyrolysis liquors, washed with water, dried, compressed, and condensed for storage. This butadiene is 99+% pure, and the yield at this point is 83% based on diacetate. The pyrolysis liquors are run to a stripping column where they are contacted with water, and the unsaturated acetate components and methyl ethyl ketone are distilled as mixed azeotropes with water. These azeotropes, which separate on condensation, are run to a decanter from which the water layer returns to the column. The oil layer is fractionally distilled to remove the methyl ethyl ketone and then dried by distillation of its water azeotropes to a decanter which returns the water to the original "stripping" column. The dried oils are then distilled to remove impurities boiling above 140° C., and are run to a second small pyrolysis unit. By controlling the water balance in the pyrolysis-liquor stripping column, the base product consists of an acetic acid solution of pyrolysis by-products boiling above 150° C. This solution is run to a still from which the distillate of essentially pure acetic acid is returned to the esterification system. The high-boiling by-products obtained as

residue from this operation consist largely of methyl acetyl acetone and a small amount of unpyrolyzed diacetate. This residue is combined with the high-boiling residues from the oils distillation and run to by-product recovery.

The distilled oils from the stripping operation, consisting of a mixture of methyl vinyl carbinol acetate, crotyl acetate, and methyl ethyl ketone enol-acetate (2-acetoxy-2-butene), are pyrolyzed at 595° C. and a contact time of 0.6 second. The butadiene is separated from the pyrolysis liquors, washed with water, dried, compressed, and fractionated to remove high- and low-boiling impurities. The purified butadiene is condensed and combined with the main product from the diacetate pyrolysis. The butadiene obtained in this operation amounts to 5% of the total, and the over-all yield from glycol diacetate is 88% of the theoretical. The pyrolysis liquor from this operation is combined with the liquors from the main pyrolysis and run to the stripping column.

The high-boiling by-products from distillation of the oils and the acetic acid still are steam-stripped to separate methyl acetyl acetone and diacetate from the tars. The water-insoluble portion of the distillate is dried and fractionally distilled, the recovered diacetate returned to the pyrolysis unit, and the methyl acetyl acetone either run to storage or hydrolyzed to methyl ethyl ketone and acetic acid.

Table IV shows the over-all materials balance of the process, in which the materials charged are those required for the production of 100 pounds of butadiene. Under products and recoveries, it is assumed that the methyl acetyl acetone will be hydrolyzed and the methyl ethyl ketone and acetic acid recovered.

LITERATURE CITED

(1) Callaham, J. R., *Chem. & Met. Eng.*, **51**, 94 (1944).
(2) Morell, S. A., Geller, H. H., and Lathrop, E. C., IND. ENG. CHEM., **37**, 877 (1945).
(3) Schniepp, L. E., Dunning, J. W., and Lathrop, E. C., *Ibid*, **37**, 872 (1945).
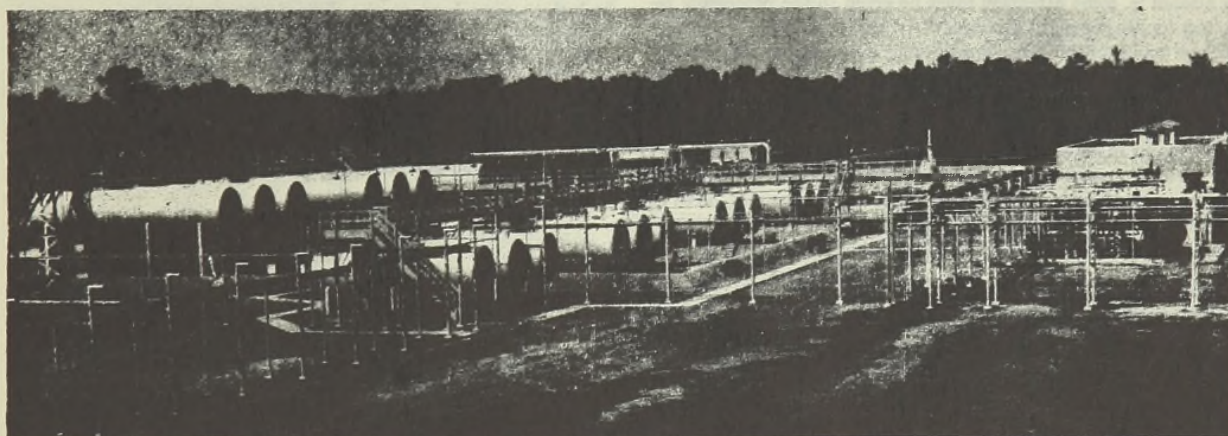
Tank Farm for Storing Butadiene and Styrene at a Synthetic Rubber Plant Operated for the Government by The Firestone Tire & Rubber Company at Lake Charles, La.

LIQUID-LIQUID EXTRACTION DATA

Systems Used in Butadiene Manufacture from Butylene Glycol[1]

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A promising source of butadiene is the pyrolysis of the diacetate of 2,3-butylene glycol. This diol comes from the fermentation of grain or molasses and may be recovered by extraction of the fermentation liquors. Various ternary liquid systems were investigated, including the diol, water, and individual solvents which might be suitable, such as butyl alcohol, butyl acetate, butylene glycol diacetate, and methyl vinyl carbinol acetate. Data were obtained for the ternary diagrams, distribution curves, and related plots, as well as for small-scale extractions at room and higher temperatures. This experimental work allowed the evaluation of respective advantages of the solvents and the desirable operating temperatures; it also formed a background for the selection and comparison of processes and the design of equipment for extraction and related steps in the large-scale manufacture of the diol, the diacetate, or butadiene, depending on which is desired as the end product.

METHODS for the production of butadiene have assumed tremendous importance. The pyrolysis of 2,3-butylene glycol diacetate gives excellent yields of butadiene in higher concentration than do other methods. 2,3-Butylene glycol is first made by the fermentation of carbohydrates (1). After separation from the fermentation liquors, the diol is esterified with acetic acid to give the diacetate, which is pyrolyzed to butadiene. (Both the diol and the diol diacetate may be removed and used for other purposes, some of which appear to have commercial possibilities.)

Since the fermented liquors contain only a few per cent of the diol along with various other materials which cause difficulty in separation, and since the diol has a much higher boiling point than that of water and therefore may not be distilled out directly as alcohol is, some attention must be given to the processing required for its recovery. Extraction from the fermentation liquors by a suitable solvent seemed to be a possible method. Furthermore, a suitable solvent extraction should leave the water-soluble impurities, such as proteins, sugars, etc., behind in the water.

Normally in an extracting operation it is most economical to work with the most dilute liquor directly; but in the present case the fermented liquors, after being exhausted of the diol, have to be evaporated substantially to dryness in order to obtain the residual food values as a stock food. Hence it is possible to con-

centrate partially by evaporation prior to the extraction operation without increasing the over-all heat cost. Thus, there is a much lower amount of solvent to be handled in the extraction step.

It is difficult to select a solvent which will choose the diol in preference to water. Few solvents will select and remove an alcohol from water, especially a dihydroxy alcohol such as glycerol or the glycols. A suitable solvent would contain oxygen, and one of the first tried was the lowest alcohol not completely miscible with water—i.e., butyl alcohol. Butyl acetate was also considered because of its possible subsequent use as an entrainer in the removal of water from the acetic acid mixture (2, 3) present in the esterification of the diol, and because of the desire to minimize the number of solvents to be added to the system. 2,3-Butylene glycol diacetate was studied because of its close structural relation to the diol, and also because it is desired as a result of acetylation of the diol. If this ester could be used, it would be possible to operate the system without an extraneous material as solvent, provided the esterification step could be operated satisfactorily in the presence of the large excess of ester which would be present in the extract. Methyl vinyl carbinol acetate, a by-product of the process, was also studied.

METHODS AND DATA

Butyl alcohol and butyl acetate were carefully fractionated from commercial materials. *meso*-2,3-butylene glycol was obtained from Schenley Research Institute, and 2,3-butylene glycol diacetate was prepared from it. Both were fractionated to give materials boiling within 1° C. of the boiling points.

Methyl vinyl carbinol acetate (MVCA) was made from methyl vinyl carbinol obtained from Shell Development Company. The alcohol was refluxed with a slight excess of acetic anhydride for 1 to 2 hours, washed with water, dried with calcium chloride, and purified by distillation. The purified MVCA distilled at 112–113° C.

Ternary systems were obtained by methods previously described for determining mutual solubility curves (5, 7). The solutions were kept at the desired temperature by a constant-temperature water bath. The indirect or synthetic method previously described (7) for taking distribution data was used.

Solubilities are indicated in Tables I and II and Figure 1 for ternary systems containing the four solvents studied. Water and diol were the other two components in each case. Distribution data were determined by methods previously described and are shown in Table III and Figure 2. The following legend applies to the numbered curves of Figures 1 to 4:

Curve	Solvent	Temp., ° C.
1	Butyl alcohol	26
2	Butyl acetate	26
3	Butylene glycol diacetate	26
4	M.V.C.A.	26
1A	Butyl alcohol	50
2A	Butyl acetate	50
3A	Butylene diacetate	50
4A	M.V.C.A.	50
3B	Butylene glycol diacetate	75
4B	M.V.C.A.	75

Butyl alcohol has excellent extractive properties at both temperatures; but the mutual miscibility of the components, especially at higher temperatures, detracts from its usefulness. Butyl acetate has poor extractive powers as shown by the distribution
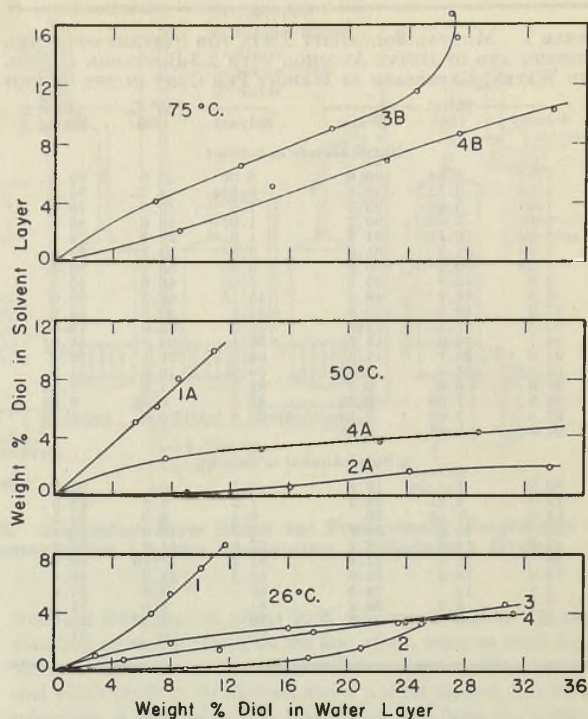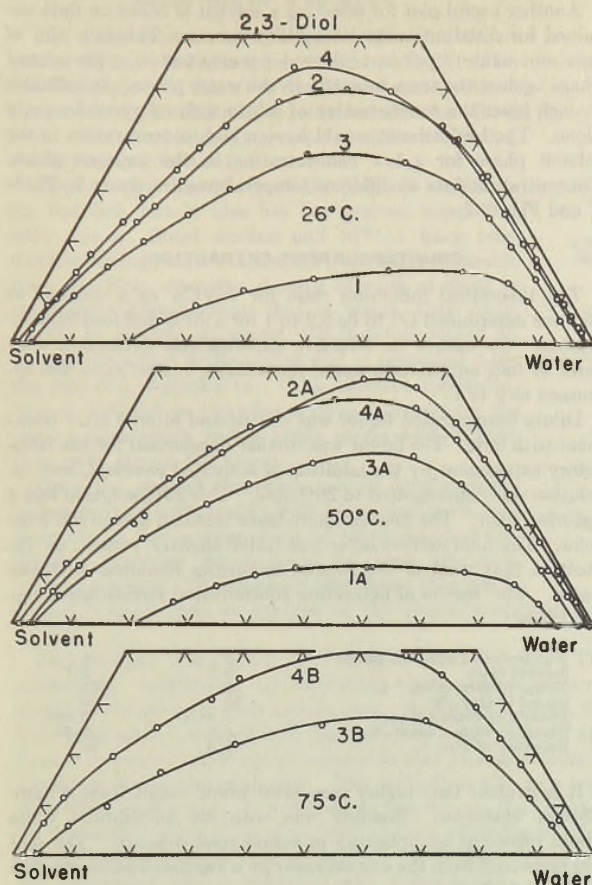
Figure 1(*Left*). Mutual Solubility Curves for Systems of
2,3-Butylene Glycol, Water, and Solvent

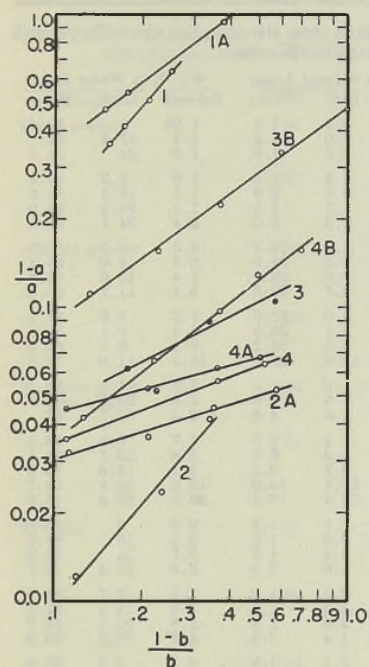Figure 2 (*Above*). Distribution of 2,3-Butylene Glycol
between Water and Solvent

Figure 3. Logarithmic Plot (*6*) of
$(1 - a)/a$ against $(1 - b)/b$ for
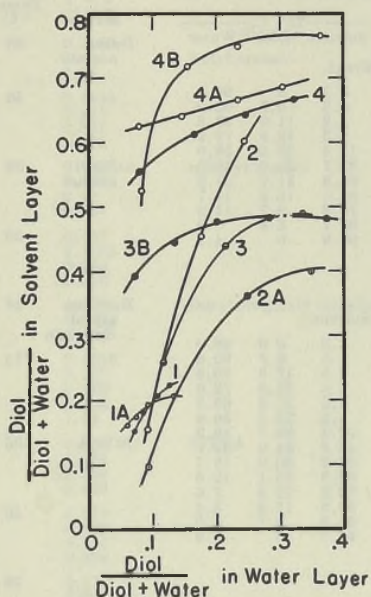Systems of 2,3-Butylene Glycol,
Water, and Solvent

Figure 4. Effective Concentration
in Systems of 2,3-Butylene Glycol,
Water, and Solvent

curves. With 2,3-butylene glycol diacetate as solvent the set-
tling rate of the two phases at 50° C. was very slow, and it did
not seem worth while to obtain the distribution data at this tem-
perature. At 26° C. the solvent layer
is the lower layer, but at 75° C. the
solvent layer is the upper layer. The
transition occurs at about 40° C. At
25° C. the settling rate is also very
slow. At 75° C., however, the two
layers form almost immediately.
MVCA had good extractive powers
at 75° C., and is immiscible with water
even in the presence of the diol.

TIE LINES AND CONCENTRATION
CURVES

The tie lines in a ternary solubility
system are useful in determining the
distribution of the solute between two
conjugate phases, the amount of sol-
vent required for a given extraction,
and the number of equilibrium units
required. Considerable data are re-
quired for plotting the lines for the
entire range of concentrations, as inter-
polation between adjacent tie lines is
difficult.

Previously, however, it was shown
(*6*) that a straight line results from
a logarithmic plot of $(1-a)/a$ against
$(1-b)/b$ where a is the fraction of sol-
vent in the solvent phase and b is
the fraction of diluent in the diluent
phase. This plot applies even to those

TABLE I. MUTUAL SOLUBILITY DATA FOR SYSTEMS OF BUTYL ACETATE AND OF BUTYL ALCOHOL WITH 2,3-BUTYLENE GLYCOL AND WATER, EXPRESSED AS WEIGHT PER CENT IN THE SYSTEM

	26° C.			50° C.	
Solvent	Diol	Water	Solvent	Diol	Water
		Butyl Acetate as Solvent			
1.01	2.34	96.6	0.69	0.0	99.3
1.08	3.55	95.4	0.824	4.76	94.5
1.22	5.38	93.4	1.0	10.7	88.4
1.36	7.89	90.7	1.07	16.6	82.3
1.78	16.45	81.6	1.6	25.5	72.6
1.99	32.9	65.3	2.3	32.7	65.0
3.22	40.0	56.7	3.85	39.7	56.3
4.6	42.5	52.8	7.06	46.6	46.3
6.8	44.2	48.8	15.15	48.3	36.6
17.2	49.8	32.9	34.8	40.3	25.9
30.3	47.1	22.7	46.9	33.9	19.45
54.7	31.6	13.7	56.4	28.5	15.0
61.8	26.7	11.5	66.5	21.1	12.4
66.3	23.8	9.95	69.0	19.9	11.2
87.6	8.8	3.5	82.3	11.8	5.88
89.9	7.09	2.72	89.8	6.52	3.86
92.5	5.09	2.52	96.8	0.0	3.19
94.9	2.86	2.18			
		n-Butyl Alcohol as Solvent			
80.2	0	19.8	6.1	0	93.9
72.4	4.51	23.2	7.2	4.4	88.5
64.8	7.25	28	9.4	8.3	82.5
55	10.3	34.7	16.7	10.9	72.4
41.7	12.4	45.8	33.6	11.2	55.2
28	14.5	57.5	31.4	11.75	56.7
15.4	14.2	70.5	45.3	11.3	43.4
8.7	12	79.5	53	9.9	36.9
7.2	8.4	84.4	61	7.6	31.2
6.5	0	93.5	70	4.35	25.6
			79	0	21

systems in which there is considerable miscibility of solvent and diluent phases; only two experimentally determined points are required to establish the tie line or distribution curve. The experimental data are calculated in Table IV, and Figure 3 shows that they correlate well by this method. Any number of tie lines may be determined from Figure 3 by picking off points on the straight lines, and then calculating the terminal points of corresponding tie lines.

Another useful plot for selecting a solvent is based on data obtained for distribution and solubility curves. This is a plot of (per cent solute)/(per cent solute + per cent water) in the solvent phase against the same quantity in the water phase. It indicates in each layer the concentration of solute with reference to water alone. The best solvent would have a high concentration in the solvent phase for a low concentration in the aqueous phase. Concentration data at different temperatures are shown in Table V and Figure 4.

COUNTERCURRENT EXTRACTION

The theoretical minimum ratio for MVCA as a solvent at 75° was determined (7) to be 3.2 to 1 for a 20% diol feed concentration. To ensure an effective experimental extraction with three or four equilibrium units, the solvent to feed ratio was increased to 5 to 1.

Dilute fermentation liquor was heated and filtered after treatment with lime. The liquor was further decolorized for the laboratory experiment by the addition of activated charcoal, and the solution was concentrated to 20% diol. This 20% solution had a red wine color. The final raffinate layer also had a deep red wine color. The final extract layer was tinted slightly yellow, an indication that most of the colored impurities remained with the water. The results of extracting concentrated fermentation liquor follow:

Number of equilibrium units	3	4
Solvent ratio	5:1	5:1
Temp. of extraction, ° C.	75	75
Glycol in feed, %	20	20
Density of extract layer	0.8415	0.842
Glycol in extract layer, %	2.6	2.86
Recovery of diol, %	84.5	96

It is evident that higher recoveries would result from a more efficient extractor. Possibly one with six equilibrium units would represent an optimum in commercial practice. The diol was recovered from the extract layer by a vacuum distillation and analyzed 94% pure diol.

TABLE II. MUTUAL SOLUBILITY DATA FOR SYSTEMS OF BUTYLENE GLYCOL DIACETATE AND OF MVCA WITH BUTYLENE GLYCOL AND WATER EXPRESSED AS WEIGHT PER CENT IN SYSTEM

	26° C.			50° C.			75° C.	
Solvent	Diol	Water	Solvent	Diol	Water	Solvent	Diol	Water
				Butylene Glycol Diacetate as Solvent				
3.62	0	96.3	2.87	0	97.2	3.7	0	96.4
3.77	4.62	91.7	3.49	5.73	90.8	4.3	5.7	90.0
3.86	12.6	83.5	3.83	10.76	85.5	5.2	11.0	83.8
4.69	19.15	76.1	5.05	19.1	75.8	8.3	18.8	72.9
5.37	24.7	69.8	8.70	27.9	63.3	15.4	26.5	58.0
7.59	30.9	61.4	14.2	33.1	52.6	33.7	25.6	40.6
14.9	35.2	50	32.2	31.8	36.0	50.8	21.9	27.3
30.4	37.1	32.4	45.2	27.7	27.0	66.1	16.2	17.7
47.2	30	22.9	54.6	23.4	21.9	78.8	9.7	11.5
57	25	18	69.0	16.9	14.2	87.7	5.4	6.9
67.2	19.75	13.1	81.6	10.0	8.24	95.9	0	4.1
76.3	14.95	9.04	89.0	5.46	5.53			
84.5	9.1	6.41	96.6	0	3.4			
96.3	0	3.7						
				Methyl Vinyl Carbinol Acetate as Solvent				
1.32	0	98.68	0.8	0	99.2	2.0	0.0	98.0
1.85	4.71	93.6	1.6	5.8	92.5	2.5	6.7	90.8
1.99	8.99	89.2	2.3	10.9	86.6	3.5	17.8	78.6
2.22	15	82.7	3.5	19.4	77.1	4.6	22.8	72.6
2.44	19.65	78	3.9	29.4	66.7	5.3	29.0	65.7
2.64	25.4	72	5.2	36.7	58.2	8.2	35.5	56.4
3	32.5	64.5	9.1	42.6	48.4	12.4	39.5	48.2
4.01	39.7	56.3	22.6	44.0	33.5	43.4	34.9	22.7
5.75	44.8	49.4	38.4	38.9	21.9	50.3	30.6	19.1
10.4	49.1	40.7	48.7	34.3	17.0	62.3	25.1	12.6
24.1	54.4	21.6	58.3	28.7	13.0	72.9	19.5	7.6
41.9	42.5	15.6	70.9	20.2	7.9	85.2	11.4	3.4
48.3	38.1	13.5	84.5	11.9	3.5	91.2	6.1	2.8
54.5	33.7	11.6	91.1	6.4	2.5	98.1	0	1.9
63	28.4	8.8	98.9	0	1.1			
68.8	23.2	7.3						
77.3	17.4	5.19						
81.5	13.8	4.64						
85.5	9.63	4.59						
92.2	5.2	2.57						
99.0	0	1.0						

TABLE III. TIE LINE DATA FOR SYSTEM SOLVENT–BUTYLENE GLYCOL–WATER

Solvent	Temp., ° C.	Wt. % in Solvent Layer			Wt. % in Water Layer		
		Solvent	Diol	Water	Solvent	Diol	Water
Butyl acetate	26	98.8	0.2	1.1	1.05	9	89.4
		97.7	1.0	1.2	1.4	17.4	81
		96.0	2.7	1.8	1.6	24	74.6
	50	96.9	0.3	2.8	1.0	9.2	89.4
		96.5	0.6	2.9	1.1	16.3	82.6
		95.3	1.7	3.0	1.5	24.5	74.0
		95.0	2.0	3.0	2.4	34.1	63.5
n-Butyl alcohol	26	73.5	4.0	22.5	6.5	6.7	86.8
		70.8	5.3	24.0	6.7	8.0	85.3
		66.3	7.0	26.7	7.4	10.0	82.6
		61.0	8.7	30.3	8.1	11.7	80.2
	50	68.0	5.0	27.0	7.2	5.6	87.2
		65.0	6.1	28.9	7.9	7.1	85.0
		58.8	8.0	33.2	9.2	8.5	82.3
		51.5	10.0	38.5	16.5	11.0	72.5
Butylene glycol diacetate	26	94.1	1.5	4.3	3.8	11.3	85
		91.8	3.6	4.6	4.8	20.5	74.7
		90.6	4.6	4.8	8.3	30.7	61
	75	90.1	3.9	6.0	4.7	6.9	88.4
		86.5	6.0	7.5	5.8	12.7	81.5
		81.8	8.7	9.5	8.2	18.8	73.0
		74.8	12.4	13.0	12.4	24.9	62.7
		65.0	16.8	18.2	28.2	26.8	45.0
MVCA	26	96.6	1.9	1.5	2.0	8	90.0
		95.1	3.0	1.9	2.2	16	81.8
		94.7	3.4	1.9	2.7	24	73.3
		94.0	4.0	2.0	3.0	31.3	65.7
	50	95.7	2.7	1.6	2.3	7.7	90.0
		95.0	3.2	1.8	3.0	14.3	82.7
		94.2	3.8	1.9	3.8	22.5	73.7
		93.7	4.4	2.0	4.5	29.2	66.3
	75	96.0	2.1	1.9	2.7	8.5	88.8
		93.8	5.1	2.0	3.2	14.8	82.0
		91.2	6.6	2.2	4.3	22.5	73.2
		88.6	8.7	2.7	5.6	27.4	67.0
		86.5	10.3	3.2	7.2	33.8	59.0

SELECTION OF A SOLVENT

The three solvents other than butyl acetate appeared to have individual advantages at 75° C. The finished acetic acid diester is the desired end point of the processing, and it, in turn, is converted to butadiene later. Hence, an esterifying step is required following the separation of the diol.

Butyl alcohol has the best distribution coefficient for the diol, but it also has the greatest miscibility with water. Butyl alcohol and MVCA have relatively low boiling points which make them easily separable from the diol; since the density of each of them is reasonably different from that of water, they settle readily in gravity extractors. 2,3-Butylene glycol diacetate has a high boiling point and is separated from the diol with difficulty (4). The effective concentration of the diol in the solvent layer is greater for the same concentration in the water layers with MVCA than with any of the others.

Since the goal of this work was to develop plant processes from comparative pilot plant studies, it was desirable to find combinations of extraction and distillation processes which could be used for each of these solvents. The proposed flow sheets (Figures 5, 6, and 7) result from an analysis of the characteristics of each solvent.

PRELIMINARY TREATMENT OF FERMENTATION LIQUORS. The preliminary treatment, concentration, and alcohol removal would be the same for each solvent used. As Figure 5 shows, the fermented mash is treated with lime (pH 8.0 – 8.5), heated, and filtered to remove solids and proteins that may promote emulsion formation during the extraction. The mash then goes to a multiple-effect evaporator. It is desired to concentrate the liquid as far as possible without loss of diol and without otherwise interfering with the subsequent extraction. A triple-effect evaporator with backward feed is indicated with a concentrate discharge

C = Condenser
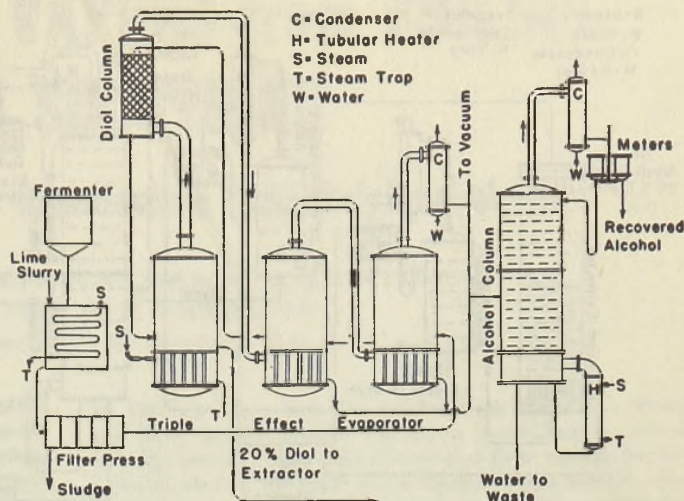H = Tubular Heater
S = Steam
T = Steam Trap
W = Water

Figure 5. Suggested Flow Sheet for Preliminary Treatment of Fermentation Liquors Containing 2,3-Butylene Glycol

from the first effect at about 20% diol concentration. A small distilling column is placed on the first effect, using as wash liquid the feed from the second effect. This column holds down any diol which tends to distill over, and is a short packed unit with a minimum of back pressure. The condensate from the three effects contains substantially all of the small amount of alcohol formed in the fermentation. It is combined from the three heating belts of the evaporator and passed to an alcohol concentrating unit, as suggested by Reich (8).

BUTYL ALCOHOL. The hot concentrated solution of approximately 20% diol (Figure 6) is sent in counterflow in a continuous liquid extractor, at about 70° C., to the n-butyl alcohol used as

TABLE IV. CALCULATIONS FOR TIE LINE CORRELATION FOR SYSTEM SOLVENT–BUTYLENE GLYCOL–WATER

Solvent	Temp., ° C.	$\frac{1-a}{a}$	$\frac{1-b}{b}$
Butyl acetate	26	0.01215	0.1185
		0.0235	0.234
		0.0417	0.34
	50	0.032	0.1135
		0.036	0.211
		0.0452	0.351
		0.0527	0.575
n-Butyl alcohol	26	0.36	0.152
		0.413	0.1725
		0.509	0.21
		0.64	0.247
	50	0.472	0.147
		0.538	0.1765
		0.70	0.215
		0.943	0.378
Butylene glycol diacetate	26	0.0615	0.177
		0.0895	0.337
		0.104	0.565
	75	0.11	0.1315
		0.156	0.227
		0.224	0.370
		0.338	0.595
		0.538	1.22
MVCA	26	0.0352	0.111
		0.0515	0.222
		0.056	0.364
		0.0638	0.522
	50	0.045	0.111
		0.0527	0.209
		0.0616	0.357
		0.067	0.505
	75	0.0417	0.126
		0.0661	0.22
		0.0965	0.366
		0.1287	0.493
		0.156	0.695

TABLE V. CONCENTRATION CURVE DATA FOR SYSTEM SOLVENT–BUTYLENE GLYCOL–WATER

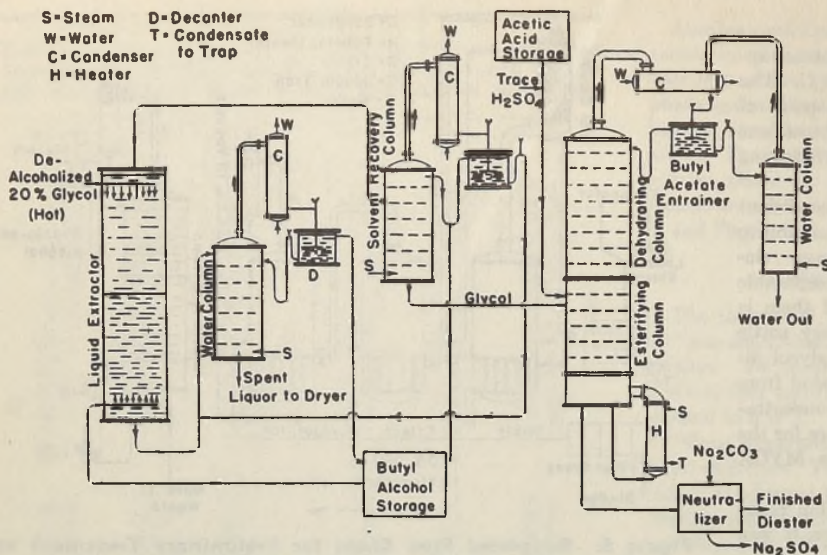|		$\left(\frac{\text{Wt. \% Diol}}{\text{Wt. \% Diol + Wt. \% Water}}\right)$	
Solvent	Temp., ° C.	Solvent layer	Water layer
Butyl acetate	26	0.154	0.0915
		0.455	0.177
		0.60	0.244
	50	0.0968	0.093
		0.362	0.249
		0.400	0.349
n-Butyl alcohol	26	0.151	0.0717
		0.181	0.0855
		0.207	0.108
		0.223	0.128
	50	0.161	0.0604
		0.174	0.074
		0.195	0.0937
		0.206	0.132
Butylene glycol diacetate	26	0.259	0.1175
		0.439	0.214
		0.49	0.335
	75	0.394	0.0724
		0.445	0.135
		0.478	0.201
		0.487	0.284
		0.48	0.374
MVCA	26	0.554	0.0815
		0.613	0.164
		0.642	0.247
		0.666	0.323
	50	0.628	0.0788
		0.64	0.1475
		0.666	0.234
		0.688	0.306
	75	0.525	0.0873
		0.719	0.153
		0.75	0.235
		0.764	0.291
		0.764	0.364

Figure 6. Suggested Flow Sheet for Process Using Butyl Alcohol as Solvent in Recovering 2,3-Butylene Glycol

extracting solvent. The resulting extract layer contains substantially all of the diol and considerable water (approximately 30% by weight). This is passed to the solvent recovery column which separates the butanol and water overhead in a steam distillation. Condensation is followed by decantation; and the top layer is divided, part to be recycled as solvent in the extractor and part to be refluxed in the distilling column, whereas the bottom layer is sent to a small water stripping column. The raffinate layer also passes to this water stripping column and is then evaporated for the recovery of solids as cattle feed.

The diol obtained as bottoms from the solvent recovery column is sent to the esterifying column. Acetic acid (containing a small amount of sulfuric acid as catalyst) is fed into the column at or near the feed plate in constant proportions to the glycol. A small amount of entrainer (butyl acetate, for example) cycles in the upper part of the system and separates itself automatically in the column from the other constituents, including acetic acid. The water formed in the esterification of butylene glycol is re-

moved in azeotropic distillation, as it would be in an acetic acid concentrating process (2, 3).

At the start of the operation, the lower part of the column (esterification section) is charged with excess acetic acid to expedite esterification. The excess would be maintained in this section of the column because of the relative boiling points of the constituents, and only the stoichiometric amount of acetic acid would be added continuously.

Butylene glycol is esterified fairly readily. The diacetate is withdrawn from the base, and the sulfuric acid is neutralized with sodium acetate. There is a small water column for exhausting the butyl acetate from the water discharged from the decanter of the distillation system.

BUTYLENE GLYCOL DIACETATE. The flow sheet for this process (Figure 7) is simpler and eliminates several auxiliary columns since an extracting solvent, extraneous to the system, is not added. Following evaporation and extraction, the extract layer goes directly to the dehydrating section of the continuous esterifying column where the small amount of dissolved water (8% by weight) is removed by an added entrainer, as before. As the diol flows downward through the esterifying section, it is acetylated and handled as in the previous case. The dissolved solvent in the raffinate layer (3–8% by weight) is removed in a small column by steam distillation.

METHYL VINYL CARBINOL ACETATE. MVCA is one of the by-products in subsequent processing of the diacetate; it would therefore be available as a solvent for the diol. It may be used as a water entraining agent in a distilling column where both the dehydrating and esterifying steps take place. Its flow sheet is otherwise generally similar to Figures 6 and 7. This solvent is almost mutually insoluble with water, which makes the solvent recovery column and the water column very small and minimizes heat consumption.

LITERATURE CITED

(1) Fulmer, E. I., and Werkman, C. H., *Proc. Iowa Acad. Sci.*, 36, 114 (1929).
(2) Othmer, D. F., *Chem. & Met. Eng.*, 48, 91 (June, 1941).
(3) Othmer, D. F., U. S. Patent 2,050,234 (Aug. 4, 1936).
(4) Othmer, D. F., Shlechter, N., and Koszalka, W. A., IND. ENG. CHEM., 37, 895 (1945).
(5) Othmer, D. F., and Tobias, P. E., *Ibid.*, 34, 690 (1942).
(6) *Ibid.*, 34, 693 (1942).
(7) Othmer, D. F., White, R. E., and Trueger, E., *Ibid.*, 33, 1240 (1941).
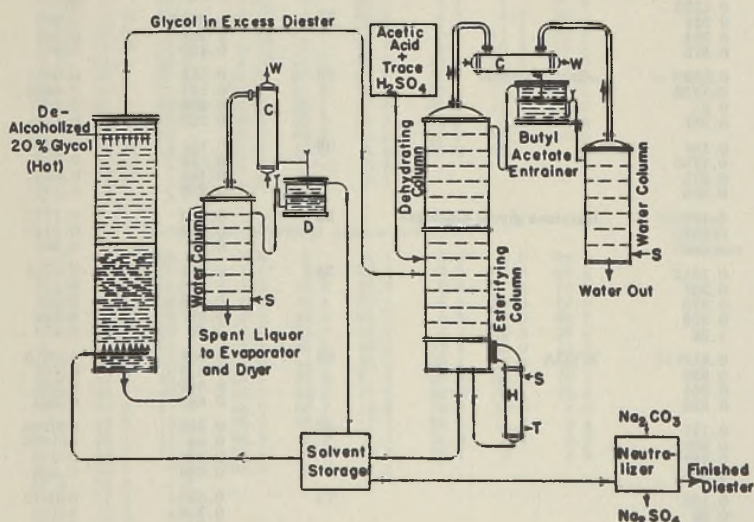(8) Reich, G. T., *Chem. & Met. Eng.*, 36, 716 (1929).

Figure 7. Suggested Flow Sheet for Process Using Butylene Glycol Diacetate as Solvent in Recovering 2,3-Butylene Glycol

COMPOSITION of VAPORS from BOILING BINARY SOLUTIONS

Systems Used in Butadiene Manufacture from Butylene Glycol

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Butylene glycol is studied as a source of butadiene for synthetic rubber manufacture. After a special fermentation of molasses or grain, extraction and distillation procedures are necessary for its subsequent recovery; then it is esterified to give the diacetate which, in turn, is pyrolyzed to give butadiene. In order to design the evaporating and distillation equipment required, vapor-liquid equilibrium relations were determined for the systems water–2,3-butylene glycol, acetic acid–2,3-butylene glycol diacetate, 2,3-butylene glycol–2,3-butylene glycol diacetate, methyl vinyl carbinol acetate–2,3-butylene glycol, and methyl vinyl carbinol acetate–acetic acid. These equilibrium data were determined at atmospheric and various subatmospheric pressures; and the data are correlated by methods previously suggested to make possible the evaluation of the several steps of the process and the design of the equipment involved.

IN 1930 Fulmer and Werkman (*1*) showed that 2,3-butylene glycol may be obtained by the fermentation of glucose. This diol has since been considered as the starting point for new plastics and has possibilities of being used as an antifreeze. In 1941 the diacetate of the diol became important as a possible source of butadiene for use in synthetic rubber manufacture; as compared with alcohol, in the pyrolysis of butadiene it gives comparatively small amounts of by-products which are readily separable. Various investigations were started on its production and conversion to butadiene.

The major steps are: (*a*) fermentation of carbohydrates (grain under present war conditions) to give liquors containing 3.5–5.5% of 2,3-diol; (*b*) recovery of the diol from fermentation liquors; (*c*) esterification of the diol to 2,3-butylene diacetate; (*d*) pyrolysis of the diacetate to butadiene; (*e*) separation of the butadiene from the other products of pyrolysis. In addition to the diol, the fermented liquors contain proteins, alcohols, polysaccharides, and other by-products of fermentation, as well as substantial amounts of suspended material resulting from dead bacteria and broken-down grain structures.

Attempted recovery of the diol, by steam distillation of filtered fermented liquor, to which has been added an excess of lime, showed that an over-all recovery of the diol of only a little over 90% could be effected. If the ferment liquor is not made basic and filtered, it is possible to obtain only a 50% recovery of the diol due to decomposition. These recoveries are not high enough for a successful commercial process. Operation is also difficult due to the precipitation of solid material, extreme foaming, and the very viscous bottoms obtained. Solvent extraction followed

by distillation as a means of recovering the diol from a filtered and limed ferment solution has shown possibilities in another investigation (*5*). This work showed that three solvents studied (*n*-butyl alcohol, butylene glycol diacetate, and methyl vinyl carbinol acetate) had desirable properties. In the esterification unit following the recovery steps, the water formed in the reaction, as well as any present with the diol, is removed in an azeotropic distillation with a suitable entrainer in the manner already described (*3*).

This work is part of a study of the recovery of 2,3-butylene glycol from fermented mash liquors. Vapor-liquid equilibria of various binary systems encountered in the distillation processes following the proposed extractions are considered in order to obtain data necessary for the comparison of these three processes and for the design and operation of final plants.

The system water–2,3-butylene glycol was studied under subatmospheric pressures and is of interest in the design of the preliminary evaporator. This unit concentrates the fermented liquor up to a strength where diol in appreciable quantities appears in the vapors or where the concentration of impurities in the liquor becomes high enough to interfere with the subsequent extraction. Since all the water in the ferment liquors is eventually removed, in order to recover the solids for fertilizer or cattle feed, no heat economy in the over-all process is to be effected by running an extraction directly on the dilute ferment liquors, as would be the case where the liquors were wasted. However, considerable saving will be expected in the extraction and distillation operation if a concentrated feed is used. This will mean a smaller extracting column and, more important, the use of considerably less solvent and lower heat costs in the subsequent distillations.

The system acetic acid–2,3-butylene glycol diacetate is of interest in the design of the esterification unit, since acetic acid
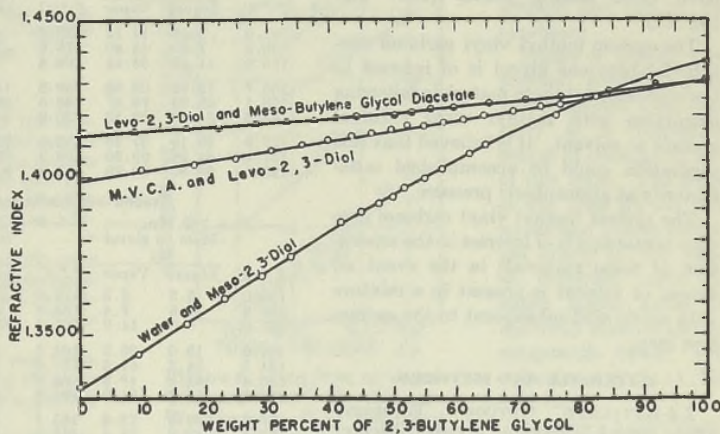

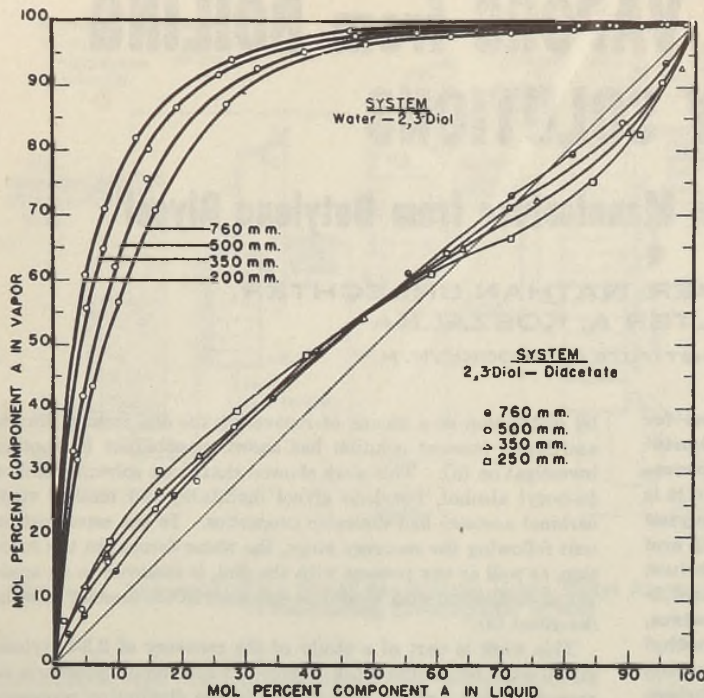**Figure 1. Refractive Indices for Three Systems**

Figure 2. Vapor-Liquid Compositions for Water–meso-2,3-Butylene Glycol and levo-2,3-Butylene Glycol–meso-2,3 Butylene Glycol Diacetate Systems

Component A is water in the upper section and levo-2,3 butylene glycol in the lower system

TABLE I. REFRACTIVE INDEX DATA

Water–meso-2,3-Butylene Glycol		levo-2,3-Butylene Glycol–meso-Butylene Glycol Diacetate	
Wt. % butylene glycol in soln.	Refractive index at 24° C.	Wt. % butylene glycol in soln.	Refractive index at 24° C.
0	1.3330	0	1.4130
9.21	1.3435	8.74	1.4140
17.01	1.3530	17.05	1.4150
23.63	1.3610	22.30	1.4155
29.12	1.3680	28.25	1.4165
33.60	1.3740	33.10	1.4170
38.26	1.3825	37.50	1.4175
41.90	1.3850	41.00	1.4185
45.01	1.3880	44.20	1.4190
47.75	1.3915	46.80	1.4195
49.86	1.3930	49.45	1.4200
50.00	1.3930	50.2	1.4195
51.97	1.3960	53.1	1.4200
55.03	1.3990	56.1	1.4210
57.90	1.4020	59.9	1.4215
62.15	1.4070	65.4	1.4230
64.90	1.4100	71.2	1.4240
70.52	1.4111	77.9	1.4255
76.10	1.4190	84.5	1.4270
82.53	1.4250	92.3	1.4290
91.13	1.4310	100	1.4300
100	1.4366		

Methyl Vinyl Carbinol Acetate–levo-2,3-Butylene Glycol		
Wt. % butylene glycol in soln.	Refractive index at 25° C.	Wt. % butylene glycol in soln.	Refractive index at 25° C.
0	1.3990	52.30	1.4155
9.92	1.4025	55.00	1.4160
18.19	1.4040	58.02	1.4168
24.96	1.4060	61.28	1.4178
30.77	1.4080	64.81	1.4190
35.61	1.4100	69.08	1.4205
39.82	1.4115	73.71	1.4220
43.42	1.4125	76.76	1.4230
46.74	1.4139	84.79	1.4260
49.70	1.4150	92.32	1.4285
52.40	1.4160	100	1.4310

and ester must be separated in the esterification still. This problem is complicated by the fact that butylene glycol diacetate tends to decompose when heated in the presence of mineral acids used for catalysts in the esterification. Therefore, data must be available for vacuum and hence, low-temperature distillation.

The system 2,3-butylene glycol–2,3-butylene glycol diacetate is also of interest in the design of the esterification unit. It is important to be able to separate any unreacted glycol in the column. The butylene glycol and the diacetate have close boiling points (180° and 192° C.).

The system methyl vinyl carbinol acetate–2,3-butylene glycol is of interest in the separation of these materials following extraction with methyl vinyl carbinol acetate as solvent; it is believed that this separation could be accomplished satisfactorily at atmospheric pressure.

The system methyl vinyl carbinol acetate–acetic acid is of interest in the separation of these materials in the event an excess of solvent is present in a mixture with acetic acid subsequent to the extraction step.

MATERIALS AND METHODS

2,3-BUTYLENE GLYCOL. Technical-grade meso-2,3-butylene glycol (Schenley Research Institute) consisted of 92% 2,3-diol and 8% impurities. The liquid was carefully rectified; and the dis-

TABLE II. VAPOR-LIQUID EQUILIBRIUM DATA

SYSTEM WATER–meso-2,3-BUTYLENE GLYCOL

P = 760 Mm.			P = 500 Mm.			P = 350 Mm.			P = 200 Mm.		
	Mole % water in:			Mole % water in:			Mole % water in:			Mole % water in:	
T ° C.	Liquid	Vapor	T ° C.	Liquid	Vapor	T ° C.	Liquid	Vapor	T ° C.	Liquid	Vapor
172.0	3.70	31.75	155.4	2.90	33.60	140.0	4.85	55.69	126.0	4.85	60.70
167.2	6.00	42.00	153.4	4.00	42.70	135.8	8.30	64.90	119.6	8.30	69.70
158.6	10.00	57.00	144.0	9.50	63.00	123.0	15.00	80.00	109.5	12.69	82.40
149.6	15.75	70.80	136.1	14.70	75.50	115.4	19.16	87.20	86.4	27.70	94.60
132.0	26.70	87.50	111.4	31.90	93.00	105.8	25.70	92.00	73.6	46.30	97.60
110.8	48.80	96.60	95.2	56.90	98.70	87.6	47.50	97.40	69.4	66.20	98.70
106.0	62.00	98.00	91.7	79.40	99.00	83.6	66.20	98.70	68.3	82.30	99.20
104.8	71.50	98.50	89.7	88.00	99.40	81.2	80.60	99.00	67.8	87.70	99.40
102.4	81.40	99.00	89.2	92.70	99.60	79.4	91.20	99.10	67.2	94.50	99.50

SYSTEM ACETIC ACID–meso-2,3-BUTYLENE GLYCOL DIACETATE

P = 760 Mm.			P = 500 Mm.			P = 300 Mm.			P = 150 Mm.		
	Mole % acid in:			Mole % acid in:			Mole % acid in:			Mole % acid in:	
T ° C.	Liquid	Vapor	T ° C.	Liquid	Vapor	T ° C.	Liquid	Vapor	T ° C.	Liquid	Vapor
191.0	2.16	14.12	177.6	1.15	9.03	157.5	2.79	16.48	137.8	0.37	2.65
180.5	7.66	43.40	173.6	2.67	21.26	153.5	5.61	30.96	136.1	1.65	16.53
175.2	11.28	55.43	168.4	7.16	37.89	145.0	10.15	55.32	129.2	6.71	48.39
166.7	13.99	68.60	159.8	13.80	59.85	139.6	14.32	65.77	119.3	13.32	70.59
158.1	23.03	76.87	138.5	29.85	86.89	119.6	35.25	89.86	106.4	26.41	86.13
145.8	34.13	89.58	120.9	54.85	96.69	113.3	45.50	93.59	98.8	36.72	91.72
127.9	69.19	97.49	112.6	70.49	98.52	103.9	63.65	97.10	85.5	61.50	96.92
121.4	84.96	99.20	109.3	79.80	98.80	94.3	82.56	99.08	81.3	71.49	98.26
120.0	90.86	99.70	106.8	84.98	99.15	89.9	96.95	99.52	75.2	89.36	99.17

SYSTEM levo-2,3-BUTYLENE GLYCOL–meso-BUTYLENE GLYCOL DIACETATE

| P = 760 Mm.			P = 500 Mm.			P = 350 Mm.			P = 250 Mm.		
	Mole % glycol in:			Mole % glycol in:			Mole % glycol in:			Mole % glycol in:	
T ° C.	Liquid	Vapor	T ° C.	Liquid	Vapor	T ° C.	Liquid	Vapor	T ° C.	Liquid	Vapor
193.0	2.5	4.5	172.0	8.5	24.0	165.2	8.0	17.0	153.8	1.0	6.5
189.8	4.8	7.4	168.5	22.2	28.5	158.9	16.0	27.0	150.6	8.5	19.0
187.0	9.6	14.0	167.2	28.0	37.0	163.9	48.0	54.0	148.0	16.2	30.0
184.0	19.0	26.0	164.7	61.0	64.0	153.0	64.0	65.0	145.8	28.5	49.5
181.5	34.2	41.5	164.6	71.0	71.0	153.0	70.0	68.8	144.4	39.5	48.0
180.4	41.0	48.8	164.6	77.0	75.0	153.1	75.5	72.5	143.5	58.5	61.0
178.6	55.0	61.0	164.8	83.0	79.0	153.2	80.5	75.0	143.5	71.5	66.5
177.6	71.3	73.0	165.1	89.0	84.5	153.7	90.0	83.0	143.8	80.5	72.5
177.6	80.8	79.5	165.2	92.5	87.5	154.0	93.3	87.5	144.0	84.0	75.0
177.7	95.5	93.8	165.4	95.0	90.5	154.5	98.0	93.0	144.5	91.5	82.5
179.0	100.0	100.0	165.8	100.0	100.0	154.8	100.0	100.0	145.0	100.0	100.0
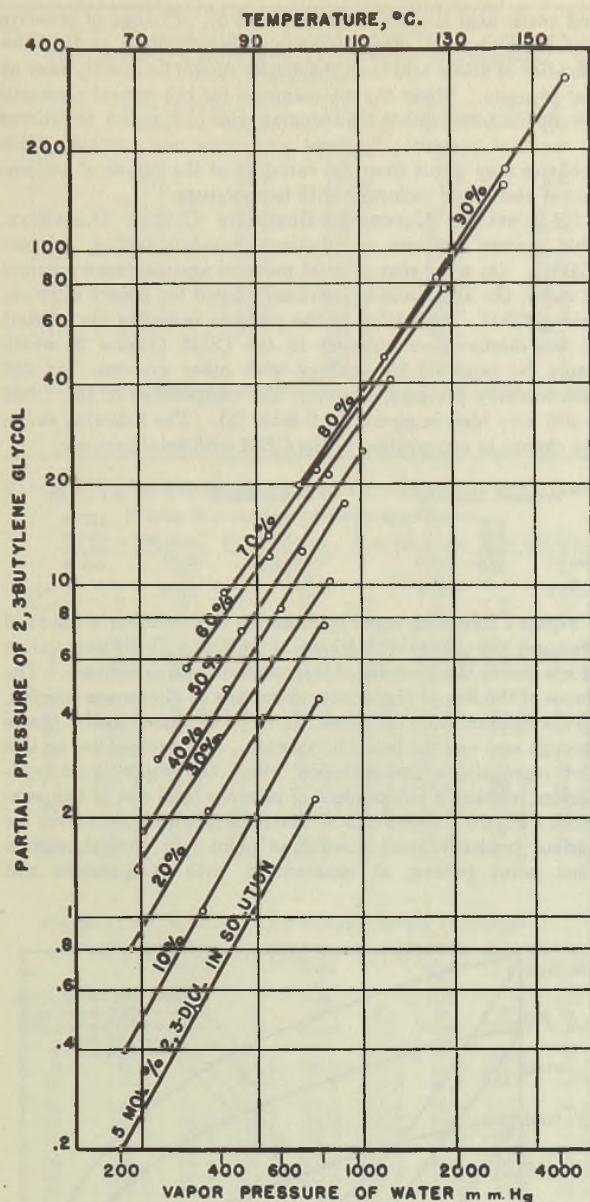
Figure 3. Log Plot of Partial Pressures of *meso*-2,3-Butylene Glycol from Aqueous Solutions *vs.* Vapor Pressures of Water at Same Temperatures

tillate coming over up to 183° and above 184° C. at 760 mm. mercury was discarded. The fraction collected had a refractive index of 1.4366. This material was used in studying the system water-diol and for making the ester used in the other two systems. The diol for the third and fourth systems was *levo*-2,3-butylene glycol similarly purified with a boiling range of 176–177° C. and a refractive index of 1.4130.

2,3-BUTYLENE GLYCOL DIACETATE. The technical-grade *meso* ester (Schenley Research Institute) was refined in the same manner as the diol. The distillate was collected over a range of 190–193° C. and had a refractive index of 1.4330 at 24° C. These values are in agreement with accepted data.

ACETIC ACID. Chemically pure glacial acetic acid was used. The trace of water present was removed by discarding foreruns of the distillations, since it steam-distilled over to give a slightly milky condensate.

METHYL VINYL CARBINOL ACETATE. This compound (M.C.V.A.) was made from methyl vinyl carbinol obtained from Shell Development Company. The alcohol was refluxed with a slight

excess of acetic anhydride for 1–2 hours, washed with water, dried with calcium chloride, and finally purified by distillation. The purified methyl vinyl carbinol acetate distilled at 112–113° C.

METHODS. The experimental apparatus and procedure were described previously (*2, 4*). Because of the high-boiling temperatures encountered, the still was heavily insulated to reduce radiation losses and errors. The three systems containing diol were analyzed in a refractometer. Refractive index data obtained for these systems from synthetic mixtures are shown in Table I and Figure 1. The two systems containing acetic acid were analyzed by titration of weighed samples for acetic acid.

CORRELATION OF DATA

The data are given in Tables II and III, and plots were made of the liquid and vapor relations with temperature (boiling point and dew point curves) and of the vapor composition as a function of liquid composition alone (*x, y* curves). Plots were also made of the logarithms of partial pressure, vapor composition, relative volatility, activity, and equilibrium constant against the logarithms of vapor pressure of water at the same temperature and against the total pressure at the same temperature. These methods of correlation of P, T, x, y data were discussed elsewhere (*6*). Only a few of these plots are included (Figures 1 to 8) to show the relative consistency of the experimental work. The smoothed values of vapor and liquid compositions of Table IV were obtained by picking off values from logarithmic plots of all the experimental data.

WATER – 2,3-BUTYLENE GLYCOL. The data for this system (Figures 2, 3, and 4) exhibit the characteristics of a normal binary mixture of two components with widely differing boiling points. No constant-boiling mixture is formed at any pressure; the relative volatility of water is always great and increases with decreasing pressure. This is important in the operation of the evaporator and a simple rectifying system which may be attached to it, since considerable water can be evaporated from the aqueous solutions without any loss of diol overhead.

Figure 4 (vapor composition plotted on log paper against total pressure) is a convenient means of correlating data of this type. The slopes of the lines on the total pressure plots shown are nearly all the same, as expected, since the molar latent heats are relatively close for the two compounds (water 9700 calories, diol 11,700 calories).

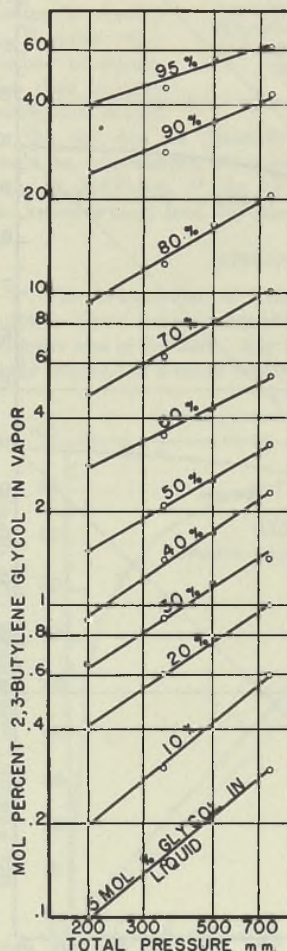ACETIC ACID–2,3-BUTYLENE GLYCOL DIACETATE. This system shows

Figure 4. Log Plot of Vapor Composition of System Water–*meso*-2,3-Butylene Glycol at Constant Liquid Compositions *vs.* Total Pressures

some irregularities, which are expected since acetic acid is known to be associated. The wide variation of the boiling points also increased experimental difficulties and probably experimental errors. The separation, however, between the diester
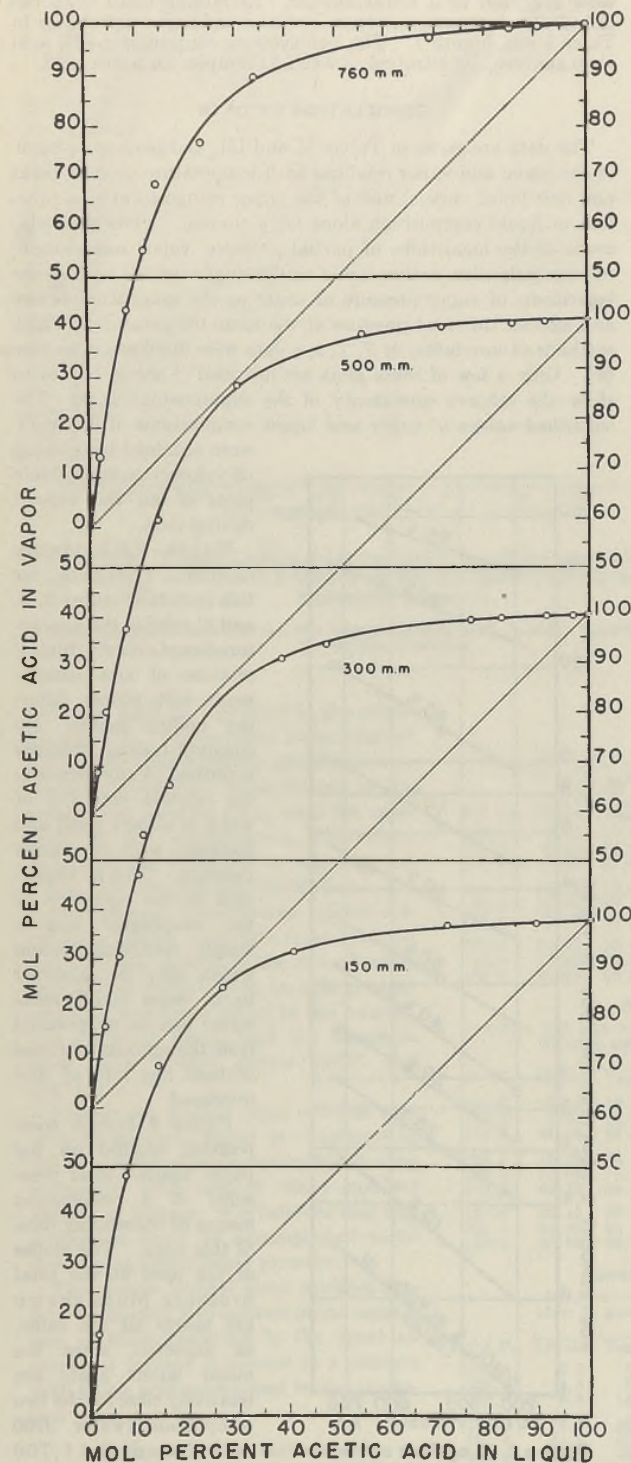
and acetic acid is good (Figures 5 and 6). Change of pressure seems to have little effect on the relative volatilities, so that rectification of acetic acid from the diester should be equally easy at any pressure. When the x-y diagrams for the several pressures are superimposed rather than separated, as in Figure 5, the curves at constant pressures intersect and cross one another. This behavior may result from the variation of the degree of association of acetic acid molecules with temperature.

2,3-Butylene Glycol–2,3-Butylene Glycol Diacetate. This system exhibits a minimum constant-boiling mixture (CBM). On a log plot of total pressure against vapor pressure of water, the lines cross as previously noted for binary mixtures having CBM. Reduction of the pressure increases the amount of the diester (less volatile) in the CBM (Figure 2) which would be expected by analogy with other systems. At 250 mm. mercury pressure, however, the composition of the CBM is still very high in glycol (63.2 mole %). The following shows the change in composition of the CBM with total pressure:

Pressure, Mm. Hg	% Diol in CBM	B.P., ° C.
760	77.0	177.6
500	71.2	164.6
350	67.5	153.0
250	63.2	143.4

Figure 7 shows log vapor composition as a function of log total pressure; the change of the slopes of the lines with different values of x is due to the presence of the constant-boiling mixture. The slopes of the line at higher concentrations of diester are positive. As the concentration decreases, the slope decreases until it passes through zero and the line is horizontal. A horizontal line on this plot represents a concentration where the vapor-liquid equilibrium relation is independent of pressure (and also of temperature). Figure 7 shows this at about 55% where the curves for various pressures cross a common point. In general, such a fixed point (where, at constant x, both temperature and
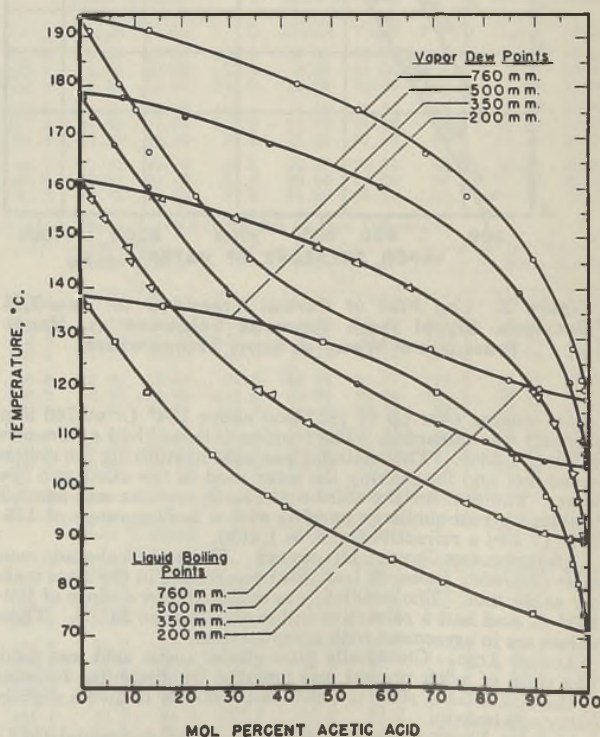

Figure 5. Vapor-Liquid Compositions for System Acetic Acid–2,3-Butylene Glycol Diacetate

Vapor compositions to 50% acetic acid are indicated on left and above 50%, on right.

Figure 6. Boiling Point and Dew Point Curves for System Acetic Acid–2,3-Butylene Glycol Diacetate

TABLE III. VAPOR-LIQUID EQUILIBRIUM DATA FOR SYSTEM MVCA-levo-2,3-BUTYLENE GLYCOL AT ATMOSPHERIC PRESSURE

Temp., ° C.	Mole % MVCA in:		Temp., ° C.	Mole % MVCA in:	
	Liquid	Vapor		Liquid	Vapor
179.0	0	0	117.8	0	0
175.5	0.8	10.0	117.1	3.8	4.6
170.4	2.4	24.8	116.8	5.9	8.0
156.0	4.7	54.8	116.4	9.1	11.9
150.4	6.9	63.5	115.7	18.2	22.2
141.2	11.6	72.5	115.5	21.0	25.0
133.9	17.9	80.4	114.9	30.7	35.2
125.5	31.2	88.0	114.4	38.7	43.5
120.5	46.4	91.7	114.1	44.2	48.6
114.9	75.7	97.5	113.3	56.3	61.5
114.0	86.5	98.6	112.7	69.4	74.2
113.5	88.3	98.8	112.3	78.7	82.2
111.8	100	100	112.0	87.5	90.0
			111.9	92.3	94.3
			111.8	100.0	100.0

TABLE IV. SMOOTHED DATA OF VAPOR-LIQUID EQUILIBRIA

SYSTEM WATER-meso-2,3-BUTYLENE GLYCOL

	P = 760 Mm.		P = 500 Mm.		P = 350 Mm.		P = 200 Mm.	
Mole % Water in Liquid	T ° C.	Mole % water in vapor	T ° C.	Mole % water in vapor	T ° C.	Mole % water in vapor	T ° C.	Mole % water in vapor
0	182.5	0.0	168.0	0.0	158.5	0.0	142.0	0.0
5	168.5	38.5	152.5	43.5	141.2	54.20	126.3	60.2
10	158.7	56.5	143.0	64.6	130.7	71.70	115.2	76.0
20	142.3	79.2	127.0	83.3	114.0	87.60	97.5	90.1
30	127.8	89.8	113.7	91.6	101.2	93.70	84.8	95.2
40	116.7	94.5	103.6	95.7	92.1	96.50	77.5	97.2
50	110.3	96.7	98.0	97.5	87.0	97.90	72.7	98.5
60	106.6	97.7	94.7	98.3	84.6	98.60	70.4	99.1
70	104.5	98.6	92.6	98.8	82.8	99.00	69.0	99.3
80	102.8	99.0	91.0	99.2	81.3	99.40	68.1	99.6
90	101.2	99.4	89.7	99.6	80.1	99.70	67.3	99.8
95	100.6	99.7	89.3	99.8	79.6	99.85	67.0	99.9
100	100.0	100.0	88.7	100.0	79.3	100.00	66.5	100.0

SYSTEM ACETIC ACID-meso-2,3-BUTYLENE GLYCOL DIACETATE

	P = 760 Mm.		P = 500 Mm.		P = 300 Mm.		P = 150 Mm.	
Mole % Acid in Liquid	T ° C.	Mole % acid in vapor	T ° C.	Mole % acid in vapor	T ° C.	Mole % acid in vapor	T ° C.	Mole % acid in vapor
0	193.7	0	178.7	0	161.0	0	138.3	0
5	185.5	30.1	171.3	29.3	153.7	31.2	131.5	40.0
10	177.5	50.2	164.3	50.0	146.8	50.5	124.7	60.0
20	162.1	75.2	150.5	75.0	134.0	75.4	112.5	79.9
30	149.7	86.8	138.6	86.4	123.7	86.1	103.3	89.0
40	141.0	92.2	130.0	92.0	116.3	91.9	96.3	93.5
50	135.5	94.7	123.5	95.0	110.5	95.1	90.7	95.8
60	131.3	96.5	118.0	97.4	105.2	96.7	86.1	97.3
70	127.0	98.1	113.0	98.4	100.1	98.2	82.0	98.3
80	123.2	99.2	108.7	99.2	95.7	99.1	78.3	99.0
90	120.0	99.7	105.7	99.7	91.7	99.7	74.7	99.7
95	118.6	99.8	104.7	99.8	90.4	99.8	73.0	99.8
100	117.8	100	104.4	100	89.6	100	71.5	100

SYSTEM levo-2,3-BUTYLENE GLYCOL-meso-2,3-BUTYLENE GLYCOL DIACETATE

	P = 760 Mm.		P = 500 Mm.		P = 350 Mm.		P = 250 Mm.	
Mole % Glycol in Liquid	T ° C.	Mole % glycol in liquid	T ° C.	Mole % glycol in liquid	T ° C.	Mole % glycol in liquid	T ° C.	Mole % glycol in liquid
0	192.7	0	177.5	0	165.6	0	154.5	0
5	189.8	7.5	173.6	10.5	162.4	12.0	152.0	12.0
10	187.2	14.7	171.8	17.5	160.5	20.0	150.0	21.5
20	184.0	28.5	168.8	28.5	158.0	29.7	147.4	32.5
30	182.0	37.7	167.0	38.7	156.3	38.7	145.5	41.2
40	180.5	46.7	165.9	47.7	154.8	47.2	144.5	48.6
50	179.3	55.7	165.2	56.0	153.7	55.7	143.7	55.5
60	178.3	63.5	164.8	63.0	153.1	62.5	143.5	62.0
70	177.7	72.0	164.7	70.5	153.0	68.5	143.5	67.3
80	177.6	79.0	164.7	76.6	153.2	74.5	143.9	72.0
90	178.0	86.8	165.1	85.0	153.8	83.5	144.5	81.8
95	178.4	92.0	165.4	90.7	154.2	90.0	144.7	89.0
100	179.0	100	165.7	100	154.8	100	145.1	100

pressure may vary without changing y) may be expected if there is a variation in slope from plus to minus, or minus to plus, in the log plots of y against total pressure or y against vapor pressure of a reference substance.

The presence of this CBM indicates the importance of complete esterification of the glycol in the esterifying column. It shows that the diacetate may be used as a solvent only if esterification in the presence of a great excess of the diester is feasible or if some other method of separation than ordinary rectification is used for the diol and its diacetate. Such an additional method would be, for example, the separation of the diol by a partial pressure distillation of the heterogeneous CBM of the diol and kerosene away from the diacetate.
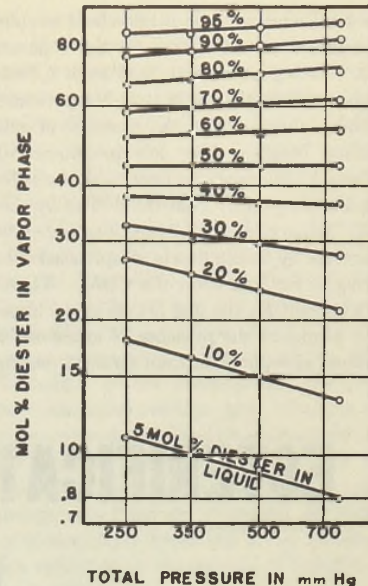
Figure 7. Log Plot of Vapor Compositions of System 2,3-Butylene Glycol–2,3-Butylene Glycol Diacetate at Constant Liquid Compositions vs. Total Pressures

CONCLUSIONS

1. The evaporation of fermented liquors containing 2,3-butylene glycol prior to extraction can be carried out without excessive loss of the diol. Any diol that may come over can be easily returned in a small rectifying column in the vapor line of
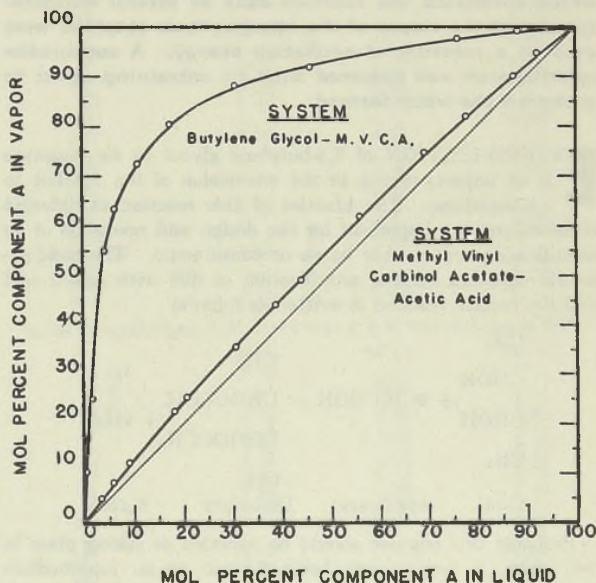
Figure 8. Vapor-Liquid Compositions for MVCA-levo-2,3-Butylene Glycol and MVCA-Acetic Acid Systems

the final effect of a multiple-effect evaporator. The use of low pressures is advantageous for this separation.

2. To separate acetic acid from 2,3-butylene glycol diacetate with a sufficiently low bottom temperature (120° C.) to minimize decomposition due to the presence of sulfuric acid as an esterification catalyst, very low pressures (100 mm.) are required. It may be necessary to neutralize the sulfuric acid before removing the acetic acid from the diester by distillation.

3. Separation of 2,3-butylene glycol and 2,3-butylene glycol diacetate by distillation is complicated even at very low pressures, owing to the formation of a CBM. Therefore, the use of diester as a solvent for the diol is dependent upon a successful esterification of diol in the presence of excess ester or the use of another method of separation than straight rectification.

LITERATURE CITED

(1) Fulmer, E. I., and Werkman, C. H., *Proc. Iowa Acad. Sci.*, **36**, 114 (1929).
(2) Gilmont, R., and Othmer, D. F., IND. ENG. CHEM., **36**, 1061 (1944).
(3) Othmer, D. F., *Chem. & Met. Eng.*, **48**, 91 (1941).
(4) Othmer, D. F., IND. ENG. CHEM., **35**, 614 (1943).
(5) Othmer, D. F., Bergen, W. S., Shlechter, N., and Bruins, P. F., *Ibid.*, **37**, 890 (1945).
(6) Othmer, D. F., and Gilmont, R., *Ibid.*, **36**, 858 (1944).

ESTERIFICATION of 2,3-BUTYLENE GLYCOL with ACETIC ACID

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The rates of esterification at different temperatures of both glycol and the glycol monoester were determined, using sulfuric acid as catalyst. The reaction was also studied in an excess of glycol diacetate equivalent to the amount which would be present in an extract layer from a liquid extraction column, using butylene glycol diacetate as a solvent for the recovery of glycol. The reaction does not appear to be a single, simple one of first, second, or third order. Equilibrium constants and heats of reactions are reported. An empirical plot was developed which correlated the reaction data at several temperatures, and the slopes of the straight lines obtained were used as a measure of activation energy. A continuous esterification was operated with an entraining agent to withdraw the water formed.

ESTERIFICATION of 2,3-butylene glycol to its diacetate is an important step in the conversion of the 2,3-diol to 1,3-butadiene. The kinetics of this reaction at different temperatures are important for the design and operation of an esterification unit (either batch or continuous). The stoichiometric equation for the esterification of diol with acetic acid and the reverse reaction is written as follows:

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
\text{CHOH} \\
| \\
\text{CHOH} \\
| \\
\text{CH}_3
\end{array}
+ 2\text{CH}_3\text{COOH} \rightleftharpoons
\begin{array}{c}
\text{CH}_3 \\
| \\
\text{CHOOCCH}_3 \\
| \\
\text{CHOOCCH}_3 \\
| \\
\text{CH}_3
\end{array}
+ 2\text{H}_2\text{O}
$$

·Diol   Acetic acid   Diacetate   Water
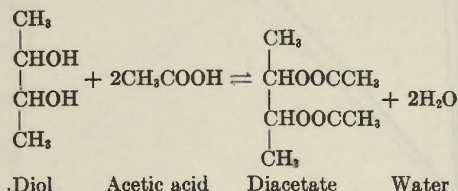
Probably this reaction should be regarded as taking place in two steps, a monoacetate being formed as an intermediate product. This mechanism would give two opposite second-order reactions forming and decomposing the monoacetate, followed by two more opposing second-order reactions forming and decomposing the diacetate. The monoacetate was actually found

in the reaction vessel (*2*); it was prepared by treating the diol with the calculated amount of acetic anhydride to give a material having the following properties (*2*): clear, colorless liquid with a mild pleasant odor; soluble in water, alcohol, ether, benzine, and acetone; sparingly soluble in aliphatic hydrocarbons; refractive index 1.4214 at 25° C.; boiling range 178–183° C.

The industrial application of the reaction to give the diacetate would be complicated by the high boiling points of the alcohol (181° C.) and the ester (192° C.). A projected method is to use a continuous esterification column fed with the stoichiometric quantities of glycol and acetic acid plus the required amount of sulfuric acid catalyst. An entrainer may be recycled in the upper or dehydration section to remove the water of reaction. The glycol and the diacetate form an azeotrope (*5*), and the reaction must proceed to complete utilization of the glycol. This can be accomplished by having excess acetic acid present as permanent holdup in the column below the feed plate.

EXPERIMENTAL METHODS

To determine conditions at equilibrium, a galvanized iron tank, $12 \times 9 \times 14$ inches ($31 \times 23 \times 36$ cm.), was set up as a constant-temperature bath and lagged with a 2-inch layer of magnesia. S.A.E. 30 motor oil was used in the bath and was heated by a 750-watt immersion heater which was connected in series with a relay and a mercury temperature regulator. The regulator and an agitator held the bath temperature constant within ±1° C. The reaction took place in a one-liter, three-neck flask immersed in the oil bath. A thermometer, water-cooled condenser, and stirrer, inserted through a mercury seal, were installed in the three openings.

The lower-boiling reactant, acetic acid, contained the required amount of sulfuric acid (optimum = 0.0162 mole per mole of glycol, *2*). It was heated in the reaction flask, and the high-boiling reactant, butylene glycol, was heated in another flask. When both liquids were at reaction temperature, the glycol was rapidly introduced into the flask. At the same instant an electric timer was started. At regular intervals samples were withdrawn by a 1-ml. pipet. Samples, 0.50 to 0.85 cc. in volume, were transferred to Erlenmeyer flasks kept at about −10° C. by immersion in a mixture of ice, water, and calcium chloride. The samples froze instantly and thus arrested further reaction. Each sample was later titrated for free acetic acid.
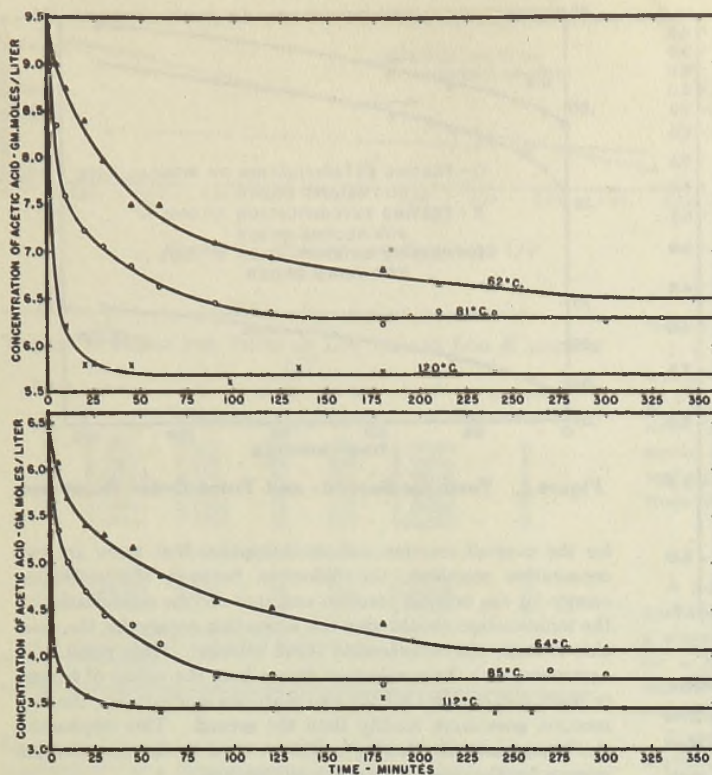
Figure 1. Esterification of 2,3-Butylene Glycol with Acetic Acid

Initial concentrations of reactants: (*above*) 4 moles acetic acid, 2 moles diol, 0.032 mole sulfuric acid (catalyst); (*below*) 3 moles acetic acid, 3 moles diol, 0.048 mole sulfuric acid

CORRELATION OF EQUILIBRIUM DATA

Runs were made for the esterification of diol with acetic acid at 120°, 85° and 65° C. The data are presented in Table I and Figure 1. At each temperature a run was made with equal molal quantities and another with two moles of acetic acid per mole of glycol in order to obtain a check on the values for k (the specific reaction velocity constant) and for K (the equilibrium constant) which was expected to be independent of initial concentrations.

An attempt to obtain values for the specific reaction velocity, k, was made by correlating the runs at 65° C. The reaction is slow at this temperature (Figure 1), and it was hoped that by correlating the data up to 2-hour reaction time, positive results could be obtained. At this temperature the effect of the reverse reaction should be negligible for the early part of the run. Even if the esterification takes place in two consecutive reversible reactions, it is possible that some simple first-, second-, or third-order equation might be identified in the early stages. This occurs in the hydrolysis of ethyl succinate, ethyl tartrate, glycol diacetate, and glycerol triacetate in the presence of hydrochloric acid as a catalyst (1).

Tables II and III and Figures 2 and 3 present data to test for order of reaction. Although smooth curves are obtained, the reaction follows no single first-, second-, or third-order equation because the curves are not straight. Therefore, even for the early part of the runs, when the reverse reactions are negligible, the consecutive mechanism for the over-all reaction is important.

The values for equilibrium constant K, as obtained by the two runs at each temperature, are in good agreement (Table IV). A plot of log K against $1/T$ (Figure 4) gives a straight line; the heat of reaction calculated from this line is 5330 calories.

In order to separate a single reaction from the mechanism of the monoacetate to diacetate, the monoacetate was prepared from butylene glycol by refluxing with the calculated amount of acetic anhydride for about 4 hours and then carefully fractionating. A fraction was collected which boiled over a range of from 178° to 180° C., and showed all the physical properties reported above. It analyzed 103% monoacetate. The monoester was then further esterified in a series of runs similar to those for the diol. Table V and Figure 5 give the results which indicate that the time to reach equilibrium for the monoacetate is about the same as for the over-all reaction. This means that the rate of formation of the monoacetate, the first step in the consecutive reaction, may be either as fast as or somewhat faster than its disappearance. This point further stresses the importance of allowing sufficient time in the esterification unit for equilibrium to be reached; otherwise, the large amount of monoacetate remaining in the product will mean a reduction in the amount of butadiene which may be obtained.

A plot of log K against $1/T$ for the monoacetate reaction is nearly a horizontal line (Figure 4) which indicates that equilibrium constant K is independent of temperature. The heat of reaction is 441 calories.

TABLE I. ESTERIFICATION OF 2,3-BUTYLENE GLYCOL

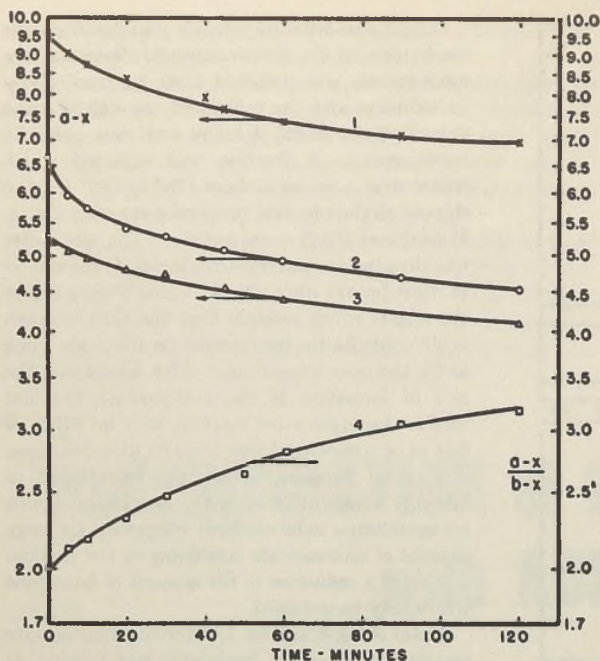| Reaction Time, Min.	Acetic Acid Concn., Gram Moles/Liter		
	62° C.	81° C.	120° C.
Initial Concentrations, 4 M Acetic Acid + 2 M Diol + 0.032 M H$_2$SO$_4$ (Catalyst)			
0.5	9.40	...	...
0.584	...	...	8.14
0.75	...	...	7.64
1.8	...	8.98	....
5	9.00	8.35	....
6	...	...	5.60
8.25	...	...	6.29
10	8.75	7.60	6.20
15	...	...	5.99
20	8.40	7.23	5.80
25	...	...	5.80
30	7.98	7.05	5.72
45	7.50	6.85	5.78
60	7.50	6.63	....
90	7.10	6.48	....
98	...	...	6.50
120	6.94	6.35	....
135	...	...	5.75
140	...	6.29	....
180	6.80	6.22	5.70
195	...	6.30	....
210	6.65	6.35	....
240	...	6.34	5.68
270	...	6.30	....
300	6.50	6.25	....
310	...	...	5.68
330	...	6.28	5.68
360	6.50	6.27	....
Initial Concentrations, 3 M Acetic Acid + 3 M Diol + 0.048 M H$_2$SO			
	64° C.	85° C.	112° C.
0.333	6.53	...	....
0.467	...	6.42	....
0.55	...	...	5.54
5	6.08	5.36	3.85
10	5.70	5.02	3.70
20	5.42	4.70	3.57
30	5.30	4.45	3.47
45	5.16	4.35	3.50
60	4.87	4.13	3.40
90	4.60	3.79	3.47
120	4.52	3.80	3.43
140	...	...	3.43
180	4.35	3.70	3.55
240	4.05	...	3.40
260	...	...	3.40
270	...	3.85	....
300	4.09	3.80	3.44
310	...	...	3.44
360	4.06	3.75	3.45

Figure 2. Tests for First- and Second-Order Reactions

1. **Esterification of diol, stoichiometric quantities of reactants (first order)**
2. **Esterification of diol, equal molar quantities of reactants (first order)**
3. **Esterification of monoacetate, equal molar quantities of reactants (first order)**
4. **Esterification of diol, stoichiometric quantities of reactants (second order)**

         a = initial concentration of diol
         b = initial concentration of acetic acid
         x = amount of acetic acid reacted at time t

Since no values were obtained for specific reaction velocity constant k, correlation of the rate of reaction with temperature by the Arrhenius equation was impossible. However, for design and operation purposes it is highly desirable to be able to predict the rate of reaction at any possible temperature; therefore, an empirical correlation was attempted by plotting the logarithm of the reciprocal of θ (the time to reach equilibrium, in minutes) against $1/T$, where T is the absolute temperature (Figure 6).

The reason for making such a plot is that specific rate constant k, for any order whatever, is a function of $1/\theta$ multiplied by some concentration factor; therefore, it was believed that $1/\theta$ could be substituted for k in the Arrhenius equation. Such a substitution could be successfully made only if the effect on k of any variation of concentration factor with temperature is negligible, as compared to the corresponding variation in θ. The data correlate well when plotted in such a manner. For the esterification of the diol, two parallel straight lines are obtained, each corresponding to a different concentration of original reactants.

ACTIVATION ENERGIES

The slope of an Arrhenius plot multiplied by 2.303 R gives the energy of activation for any specific reaction. The slopes of the lines in Figure 6 were multiplied by 2.303 R, and the results are given in Table VI. The energy of activation for the particular reaction involved is considerably greater than the heats of reaction as obtained from the equilibrium constant, which would be expected. For the same reaction run at different initial concentrations, the same slope is obtained, as would also be expected.

The energy of activation so calculated for the esterification of the monoacetate is slightly greater than one half that obtained
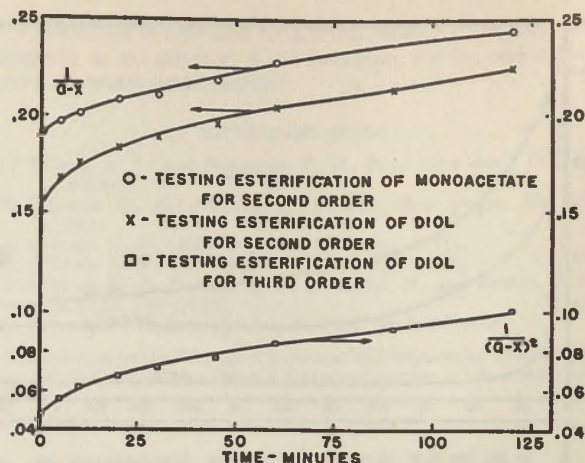
Figure 3. Tests for Second- and Third-Order Reactions

for the over-all reaction. Since it appears that there are two consecutive reactions, the difference between the activation energy for the over-all reaction and that for the esterification of the monoacetate should give the activation energy for the reaction to form the monoacetate (4965 calories). This result is in agreement with the conclusions drawn from the values of θ (time to reach equilibrium) for the two reactions studied; i.e., the first reaction goes more readily than the second. This emphasizes the importance of allowing sufficient time in the esterification column for the reaction to reach equilibrium.

Previous papers (4, 5) have discussed the recovery of glycol from fermentation liquors by solvent extraction and then by distillation, and several solvents were suggested. One was the

TABLE II. DATA TO TEST FOR ORDER OF REACTION[a] OF ESTERIFICATION OF 2,3-BUTYLENE GLYCOL

EQUAL MOLAR CONCENTRATIONS AT 61 ± 1° C.

Time, Min.	$a - x$	$1/(a - x)$	$1/(a - x)^2$
0	6.63	0.150	0.0225
0.33	6.53	0.155	0.0240
5	5.98	0.167	0.0279
10	5.72	0.175	0.0306
20	5.44	0.183	0.0335
30	5.30	0.189	0.0357
45	5.10	0.196	0.0384
60	4.88	0.205	0.0420
90	4.66	0.214	0.0453
120	4.52	0.224	0.0502

STOICHIOMETRIC CONCENTRATIONS AT 65 ± 1° C.

	$a - x$	x	$b - x$	$(a - x)/(b - x)$
0	9.50	0	4.75	1.99
0.5	9.40	0.10	4.65	2.02
5	9.00	0.50	4.25	2.12
10	8.75	0.75	4.00	2.18
20	8.34	1.16	3.59	2.32
30	7.98	1.52	3.23	2.48
45	7.64	1.86	2.89	2.64
60	7.38	2.12	2.63	2.81
90	7.08	2.42	2.33	3.04
120	6.94	2.56	2.19	3.17

[a] Where a = initial concentration of acetic acid, b = initial concentration of 2,3-butylene glycol, and x = amount of acetic acid reacted at time t (all in gram moles/liter).

TABLE III. DATA TO TEST FOR ORDER OF REACTION OF ESTERIFICATION OF 2,3-BUTYLENE GLYCOL MONOACETATE AT 64 ± 1° C.

Time, Min.	$a - x$	$1/(a - x)$
0	5.30	0.189
0.358	5.24	0.191
5	5.07	0.197
10	4.99	0.201
20	4.80	0.208
30	4.75	0.211
45	4.55	0.219
60	4.39	0.228
120	4.10	0.244
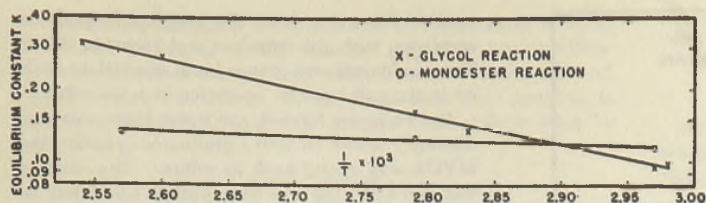
Figure 4. Plot of Log K against $1/T$

TABLE IV. DATA FOR PLOTS OF LOG $1/\theta$ AND LOG K AGAINST $1/T$

θ^a	$1/\theta$	K	$t°$ C.	$T°$ K.	$1/T$	Remarks[b]
Esterification of Glycol						
33	0.0300	0.278	112	385	0.00260	E
30	0.0333	0.308	120	393	0.00254	S
130	0.00768	0.136	81	354	0.00283	S
90	0.0111	0.162	85	358	0.00279	E
290	0.00345	0.0984	62	335	0.00298	S
240	0.00416	0.0965	64	337	0.00297	E
Esterification of Monoacetate						
60	0.0167	0.132	116	389	0.00257	E
120	0.00833	0.126	85	358	0.00279	E
230	0.00434	0.115	64	337	0.00297	E

[a] Time to reach equilibrium, min.
[b] S = stoichiometric quantities of reactants; E = equal molar concentrations of reactants.

diacetate of the diol; its successful use was predicated upon the practicability of a direct esterification of the diol in the extract layer, as it came from a liquid-liquid extractor. Table VII and Figure 7 give the results of esterification of the diol in an excess of diacetate equal to the amount which would be obtained from an extraction column. The time to reach equilibrium at 120°C. is twice that of the normal reaction, using stoichiometric quantities. The amount of esterification which has occurred at equilibrium is only 18% as against 40% for the normal reaction. Thus, when the reaction is carried out in the presence of excess ester, more time must be allowed for equilibrium to be reached; furthermore, to obtain 100% esterification will be more difficult, take a greater length of time, and require a larger column.

ENTRAINERS FOR WATER OF ESTERIFICATION

In the previous papers (4, 5), two of three suggested solvents were also proposed as possible water-removing agents or entrainers in the dehydrating section of the esterification column. If either the butylene glycol diacetate (BGD) or the methyl vinyl carbinol acetate (MVCA) could be used as entrainer to remove the water of esterification, the process would be simplified by avoiding the introduction of an outside material, such as butyl acetate (5).

The water-entraining properties of the two solvents were studied in an apparatus consisting of four 500-cc. round-bottom flasks connected with 8-mm. tubing so that the vapors from one passed to the bottom of the next. The vapors from the last flask were passed into a condenser. Thermometers were inserted in the vapor space of each flask. Several hundred milliliters of distilled water were placed in the first flask, and mixtures of solvent and distilled water in the others. The water in the first flask was boiled, and the steam led into the second flask below the surface of the liquid. The vapors from this flask were passed into the third flask, and so on to the condenser. The condensate separated into two layers, solvent and water, and the amount of each was readily determined.

Table VIII gives the results obtained and compares the three proposed entrainers. MVCA compares favorably with butyl acetate. The former distills over with water at a lower temperature (87.2° compared to 90.6° C.) which, from the standpoint of ease of separation of water from acetic acid, is an important factor. MVCA requires approximately 8% more heat per pound of water removed than does butyl acetate. MVCA is a by-product of the diacetate pyrolysis and can be fed directly to the esterification unit. Water is readily decanted from MVCA, which is important since any entrainer dissolved will be returned to the column as reflux.

It is apparent from Table VIII that BGD has the lowest entrainer-water ratio and heat requirements. However, separation of water from acetic acid by the BGD–water azeotrope is not much better than separation by direct distillation of a water–acetic acid mixture. The azeotrope temperature is 99.6° C. and an efficient long column would be needed to obtain the azeotrope overhead.

STUDIES IN DISTILLING COLUMN

A 2-liter distilling flask, a 90-cm. glass laboratory column packed with small glass helices, and a still head, which included a water-cooled condenser, were assembled. Heat was supplied by a hot plate. To overcome heat losses, the column was heated by a Nichrome resistance wire in an air space inside an outer jacket.

A stoichiometric mixture of glycol and acetic acid, plus the required amount of catalyst (0.0162 mole sulfuric acid per mole of glycol) were charged. MVCA as entrainer was also charged into the still. The still was maintained at 120° C., or below, to minimize diacetate decomposition. As the esterification pro-

TABLE V. ESTERIFICATION OF 2,3-BUTYLENE GLYCOL MONOACETATE

Reaction Time, Min.	Acetic Acid Concn. Gram Moles/Liter[a]		
	64° C.	85° C.	116° C.
0.358	5.24	...	...
0.368	...	5.84	...
0.467	...	...	5.16
5	5.07	5.58	4.59
10	4.99	5.33	4.33
20	4.80	5.06	4.09
30	4.75	4.88	3.95
45	4.55	4.74	3.92
60	4.39	4.65	3.86
120	4.10	4.65	3.86
180	4.01	4.51	3.82
240	3.93	4.44	3.82
300	3.93	4.49	3.78
330	3.90	...	3.78
360	3.93	4.43	3.78

[a] Initial concentrations:

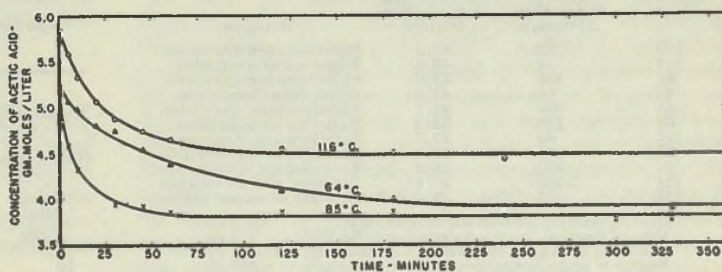|	Monoacetate	Acetic Acid	H_2SO_4 (Catalyst)
64° C.	1.18 M	1.18 M	0.018 M
85° C.	1.25 M	1.50 M	0.012 M
116° C.	1.50 M	1.50 M	0.012 M

Figure 5. Esterification of 2,3-Butylene Glycol Monoacetate with Acetic Acid

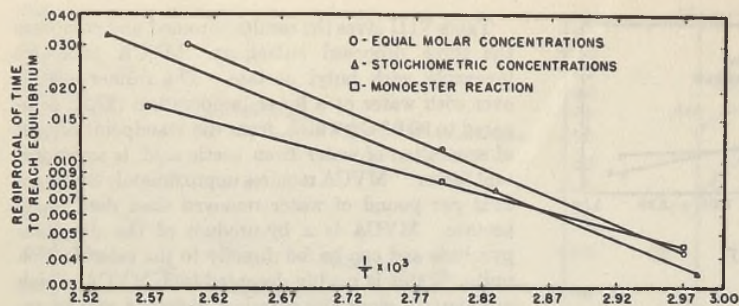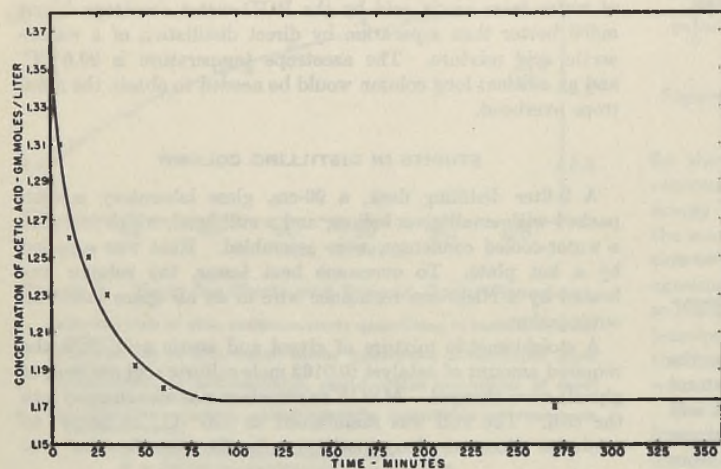Figure 6. Plot of Log $1/\theta$ against $1/T$

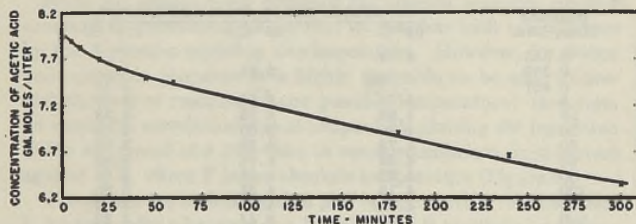Figure 7. Esterification of 2,3-Butylene Glycol in Excess Diacetate

Figure 8. Esterification of 2,3-Butylene Glycol without Catalyst

ceeded, the water from the reaction formed the azeotrope with the entrainer and began to distill. The condensate was trapped and allowed to build up in the still head by operating at total reflux.

As two layers formed, the water layer was continuously drawn off into a graduated cylinder, and MVCA was cycled back as reflux. The reaction was run until the top temperature could not be kept below 90° C. The completeness of reaction was measured by the amount of water collected in the receiver.

Analyses were made for free acetic acid in the overhead water, for free acetic acid (corrected for sulfuric acid) in the hot residue, for removal of MVCA and free acetic acid from the product mixture by fractionation in the laboratory column, and for diacetate by saponification of the product.

The results show that with a fairly efficient short column and careful control, at least 95% conversion to the diacetate is obtainable. The remainder is either decomposed under the conditions of the experiment or is represented by presence of the monoacetate:

% reaction (based on total water collected overhead)	98.3
% of original acetic acid collected overhead	2.2
% of original acetic acid remaining in bottoms	1.7
Total acetic acid accounted for, %	102.2
Total MVCA recovered, %	97.5
% conversion to diester	95.0

When the temperature in the still pot was permitted to go above 120° C. for any extended time (particularly in the latter stages of the

TABLE VII. ESTERIFICATION OF 2,3-BUTYLENE GLYCOOL IN EXCESS DIACETATE

(Initial concentrations: 0.4 M acetic acid + 0.2 M diol, + 1.42 M diacetate + 0.0032 M H_2SO_4; temperature 117 ± 1° C.)

Time, Min.	Acetic Acid Concn., Gram Moles/Liter	Time, Min.	Acetic Acid Concn., Gram Moles/Liter
0.417	1.345	45	1.19
5	1.31	60	1.18
10	1.26	270	1.17
20	1.25	300	1.175
30	1.23		

TABLE VIII. RESULTS OF STEAM DISTILLATION EXPERIMENTS

	Butyl Acetate[a]	MVCA	BGD
Entrainer, lb./lb. water	2.57	3.28	0.185
Azeotrope temp., ° C.	90.6	87	99.6
Latent heat, B.t.u./lb. water removed			
Entrainer	358	463	23
Entrainer-water azeotrope	1336	1445	993
Sp. vol. of steam at azeotrope temp.	37.0	40	26.8

[a] The data for butyl acetate have been previously reported (3).

TABLE IX. ESTERIFICATION OF 2,3-BUTYLENE GLYCOL WITHOUT CATALYST

(Initial concentration: 1.80 moles butylene glycol and 2.50 moles acetic; temperature 114 ± 1° C.)

Time, Min.	Acetic Acid Concn., Gram Moles/Liter	Time, Min.	Acetic Acid Concn., Gram Moles/Liter
0.493	7.98	45	7.50
5	6.89	60	7.45
10	7.83	180	6.90
20	7.70	240	6.64
30	7.60	300	6.34

TABLE VI. SUMMARY OF RESULTS OF ESTERIFICATION EXPERIMENTS

Reaction Temp., ° C.	Min. to Reach Equilibrium, θ	% Esterification at Equilibrium	Remarks
120	30	40.3	Stoichiometric quantities
112	33	48.3	Equal molar quantities
81	130	33.9	Stoichiometric quantities
85	90	43.4	Equal molar quantities
62	290	31.7	Stoichiometric quantities
64	240	38.8	Equal molar quantities
116	60	26.7	Esterification of monoester
85	120	29.1	Esterification of monoester
64	230	25.3	Esterification of monoester
114	>300	20.6[a]	Reaction with no catalyst
117	70	17.6	Reaction in excess diester

Heat of reaction for over-all esterification:	5,330 cal.
Heat of reaction for monoacetate esterification:	441 cal.
Energy of activation for over-all esterification:	10,425 cal.
Energy of activation monoacetate esterification:	5,460 cal.

[a] Per cent reacted after 3 hours.

esterification), increased decomposition of the product resulted in marked darkening of the reaction mixture. An esterification was therefore run without sulfuric acid. Table IX and Figure 8 give the results which show that the reaction is slow even at 120° C., and that sulfuric acid catalyst must be used.

CONCLUSIONS

1. The mechanism for esterification of diol to diacetate proceeds via two pairs of consecutive, reversible reactions of approximately equal speed.

2. The presence of excess diacetate is disadvantageous to the esterification reaction.

3. An empirical method of correlating kinetic data with temperature of reaction consists of plotting the logarithm of $1/\theta$ against $1/T$. The slopes of the straight lines obtained should give the energy of activation for the reaction involved.

4. MVCA can be used for an entrainer of water formed. It is preferred because it is obtained during the pyrolysis of the diacetate to butadiene.

5. Ninety-five per cent conversion to the diacetate is obtained on a laboratory column using MVCA as an entrainer to remove the water of reaction. In the operation of an esterification column, the temperature in the lower sections of the column can be prevented from going above 120° C. for any extended period by the use of vacuum.

LITERATURE CITED

(1) Glasstone, S., "Textbook of Physical Chemistry", p. 1057, New York, D. Van Nostrand Co., 1941.
(2) Northern Regional Research Lab., Summary of Research on Production of Butadiene from 2,3-Butylene Glycol by Pyrolysis of Diacetate, Aug., 1942.
(3) Othmer, D. F., U. S. Patent 2,050,234 (Aug. 4, 1936).
(4) Othmer, D. F., Bergen, W. S., Shlechter, N., and Bruins, P. F., *Ibid.*, 37, 890 (1945).
(5) Othmer, D. F., Shlechter, N., and Koszalka, W., *Ibid.*, 37, 895 (1945).

PYROLYSIS of 2,3-BUTYLENE GLYCOL DIACETATE to BUTADIENE

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The final stage in the production of butadiene by fermentation of carbohydrate materials is the pyrolysis of butylene glycol diacetate to give butadiene and acetic acid, with the ultimate purification of butadiene for synthetic rubber manufacture. The pyrolysis of butylene glycol diacetate was studied, and yields were determined under various temperatures and other operating conditions. Optimum conditions appeared to be a contact time of 7.1 seconds and a temperature of about 585° C. in an atmosphere of nitrogen. The yield at these conditions was 84.9% conversion to butadiene. Acetic acid recovery was good; polymerization of butadiene and formation of unsaturated esters during the pyrolysis reaction seem to be the most important factor in determining yields, particularly at higher temperatures and higher contact times. The amount of polymerization was reduced to a minimum by diluting the gases with sufficient nitrogen to reduce the concentration of diacetate in the vapors to about 40 mole %. Incomplete pyrolysis and formation of unsaturated esters may be minimized by subsequent passes of the condensate liquor following pyrolysis.

THE recovery of 2,3-butylene glycol and its esterification to the diacetate have been reported (3, 4, 6). The structural formula of this diol indicated that butadiene might be obtained by the removal of two molecules of water. To assist this reaction, many catalysts, selected for dehydration properties, have been tried by other investigators (2). The maximum conversion (20%) is too low for commercial application.

Hill and Isaacs (1) claim much higher yields of butadiene by the pyrolysis of 2,3-butylene glycol diacetate. This pyrolysis probably proceeds by way of an unsaturated ester according to the following equation:

$$
\begin{array}{c}
\mathrm{CH_3} \\
| \\
\mathrm{CHOOCCH_3} \\
| \\
\mathrm{CHOOCCH_3} \\
| \\
\mathrm{CH_3}
\end{array}
\xrightarrow[\text{heat}]{-\mathrm{CH_3COOH}}
\begin{array}{c}
\mathrm{CH_3} \\
| \\
\mathrm{CH} \\
\| \\
\mathrm{C-OOCCH_3} \\
| \\
\mathrm{CH_3}
\end{array}
+
\begin{array}{c}
\mathrm{CH_2} \\
\| \\
\mathrm{CH} \\
| \\
\mathrm{CHOOCCH_3} \\
| \\
\mathrm{CH_3}
\end{array}
\xrightarrow[\text{heat}]{-\mathrm{CH_3COOH}}
\begin{array}{c}
\mathrm{CH_2} \\
\| \\
\mathrm{CH} \\
| \\
\mathrm{CH} \\
\| \\
\mathrm{CH_2}
\end{array}
$$

2,3-Butylene glycol diacetate → Acetate of enolic methyl ethyl ketone + Methyl vinyl carbinol acetate → 1,3-Butadiene
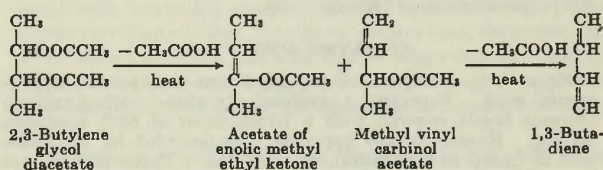
No butylenes are formed, although incomplete cracking yields unsaturated esters which boil around 115° C. Butylenes form during the pyrolysis of other materials to give butadiene; since they boil (−6° C.) very close to butadiene (−5° C.), they are separated from butadiene only with great difficulty.

Original work on this pyrolytic reaction, particularly that at the Northern Regional Research Laboratory, has shown that temperature in the reaction tube and rate of feed are the important factors in determining the extent to which 2,3-butylene glycol diacetate is converted to butadiene and to by-products. Hill and Isaacs (1) indicate that 475° C. is about the lowest limit for butadiene production; above 600° C. decomposition of butadiene is serious. At the lower temperatures, evidently, unsaturated esters are formed. To crack these unsaturated compounds further to butadiene, higher temperatures are necessary. Since butadiene polymerization begins to take place at the higher temperatures, some optimum temperature for the operation of the pyrolytic reaction must be found. Northern Regional Research Laboratory has also demonstrated that the slower the rate of feed at a given temperature, the greater the amount of polymerization which takes place, whereas the unsaturated ester formation decreases with slower feed rates.
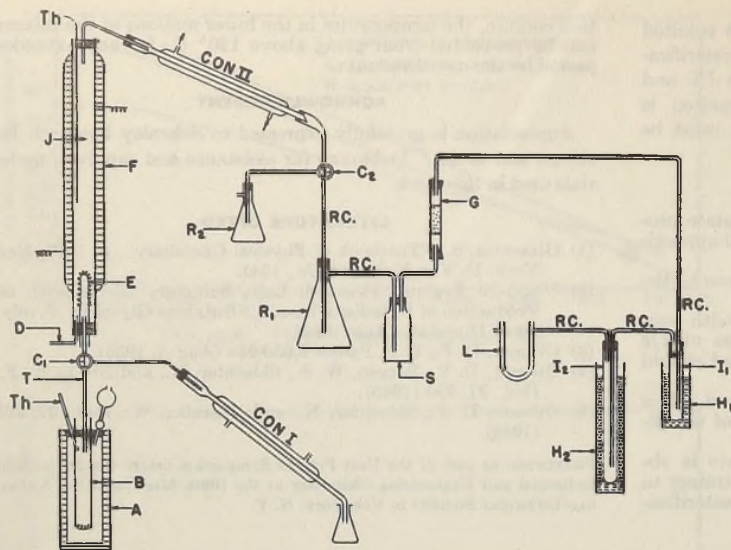
Figure 1. Apparatus for Pyrolysis Experiments

A. Vaporizer
B. Heater for vaporizer
C. Three-way stopcocks
D. Nitrogen inlet
E. Superheater
F. Furnace
G. Calcium chloride drier
H. Cold traps
I. Butadiene receivers
J. Reaction chamber
L. Carbon trap
R. Liquid take-off receivers
S. Water scrubber
T. Glass tubing
TH. Thermometer or thermocouple
CON. Condenser
RC. Rubber connections

The commercial possibilities of this process depend largely on the efficiency of the cracking operation and the attainment of maximum conversion. From theoretical considerations, it was concluded that the use of a hot inert gas (nitrogen) might be advantageous and useful in obtaining higher yields. Since nitrogen is a diluent, it reduces the partial pressure of the resulting butadiene and thus tends to retard the polymerization reaction. The presence of air or any oxidizing material greatly facilitates the polymerization of butadiene (5).

PYROLYSIS APPARATUS

Figure 1 is a diagram of the apparatus used for the experimental work. Vaporizer A consisted of a wide-mouthed vacuum thermos bottle covered with a 1-inch layer of 85% magnesia lagging. Heater for the vaporizer was provided by Nichrome wire B (rated at 600 watts), inserted into a Pyrex tubing bent into a U. Current for the vaporizer was supplied from the 110-volt d.c. line and was regulated to control the rate of vaporization. A chromel-alumel thermocouple was used to read furnace temperatures. It was inserted in a silica tube to insulate it from the hot vapors.

Superheater E was an electrical heater which extended for a height of 8 inches into the reaction chamber; the heat input was controlled by a Variac transformer. Electrically heated furnace F was 2 feet long with a 2-inch inside-diameter bore. The heating element was a heavy-duty Nichrome resistance coil (1500 watts capacity) wound around a ceramic core and then covered with a 2-inch layer of 85% magnesia lagging. Reaction chamber J was a 47-mm. unpacked Pyrex tube, 32 inches long. It was inserted into the vertical furnace. Wide-mouthed thermos bottles H, containing a saturated solution of solid carbon dioxide and acetone, where used as butadiene condensers.

The vaporizer was calibrated for the relation between electrical power (watts) input and rate of vaporization (grams per minute). Thus ammeter and voltmeter readings indicated the amount of vapor fed to the cracking unit by use of a calibration chart.

Experiments were run at several temperatures to find the effective reaction zone for estimating contact times. This zone was considered that portion included in a range 25° C. below the maximum, and was assumed equal to 7 inches in length. During a run the thermocouple was inserted to a position 16 inches from the bottom, which is at the maximum temperature region. The temperature gradient across the diameter of the tube was negligible.

OPERATION. Furnace F was brought to the desired temperature. Vaporizer A was charged with a weighed amount of butylene glycol diacetate; and the desired feed rate was set. Cold traps H_1 and H_2 were cooled to about −75° C. When the thermometer in the vaporizer reached the boiling point of the diacetate (191° C.), cock C_1 was turned to admit vapors into the reaction tube. A hot Nichrome wire was wrapped around glass tubing T to prevent condensation. The vapors were heated to about 430° C. by superheater E.

The moment cock C_1 was opened, an electric timer was started. The reaction was permitted to reach steady state conditions by running for about 5 minutes. At the end of this period cock C_2 was turned to permit the products to enter the main receiver, R, and the time was noted.

At the end of a run the condensed liquid take-off was carefully heated to the boiling point to remove dissolved butadiene, which was subsequently collected in a cold trap. The products collected in R_1, I_1, I_2, and L were weighed.

Three independent checks were obtained on the feed rate of vapors to the reaction chamber: (a) The voltmeter and ammeter readings and the calibration chart showed the amount vaporized. (b) A check rate was run either before or after the actual run, when cock C_1 was so turned that the vapors were going to condenser I. The condensed vapors were collected in a tared receiver over a measured time interval and weighed. (c) An overall material balance was obtained with the original charge to the vaporizer. The residue at the end of the run and the material collected in receivers beneath condenser I were measured. The difference was the input to the reaction chamber during the run.

Analyses were also made on the liquid take-off and the butadiene fractions. The take-off liquors from the pyrolysis contained acetic acid, unsaturated acetates, hydrocarbons (polymers of butadiene), unreacted diacetate, and dissolved butadiene. The following analytical method was used to determine the amount of the various materials present. It is based mainly on a method worked out at the Northern Regional Research Laboratory (2).

TABLE I. PYROLYSIS OF DIACETATE WITHOUT NITROGEN

Temp., °C.	Feed Rate, Grams/Min.	Contact Time, Sec.	Diacetate Input, Grams	Liquid Take-off Total, grams	Unsatd. esters Grams	Unsatd. esters %[a]	Polymer Grams	Polymer %[a]	Unreacted Diester Grams	Unreacted Diester %[b]	Acetic Acid Free, Grams	Acetic Acid Total input, grams	Acetic Acid % recovery	Butadiene Grams	Butadiene % conversion	Material Recovered, Wt. %
500	5.20	9.2	210.7	169.4	23.8	12.4	11.2	5.8	19.2	9.2	115.2	145.0	96.9	37.1	62.5	98.0
500	3.20	15.0	202.1	154.5	16.1	6.2	8.9	4.6	6.6	3.3	122.9	139.0	97.6	44.5	73.4	98.5
500	0.87	54.3	103.9	77.6	0.76	0.74	11.1	10.8	1.7	1.6	64.0	71.7	91.5	20.2	63.5	94.4
500	1.70	27.2	104.1	79.0	3.43	3.38	7.7	7.6	2.7	2.6	65.2	72.0	95.6	22.1	70.4	96.7
550	4.50	9.9	121.3	90.1	4.52	3.78	7.1	6.0	2.0	1.6	76.5	83.7	95.7	27.9	75.3	97.2
550	5.80	7.7	116.2	87.8	5.14	4.52	7.3	6.3	2.4	2.1	72.8	80.0	95.1	25.2	71.5	97.4
550	0.77	57.8	94.8	73.5	0.76	0.82	12.9	13.8	1.5	1.6	58.2	65.4	90.3	15.6	54.0	94.0
550	1.95	22.9	116.6	90.1	2.36	2.50	11.8	10.3	1.9	1.6	74.4	80.5	96.0	24.0	66.7	98.0
585	2.70	15.8	121.1	91.8	3.61	3.02	10.7	8.9	1.2	1.0	76.3	83.7	94.0	24.4	65.7	96.1
585	1.85	23.2	164.8	127.3	2.85	1.73	19.3	11.8	0.8	0.5	104.3	113.5	93.7	30.2	59.4	95.6
585	1.05	40.7	167.0	127.6	1.71	1.03	23.3	14.0	Negl.	0	102.6	115.0	90.0	27.9	63.8	93.1
585	5.03	8.5	160.9	118.7	5.75	3.62	13.5	8.5	2.1	1.3	97.3	110.0	91.7	37.4	76.0	97.3

[a] Weight per cent of diester reacted.
[b] Weight per cent of diester input.

TABLE II. PYROLYSIS OF DIACETATE IN PRESENCE OF NITROGEN

Temp., °C.	Flow Rates Diester, grams/min.	N₂, cc./min.	Contact Time, Sec.	Diacetate Input Grams	Mole % in mixt.	Liquid Take-off Total, grams	Unsatd. esters Grams	%ᵃ	Polymer Grams	%ᵃ	Unreacted Diester Grams	%ᵇ	Acetic Acid Free grams	Total input, grams	% recovery	Butadiene Grams	% conversion	Material Recovered Wt. %
585	1.1	550	8.5	76.7	22	56.7	8.2	8.2	2.7	3.6	1.1	1.4	46.7	53.0	95.5	19.5	83.2	99.2
585	3.8	615	5.2	144.7	46	107.3	14.0	9.9	3.1	2.2	2.8	1.9	87.4	99.6	97.1	34.7	78.9	98.2
585	2.1	550	7.1	126.5	35	92.5	11.5	9.2	3.9	3.1	1.9	1.5	75.2	87.1	95.0	32.5	83.9	98.9
550	5.4	595	4.6	221.0	56	177.0	41.5	20.3	2.4	2.1	16.4	7.4	116.7	152.5	98.1	43.0	67.8	99.5
550	1.3	580	8.1	94.6	25	71.4	14.9	16.6	1.4	1.6	4.0	4.4	51.1	65.3	94.8	22.5	79.5	99.1
550	0.79	530	9.7	87.4	17	66.7	12.5	14.7	2.1	2.5	2.2	2.5	49.9	60.2	96.2	20.3	77.1	99.6

ᵃ Weight per cent of diester reacted.
ᵇ Weight per cent of diester input.

The dissolved butadiene was boiled out of the take-off liquors and collected in a cold trap. A sample of the butadiene-free liquors was analyzed for total free and combined acetic acid; this provided an over-all check on the analysis. These liquors were then fractionated. One fraction boiled below 145° C. and the other above. Each portion was weighed and analyzed for free and combined acetic acid.

From these analyses, it was possible to calculate the acetic acid, unsaturated acetates (molecular weight 114), and unreacted diacetates in the liquid take-off. The combined acetic acid in the distillate boiling up to 145° C. was considered to be from the unsaturated acetate, while the combined acid in the fraction boiling above 145° C. was considered to be from glycol diacetate. The difference between the sum of calculated values of percentage content of free acetic acid plus unsaturated acetates plus unreacted diacetate, and 100% was considered to be the percentage hydrocarbon in the take-off liquors.
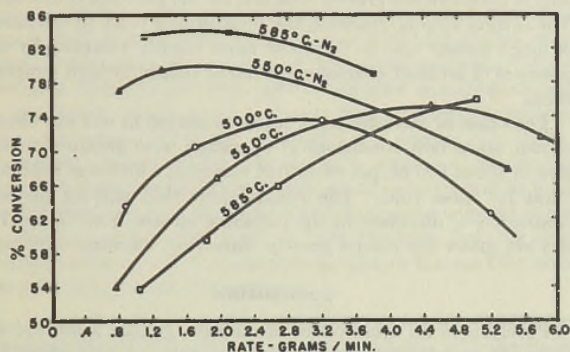
Figure 2. Conversion to Butadiene vs. Rate of Flow

Assuming these hydrocarbons to be polymers of butadiene, it was possible to calculate the percentage yield of each of the products from the diacetate fed into the pyrolysis system. The butadiene was analyzed by careful fractionation; and a fraction was collected boiling from −5° to 0° C. The nonvolatile material remaining was recorded. The butadiene analyzed in this manner was 98–99% pure.

PYROLYSIS REACTION

A complete study was first made of the pyrolysis reaction at various temperatures and feed rates to obtain information as to butadiene yields, unsaturated ester formation, hydrocarbon production, and acetic acid recoveries (Table I). Then a series of experiments was run at selected temperatures and feed rates to illustrate the effect of cracking in an atmosphere of nitrogen (Table II). The flow of nitrogen was measured by a calibrated orifice meter.

To compare results obtained by various investigators in equipment of varying sizes and to use laboratory and pilot plant results for plant design, a common expression for the rate of feed must be used. The general term is contact time, which is an attempt to approximate the time spent by the reactants in the reaction zone:

$$\text{contact time} = V_R/V_0$$

where V_R = volume of reaction zone
V_0 = volume of incoming stream per unit time at temperature and pressure of reaction zone

The lack of exact material balance is attributed to the destruction of some acetic acid at the temperature of the reaction. The recoveries for the runs without nitrogen, however, are good, ranging from 93.1 to 98.0% and averaging 96.4%. Important also from an economic viewpoint is the recovery of acetic acid which is also good, 90.0–97.6%, with an average of about 94%. Pyrolysis with nitrogen resulted in increased weight recoveries of 96.4 to 99.1%, and acetic acid recoveries from 94.0 to 96.1%. This is probably due to the retardation of acetic acid destruction at the higher temperatures by the presence of nitrogen.

Figures 2 and 3 show that for each temperature there is an optimum rate of feed at which a maximum yield of butadiene is obtained. At the slow rates lower temperatures result in larger yields of butadiene; at the faster rates, the curves cross and show higher yields. This is in line with theoretical considerations. At higher temperatures and slow rates, butadiene polymerization dominates the reaction; at lower temperatures and faster rates, incomplete cracking (only to the unsaturated ester) prevails.

Figures 4 and 5 show that at each temperature there is a steady increase in the amount of unreacted diacetate and unsaturated esters with decreasing contact times (increasing rates). These curves also illustrate that, for a given contact time, the percentage of unreacted diacetate and unsaturated esters decrease with increasing temperatures. In general, the percentage of unreacted diacetate is much less than the quantities of unsaturated esters formed.

The data for polymer formation (Figure 6) are not so regular as are the rest of the data, since the amount of polymer was ob-
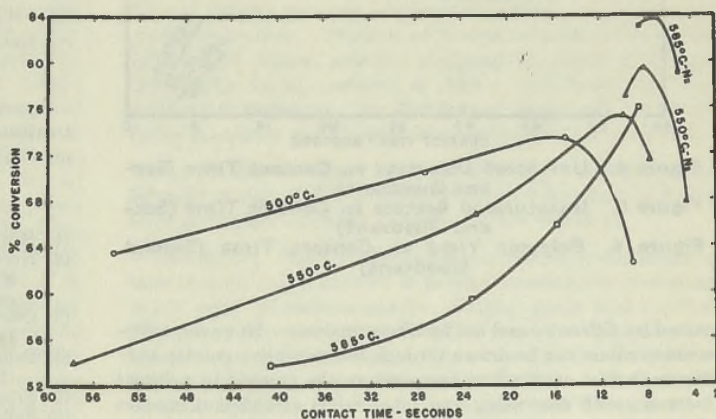

Figure 3. Conversion to Butadiene vs. Contact Time

This plot is in second quadrant because a high contact time is equivalent to a low flow rate.
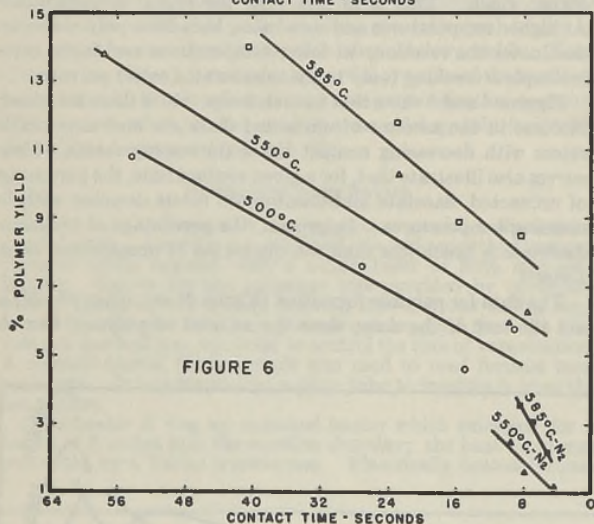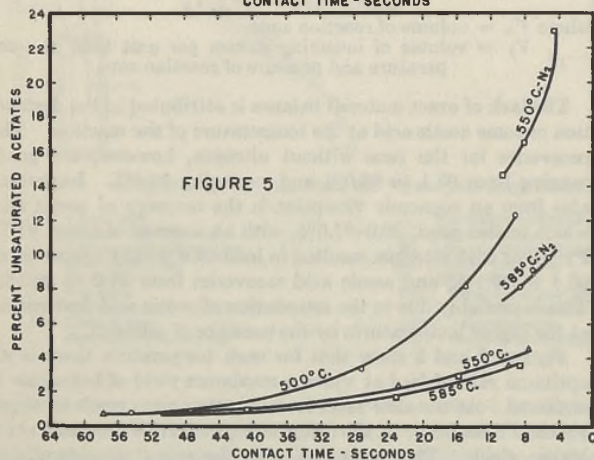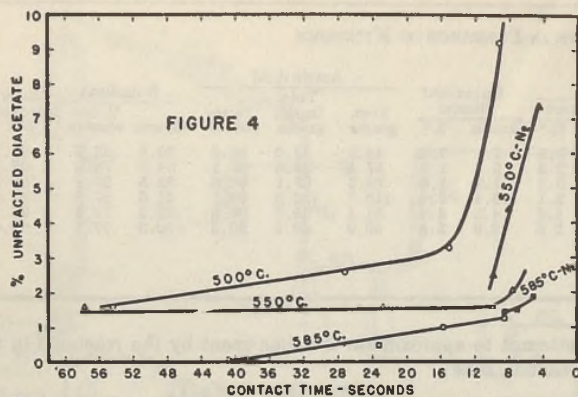
Figure 4. Unreacted Diacetate vs. Contact Time (Second Quadrant)

Figure 5. Unsaturated Acetate vs. Contact Time (Second Quadrant)

Figure 6. Polymer Yield vs. Contact Time (Second Quadrant)

greatest deterring factor for high butadiene yields. Thus, any scheme of operation which cuts polymer formation will greatly increase the efficiency of pyrolysis.

Pyrolysis in an atmosphere of nitrogen increased the optimum convers'on to butadiene (Figures 2 and 3) from 76% without to 84% with nitrogen. Most important, however, is the reduced amounts of polymer obtained under these conditions. At the optimum conditions of a contact time of 7.1 seconds and a temperature of 585° C. (Figure 6), only 3.1% polymer was formed, whereas cracking without nitrogen resulted in 9.0% polymer.

Simultaneously with decreased polymer yield, a greatly increased yie'd of unsaturated esters was obtained. Thus, at the optimum operating conditions for each method of pyrolysis (Figure 5), the percentage of unsaturates increased from 3.7 to 9.3%. The unsaturated esters can·be cracked further under the same conditions as the diester to give increased yields of butadiene.

The above results can be explained from the kinetic theory of gaseous reactions. Nitrogen is effective in reducing the amount of polymer formation because it lowers the butadiene concentration in the reaction chamber and also because the presence of oxygen, which is believed to be a catalyst for the polymerization reaction, has been eliminated entirely. The increased amount of unsaturated esters was attributed to the fact that the over-all reaction is a result of two consecutive reactions. The cracking of the diacetate to the unsaturated acetate is rapid and is the normal reaction below 500° C. where no butadiene is formed. This step is therefore not greatly retarded by the presence of nitrogen. The second step of cracking the unsaturated ester to butadiene is much slower and is therefore more readily retarded by the presence of an inert component, even at relatively high temperatures.

The effect of the amount of nitrogen passed in was not clearly shown, since best conditions of operation were obtained with a flow of about 600 cc. per minute of nitrogen, which was kept constant for these runs. The results show that varying the concentration of diacetate in the incoming stream from 50 to 17% did not affect the results greatly since they correlate very well.

CONCLUSION

Pyrolysis in an atmosphere of nitrogen greatly improved the performance of a laboratory cracking unit for converting 2,3-butylene glycol diacetate to 1,3-butadiene, and is recommended for commercial consideration. An optimum yield for one-pass unit of 83.9% conversion obtained, which probably could be raised to at least 90% by subsequent cracking. The optimum conditions of operation, as obtained in the laboratory, are pyrolysis to 585° C. at a contact time of 7.1 seconds, the diacetate being diluted by nitrogen to a concentration of about 40 mole % in the reaction zone.

LITERATURE CITED

(1) Hill and Isaacs, U. S. Patent 2,224,914 (Feb. 17, 1940).
(2) Northern Regional Research Lab., Summary of Research on Production of Butadiene from 2,3-Butylene Glycol by Pyrolysis of Diacetate, Aug., 1942.
(3) Othmer, D. F., Bergen, W. S., Shlechter, N., and Bruins, P. F., Ind. Eng. Chem., 37, 890 (1945).
(4) Othmer, D. F., Shlechter, N., and Koszalka, W. A., Ibid., 37, 895 (1945).
(5) Pittsburgh–Des Moines Steel Co., Research Bull. 7381-B (1942).
(6) Shlechter, N., Othmer, D. F., and Marshak, W. B., Ind. Eng. Chem., 37, 900 (1945).

tained by difference and not by direct analysis. However, representative lines can be drawn through the respective points; they illustrate that at constant temperature the amount of polymer increases with decreasing feed rates, while at constant contact time the polymer formation increases sharply with increasing temperature. A comparison between the amount.of polymer formed as against the amount of unsaturated esters (particularly at higher temperatures) shows that polymer formation is the

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors
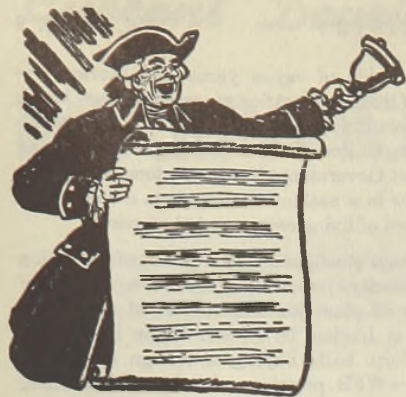
¶ AUGUST 3. Celanese Corp. of America announces formation of Viscosa Mexicana S.A., in Mexico City.

¶ AUGUST 5. Wm. H. Davis, director of Economic Stabilization, says President's Committee on Patent System is considering action to make patent rights more effective and will re-examine system in light of objectives to promote scientific progress.~~ A. W. Peake, president, Standard Oil of Indiana, says company is organizing chemical products department with Bruce K. Brown in charge of development and Wm. B. Plummer as manager.

¶ AUGUST 6. President Truman and War Department release information on use of atomic disintegration as a weapon against Japan. Power of bomb is said to equal 20,000 tons of TNT or have more than 2,000 times the blast power of what previously was world's most devastating bomb.~~WPB says limited quantities of nitrogen compounds and anhydrous ammonia for distribution without allocation will be released monthly, starting in September, for shipment to Puerto Rico and into States lying east of Montana, Wyoming, Colorado, and Arizona.~~Deputy Petroleum Administrator Davies says technical information collected from secret records of German oil industry will be made available immediately to American oil companies engaged in war program.~~Pekin, Ill., plant of Corn Products Refining shuts down because of corn shortage and company's Kansas City plant operates at half capacity for week.

¶ AUGUST 7. Aluminum Co. of America makes offer to Surplus Property Board to purchase and operate Jones Mill aluminum ingot plant on Lake Catherine and the Hurricane Creek alumina plant near Bauxite, both in central Kansas.~~Alfred P. Sloan, Jr., announces grant of $4,000,000 by Alfred P. Sloan Foundation for establishment and partial maintenance of a projected Sloan-Kettering Institute for Cancer Research, to be organized in conjunction with Memorial Hospital in N. Y. Charles F. Kettering, vice president and director of research, General Motors, will concentrate on organization of industrial techniques for cancer research. It will be a personal undertaking not connected with General Motors.~~P. F. Layedan, president Liquid Carbonic Corp., announces acquisition of Carbo Ice Ontario (Ltd.) of Toronto, Canada.~~J. Ward Keener, assistant to president of B. F. Goodrich, says since Pearl Harbor, U. S. has produced as much synthetic rubber as entire world's natural rubber supply from 1900 through 1917.~~Texas and Standard Oil jointly form a second Arabian Corp., Trans-Arabian Pipe Line Co. of Delaware, in connection with plans to build pipe line from Persian Gulf to eastern end of Mediterranean, W. S. S. Rodgers, chairman, board of Texas Co., reveals.~~PAW say present quantity of high-test automotive gasoline will be doubled immediately.~~WPB ways reconversion of industry will be made more orderly and millions saved by plan to turn over unfinished parts of some cancelled war contracts to agencies that need item being produced.

¶ AUGUST 8. Russia goes to war against Japan at 5 P.M. (EWT). ~~WPB places new restrictions on uses and permitted inventories of tin to conserve Nation's dwindling stockpile.~~WPB amends L-317 governing manufacture, delivery, and use of fiber shipping containers to increase small-user exemption.~~ Tennessee Eastman and Eastman Kodak reveal that they played a part in developing atomic bomb.~~OPA authorizes increase of 95 cents per 100 pounds in ceiling price on gum rosin.~~Board of directors of Magnesium Association accept invitation of Col. W. H. Jaeger, director of research, Army Industrial College, to form permanent industrial advisory committee on economic planning and research.~~M. W. Kellogg, president M. W. Kellogg Co., discloses formation of subsidiary 2.5 years ago to design one of major atomic bomb plants at Oak Ridge, Tenn.~~War Department denies reports that areas devastated by atomic bomb continue for years to react with death-dealing radioactivity.

¶ AUGUST 9. Navy starts construction work to house Navy Bureau of Ordnance research laboratories on a 938-acre project at White Oak, Md.[1]~~President Truman asks WPB to extend into the reconversion program five spurs and controls it applied in building up production for war, and calls in top military, diplomatic, and scientific advisers to discuss atomic bomb.~~ Aluminum Co. of America receives order from Army for 400,000 pounds of aluminum for manufacture of containers to store guns and ammunition.~~P. W. Litchfield, chairman, Goodyear Tire and Rubber, announces establishment of new rubber manufacturing plant in Union of South Africa.~~WPB says dyestuff consumers may increase color quotas for civilian use.~~Monsanto Chemical says many of its leading scientists have been closely identified with development of atomic bomb.~~War Department discloses that Brig. Gen. Thomas F. Farrell left Washington, by air, with atomic bomb 9 days before it was dropped on Japan.~~Chancellor Robert M. Hutchins of the University of Chicago announces that research which led to invention of atomic bomb will be continued at University of Chicago through two new institutes devoted to study of nuclear physics and metals. Institute of Nuclear Studies will be headed by Samuel K. Allison, professor of physics, University of Chicago, with Enrico Fermi, professor of physics, and Harold C. Urey, professor of chemistry. The Institute of Metals will have Cyril Smith as director and Clarence Zener as professor of metallurgy[1].

¶ AUGUST 10. President Edmund Ezra Day announces establishment of four $1,500 research fellowships for study of frozen foods at Cornell University's new School of Nutrition.

¶ AUGUST 11. Ralph K. Davies says several domestic refineries have received orders from PAW to begin immediately production of new superfuel aviation gasoline of higher grade than standard 100-octane rating.~~Administration calls for cooperation of management and labor to find jobs in face of tremendous cutbacks estimated as approaching $4,000,000,000.~~C. D. Howe, Canadian Minister Munitions and Supply and Reconstruction, says Canada has taken ownership of mines and extraction plants at one of world's two most important deposits of uranium.

[1] *Chem. Eng. News*, **23**, 1444 (Aug. 25, 1945).

¶ August 13. WPB promises industry aid in building additional manufacturing facilities for civilian products.~~War Department reveals that it borrowed more than 1,000,000 pounds of silver from U. S. Treasury to use in electromagnets at atomic bomb plant in Oak Ridge, Tenn., and that three different processing methods in separate plants are used in making atomic bomb material.~~Du Pont says it handled expenditure of $350,000,000 designing and constructing atomic bomb plants for Government through a profitless contract.~~Carboloy Co. reveals that a metal of unprecedented hardness was used in atomic bomb.~~Canadian Minister Howe says only the United States knows details of atomic bomb's manufacture.

¶ August 14. White House announces war ends.~~War Manpower Commission abolishes all manpower controls.~~WPB lifts controls on allocation of arsenic.~~OPA eases rules on methyl methacrylate and vinyl scrap.~~Department of Justice files civil action suit in U. S. District Court for Southern District of California, charging International Precipitation Co., Western Precipitation Corp., Research Corp., and an individual with violation of Sherman Antitrust Act in connection with electrical precipitation gas-cleaning units.~~Secretary of Interior Ickes suspends helium production activities at Cunningham, Kans., and Amarillo, Tex., plants.

¶ August 15. WPB lifts controls on all but a few raw materials. ~~U. S. Rubber announces it will double output of tires for farm vehicles.~~President Truman orders voluntary news censorship abolished.

¶ August 16. Goodrich Chemical awards construction contract for new semi-works plants at Avon Lake, Ohio, to cost about $600,000.~~WPB outlines broad plan for removal of production and materials controls.~~Six British and American companies and 10 of 11 executives charged with conspiring to violate Sherman Antitrust Law by monopolizing world supply of borax fined $146,000.~~Ira Mosher, president, National Association of Manufacturers, predicts very small percentage of workers need be out of employment for more than month as industry converts to peacetime production.~~Southern Regional Research Laboratory, U. S. Department of Agriculture, develops modified cotton fabric that does not mildew or rot.~~American Association of Scientific Workers submits eight recommendations to President Truman to help prevent use of atomic bombs in warfare and to facilitate application of atomic energy to peacetime uses.

¶ August 17. WPB drops controls on copper, aluminum, and steel for civilian production.~~Rubber companies in Akron area resume full-scale production of civilian tires.~~WPB announces partial relaxation of Controlled Materials Plan which does not affect outstanding civilian allotments or preference ratings.

¶ August 18. President Truman delegates broad powers to price, wage, and production agencies for return to free economy.

¶ August 20. WPB modifies glycol ether controls so consumers may buy up to 25 drums by offering end-use certificates and lifts almost 100 controls on production and allocating distribution of chemicals.~~Du Pont buys site outside Parkersburg, W. Va., for new plastics plant.~~Army and Navy give Department of Justice all-clear signal to proceed with 25 major antitrust suits heretofore postponed lest their trial inferfere with conduct of war.~~WPB cancels 210 controls.

¶ August 21. WPB says tin controls will stay until shipments from Far East are restored.~~J. K. Plummer, general manager Southern Agricultural Chemical Corp.'s southern division, says corporation will erect immediately $125,000 zinc sulfate plant at East Point to quadruple operations.~~Reconstruction Finance Corp. offers new rubber tube manufacturing plant located at Tuscumbia, Ala., for sale.~~WPB says all controls on DDT will be lifted August 31.~~WPB ends freeze for nylon yarns and

terminates export set aside of rayon yarns and fabrics.~~Irving Langmuir, of General Electric, at reception at Men's Faculty Club of Columbia University to honor six American scientists just returned from United Nations Congress of Scientists in Moscow, says "Soviet Government has a very long range view of importance of science in a nation which expects a continuous improvement in standard of living over a period of years".

¶ August 22. WPB says it will scrap its network of allocation controls and complex priority system September 30.~~Standard Oil of New Jersey reveals plans for construction of two petroleum research centers at Linden, N. J., and Baton Rouge, La. ~~Metals Reserve Corp. halts buying of foreign copper for November delivery.~~WPB promises retention of Combined Materials and Resources Boards for allocation of raw materials still in scarce supply, early revocation of construction order, and continued inventory controls.~~WPB removes restrictions on special sales of most idle, excess, and surplus materials.

¶ August 23. Sherwin Williams Co. announces development of wall paint mixed with DDT which will chase flies, mosquitoes, and other insects from a room.~~Streptomycin, new mold-made drug similar to penicillin, will be produced in new $3,500,000 plant at Elkton, Va., by Merck & Co.~~W. A. Gibbons, research director, U. S. Rubber, announces development of fabric made principally from chicken feathers.~~Du Pont resumes production of nylon yarn for women's hosiery and other textiles.

¶ August 24. Department of Agriculture says distillers may use 3,000,000 bushels of grain other than corn and grain sorghums for beverage alcohol and feed stuffs from September through December.~~United Nations Standards Coordinating Committee calls meeting to plan new international organization to harmonize industrial standards on world basis.~~WPB removes penicillin from restrictions on use and allocations, and lifts seven orders restricting use of paper by all branches of printing and publishing industry except newspapers, effective immediately.~~B. F. Goodrich develops new plastic claimed to be impervious to corrosive materials.

¶ August 26. WPB withdraws sponsorship of four proposed guayule rubber mills in California and cancels three projects to increase output of carbon black.~~Shell Oil plans construction of large recycling plant at Sheridan, Tex., to cost $3,000,000.

¶ August 27. Celanese Corp. will concentrate technological and research activities in textiles, plastics, and chemicals in central laboratory at Summit, N. J.

¶ August 28. House committee on executive expenditures unanimously votes for single surplus administrator to replace present 3-man Surplus Property Board.~~WPB's Rubber Bureau lifts restrictions on products manufactured of reclaimed and scrap and all synthetic rubber except butyl.~~NAM presents to Senate Banking and Currency Committee substitute program for Murray Wagner full employment bill.

¶ August 29. President Truman says combined Production and Resources Board, Combined Raw Materials Board, and Combined Food Board will continue for time being without change in authority or procedure.~~War Department reveals that Kellex Corp., a secret subsidiary of M. W. Kellogg Co., designed, engineered, and supervised construction of one of major plants at Oak Ridge, Tenn., and assigned title to patents on atomic bomb to Government.~~H. L. Derby, president, Manufacturing Chemists Association, warns that shortage of scientific and engineering manpower is bottleneck in reconversion and re-employment efforts of chemical and allied industries.~~Justice Department charges 13 mica corporations and 15 officials with violating the antitrust act.~~Rensselaer Polytechnic Institute establishes cooperative plan with industry to help replenish Nation's supply of scientific and technological personnel.

Current Developments in
EQUIPMENT AND DESIGN

Considering its small size, weight, and cost, the ordinary gasket has become a most important, specialized appliance.

Discussed by Charles Owen Brown

IN MODERN industry asbestos in various forms has properly displaced most of the old-fashioned leather gaskets, but even the finest asbestos product has limited use. Although far superior to leather and rubber at higher temperatures, it has definite limits at higher pressures. Rubber and asbestos have followed leather in general use. Harder, metalized gaskets and even solid metal gained in usefulness over rubber and asbestos. Although all of these types except leather are still employed, occasionally we find the gasket eliminated completely where joints are welded solidly, metal to metal.

The specifications which must be met by a satisfactory gasket are reasonably simple. The material selected must harmonize with conditions—inertness to the confined fluid, resistance to the working temperature, and sufficient fiber strength to permit confinement by a unit pressure of two to four times the working pressure without permanent set.

A glance through any of the catalogs of manufacturers in this country will reveal the diversity of gasket materials. Asbestos and rubber, usually in combination, are most frequently found. If some movement of the gasket is required in use, or if it must be removed and replaced frequently, the surface is impregnated with graphite. Where the wear and tear are particularly rough, or the configuration of the surface being sealed is complicated, an asbestos base may be partly covered or completely sealed in sheet metal. Such gaskets are used in spark plugs and motor cylinder heads. The chemist has a wide choice of thickness, both for the base filler sheet and for the covering metal, which may be of iron, steel, tin, lead, zinc, copper, brass, bronze, aluminum, nickel, Monel, chrome alloys, silver, or gold. Metal-bound gaskets are particularly valuable in chemical work because salt solutions will not penetrate the gasket to cause rupture by crystallization and loss by "creeping". Most joints can be made tight against low-temperature fluids at relatively low pressures with a soft gasket. This type of gasket should be filled with rubber or pitch to close porosity so that there is no seepage or crystallization. Whenever two smoothly machined surfaces are sealed, the gasket may be thinner, harder, and narrower. When the surfaces are rough and uneven—for example, at the angle flange top of a steel scrubbing tower—the gasket must be soft, thick, and of appreciable width. It is difficult to make such a joint tight when the flange is too rough and the gasket is unusually wide. If the bolts are stressed too highly, the flange and top cover will be deformed unevenly, after which it is even more difficult to remake the joint tight.

There are two ways to correct such a condition. One is to machine the flange and cover, which is difficult on large towers. The second is to use two gaskets—the outer, larger one is very hard and thin, the inner one is soft, resilient, and thicker. Figure 1 shows a cross section of the assembly. The outer thin gasket is so hard that the bolts cannot bend the flange or cover. If already bent it probably will straighten out as level as the hard gasket surface. The softer, thicker gasket is compressed to conform to the three sides of the enclosure made by the flange, inner surface of the hard gasket, and cover. As the pressure increases, this joint becomes self-sealing. Many gasket troubles arise from the type of joint and may be corrected by good design. For example, Figure 2 compares the treatment of two gaskets sealing the same level sight glass against 150 pounds steam pressure. In this type of gasket (or packing) the pressure between the gasket and the confining material should be over 150 pounds per square inch. Even then some steam may penetrate between the gasket and body for a quarter of an inch or so, until the 150-pound pressure has been broken down to a negligible value. This principle is used widely in both static and sliding seals. The gaskets of Figure 2 are solidly supported at D. In both designs even pressure is developed in the gasket by the tightening of nut E. The unit pressure on A, B, and C is the same in both designs, but in Figure 2a any penetration of fluid across the narrow joint at A

causes a leak at the threads to atmosphere, and the long sealed joint at C is useless. In the design of Figure 2b no leakage can occur until the long sealed joint at A plus C or the ample length at B have been broken down. The unit pressure on B in Figure 2b can be lower than in a and still make a tight joint. This point is an excellent reward for good design because glass is a supercooled liquid. There is the danger that the pressure required in the design of Figure 2a might induce the glass to flow.

Current design plays a most important part in specifying gaskets for high-pressure gas handling equipment. Too many types of high-pressure gaskets have been used and proposed to permit analysis here. One design, however, deserves mention as it is an improvement upon other high-pressure gaskets. This gasket (Figure 3) is known as the lens. Figure 4 shows its recent application to high-pressure tubing. It is made of the same materials as the body of the joint. The contact required for a perfect seal is almost a "line". Two important practical advantages result. The joint is easily made or unmade and the gasket falls out by gravity. The line contact surface area is so small that only a slight increase in total bolt load over that required to hold the end reaction will develop a unit pressure at the actual contact surface of twice to three times the working pressure. Under these conditions
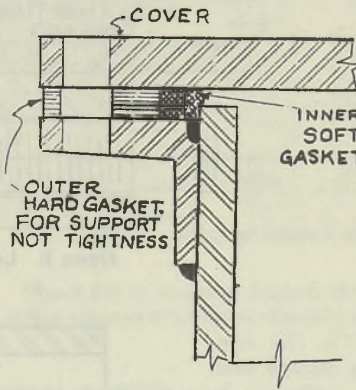

Figure 1. Cross Section of Gasketed Assembly

COVER

INNER SOFT GASKET

OUTER HARD GASKET. FOR SUPPORT NOT TIGHTNESS
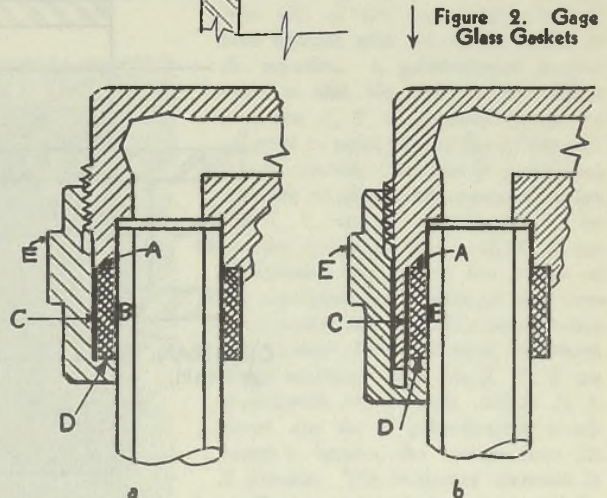
Figure 2. Gage Glass Gaskets

a   b

85

the joint is amply tight. Since the contact is only a narrow line, the elastic properties of the steel in the gasket and body material are easily used. The lens gasket need not be closely dimensioned, and there are no small grooves, rings, or recesses to machine in the body—just a flat surface to grind mirror smooth and a curved lens surface similarly treated on the gasket. Two pieces of tubing may be joined with a large, visible angle at the gasket. This is impossible with any flat gasket or step joint gasket, where the slightest deviation from a straight line must be corrected. When worn, this gasket can be reconditioned by a simple grinding operation, which shortens the tubing less than $1/_{64}$ inch. Reconditioning a step joint, after the edges of both steps have become upset and distorted, may shorten each tube end by $1/_8$ to $3/_8$ inch. In Figure 3 the limiting factor which fixes the thickness of the flanges is the thread between the flange and tubing. The metal removed by cutting the threads also lowers the tubing strength. These two features have recently been improved by the method of assembly shown in Figure 4. Tubing with a lighter wall may be used for any given pressure and the gasket area is strengthened at the same time. The forces in compression developed by the bolting can be directed inward through the gasket contact point. The use of this gasket and type of joint not only simplifies, but greatly lowers the cost of an excellent gasketed joint for gases at high pressures.
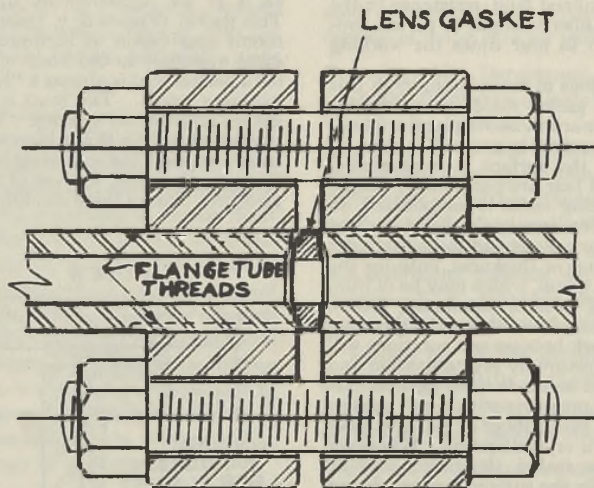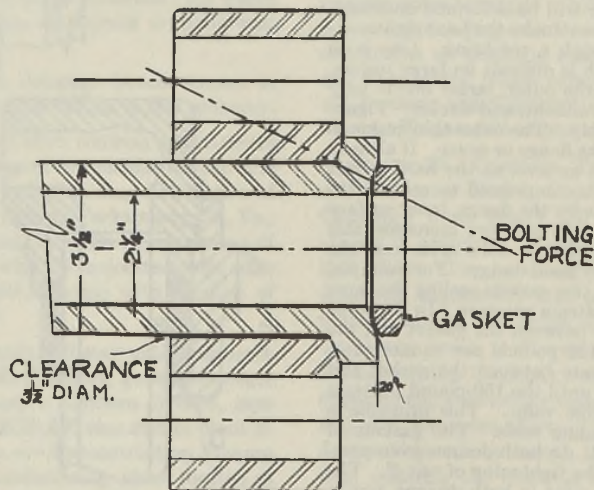

Figure 3. Lens Type of Gasket

Figure 4. Application of Lens Gasket to High-Pressure Tubing

Current Developments in

INSTRUMENTATION

Electrical computer speeds calculation of the results of instrumental analyses.

Discussed by Ralph H. Munch

MODERN methods of instrumental analysis such as infrared spectroscopy and mass spectroscopy are often capable of analyzing complex mixtures containing several components with great rapidity. Complete infrared or mass spectra can be recorded with some automatic instruments in 10 minutes. In simple cases qualitative and semiquantitative results can be obtained by an experienced worker merely by inspecting such records. However, where quantitative results for all the components of a mixture are required, it is necessary to solve a system of n linear simultaneous equations in n unknowns, where n is the number of components. In cases of this kind an hour or more of computation may be required to obtain the desired results from the instrument record.

The Spectro Computer, made by Engineering Laboratories, Inc. (610 East Fourth Street, Tulsa 3, Okla.), is an electrical device (Figure 1) for solving systems of simultaneous equations such as are encountered in infrared and mass spectroscopy. The analysis of a four-component mixture by infrared methods may be taken as an example. The optical density of the mixture is measured at four wave lengths, chosen so that one of the constituents has high and the other three have low absorption. The absorption coefficients of the pure components for each of the four wave lengths are also measured. From these data four simultaneous equations are obtained:

$$A_1W + B_1X + C_1Y + D_1Z = K_1$$
$$A_2W + B_2X + C_2Y + D_2Z = K_2$$
$$A_3W + B_3X + C_3Y + D_3Z = K_3$$
$$A_4W + B_4X + C_4Y + D_4Z = K_4$$

where K = optical density of mixture
A, B, C, D = absorption coefficients of components
W, X, Y, Z = concentrations of components
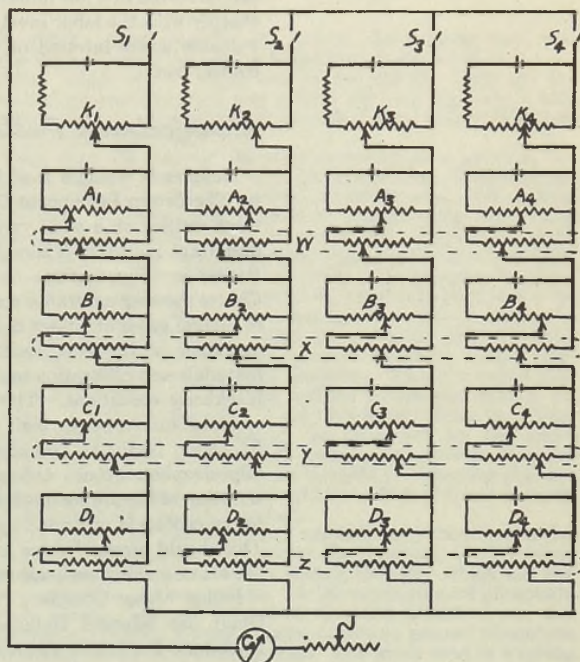Subscripts 1, 2, 3, 4 = wave lengths

Figure 2. Electrical Diagram of Spectro Computer

Figure 2 is an electrical diagram of the computer. It consists of four columns of electrical elements, each column corresponding with one of the four equations, and each element with one of the terms of the equation. A galvanometer is provided so that the sum of the voltages from the A, B, C, D elements can be adjusted to equal that of the corresponding K element. The four W potentiometers are simultaneously operated, as are the X, Y, and Z potentiometers. To use the computer, the A, B, C, D potentiometers are set to the values of the absorption coefficients of the pure components, and the K potentiometers to the values of the extinction coefficients of the mixture. With the X, Y, Z potentiometers set to zero, switch S_1 is closed, and the W potentiometer is adjusted to balance the voltage from its K element. The balancing operation is repeated for each column in turn, making
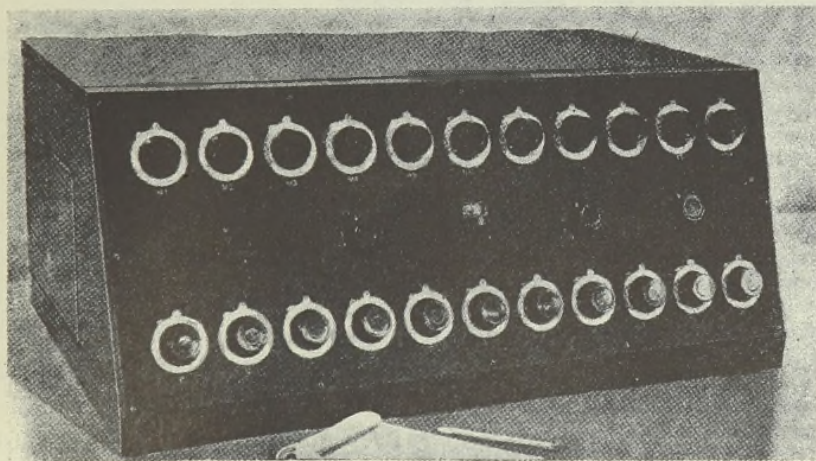

Figure 1. Spectro Computer

the adjustment with the X potentiometer for the second, the Y for the third, and the Z for the fourth. This cycle of operations is repeated until the galvanometer reads zero without further adjustment when any of the circuits is checked. Values of W, X, Y, and Z can then be read from the corresponding dials. The method of operation is equivalent to solving the equations by successive approximations. The computer can be obtained in two models, one to solve up to seven simultaneous equations, and the other up to eleven. Since seven circuits can be balanced in about one minute and three cycles are usually enough to give the answer with the required accuracy, seven simultaneous equations can be solved in a few minutes by this computer. This contrasts sharply with the labor involved in other methods, and should be valuable where infrared or mass spectroscopy is used for plant control work.

Manufacturers Publications

Number 5, Volume I, of *Instrumentation*, published quarterly by The Brown Instrument Company (Philadelphia 44, Pa) contains articles on a wide variety of subjects. Perhaps the most important is one by Thomas R. Harrison on "Industrial Use of Radiation Pyrometers under Non-blackbody Conditions". Charts showing emittance corrections to be added to the readings of several types of Brown radiation pyrometers are given, as well as tables of the best available data on emittance of various materials and calibration tables for Radiamatic pyrometers under blackbody conditions. The data presented should be valuable to those interested in high temperature measurements. A. O. Beckman, National Technical Laboratories, covers the subject, "Spectrophotometric Automatic Chemical Analysis". A description of the proper method of adjusting pneumatic controllers to the process is presented by E. D. Nunviller and J. P. Vollrath. This should prove of value to workers without long experience in the art of making such adjustments.

Bailey Meter Company (1050 Ivanhoe Road, Cleveland 10, Ohio) has released Bulletin 83-C, entitled "Bailey Thermo-Hydraulic Feedwater Regulators". It describes and illustrates improved designs of thermohydraulic generators and bellows-operated feedwater regulator valves, suitable for feed lines from $^3/_4$ to 6 inches in diameter. A clear explanation of the operating principle of this feedwater regulator is presented. Bull tin 62 describes Bailey open-channel meters for industrial wastes, sludge, and irrigation water. Meters of this type are generally used to measure flows of the order of millions of gallons per day. They are of both the direct mechanically operated type and the electronic telemeter type. A wide selection of registers having various combinations of indicating, recording, and integrating features is illustrated. Registers may be mounted on wall, panel, or pedestal and are said to be suitable for use with flumes, weirs, and atmospheric discharge nozzles.

Leeds & Northrup Company (4934 Stenton Avenue, Philadelphia 44, Pa.) has issued a revised edition of Catalog E-50B(1) describing its students' potentiometer. This inexpensive but versatile and accurate instrument is most generally used for meter calibration, thermocouple, pH, and electrolytic conductivity measurements. It is widely used not only in educational institutions but in industrial laboratories. Catalog N-00-664(1), just released, describes for the first time their complete line of instruments for the control of rotary kilns. This publication features a two-page schematic diagram of a typical kiln, showing the various points to which instrumentation is being applied. It should be helpful to those concerned with the more efficient operation of this type of equipment

Current Developments in
WASTE UTILIZATION

Chemical and engineering research can be depended upon to solve the waste disposal problems of industry.

*I*NDUSTRY will always have the problem of disposing of its waste materials. As new processes are developed, new wastes are created and older processes, together with their waste substances, are often made obsolete. Consequently the residual substances coming out of our industrial fabric are changing constantly in amount, type, and kind.

Utilization of the wastes of industry can be attained either within or without the industry producing the residual substance. The most desirable method is to use the waste in the plant producing it. Tremendous amounts of materials are being used in plants where, not many years ago, they were considered uneconomic materials. There are instances within every industry where a waste has been used advantageously. The substance, which was once a residue, now becomes the by-product. Each by-product was once a humble industrial waste which passed through the stages of technological investigation in order to become elevated to the status of a by-product. Cases can be cited where such by-products have often become the main product in an industry as a result of technological progress and change.

Rubber manufacture is an interesting example of an industry which consumes its own waste. About thirty years ago when automobiles became rather plentiful, the accumulation of worn tires became a problem. Rubber tires are composed of three major parts, the tread which is solid rubber, the carcass or fabric portion containing high-quality rubber in which the tire fabric is embedded, and the rim or "bead" which consists of steel wires set in a core of hard rubber wrapped with a rubber-coated fabric as the outer cover. At first only the tread portion was considered usable. Operators placed the tire over a wooden circular frame and skived the tread from the carcass with sharp knives whetted with water. After the tread was ground into small crumbs, it was mixed with mineral and vegetable oils, and then heated in open steam autoclaves to soften the rubber. After drying, this product was milled to a uniform plastic mass for incorporation into standard rubber tire formulations. It was necessary at that time to dispose of the carcass and bead portion of the tire as a waste material. When large piles of this residue were burned, they made spectacular raging bonfires which challenged the ingenuity of the few chemists within the organization. Research soon found the answer. The rims were cut from the carcass, and the carcass was ground to small pieces and heated in a strong caustic solution under pressure, with oils added to soften the rubber. After washing and drying, the product from this digestion was milled to a uniform mass which was good reclaimed rubber. Later it was found best to cut the rim from the old tires and process the tread and carcass portions together in this caustic solution. A substantial amount of reclaimed rubber has been produced by this method.

Then only the rims of the tires remained as a problem for disposal, because the steel wire reinforcement was difficult to remove, and the hard rubber core was not readily softened by known chemicals. The rims were carried to dumps along with other plant refuse and buried in the dirt and ashes. Huge dump areas were created. Here again chemistry came to the front with its ally engineering. Equipment was devised for stripping the steel wire from the rims, and new softening chemicals were found for the hard rubber portion. The disintegrated rims, without the steel wire, were heated with alkali and softening oils for a long period in steam, under pressure, to make a reclaim rubber suitable for use in many mechanical products. Thus the entire portion of old automobile tires was utilized within the rubber industry. But the reclamation of old tires is now about to change again. Synthetic rubber cannot be processed by the same methods as natural rubber. New reclaiming methods must be found in the laboratory which are capable of softening and desulfurizing vulcanized synthetic rubbers. This will not be easy but chemistry will find the answer.

Some may think that chemistry can help only those industries engaged in chemical manufacture or those related to chemistry. Let them consider the case of a mining industry which did not use chemicals in any operations. In the production of phosphate rock in Florida, the rock is crushed, the sand is washed out, and the crushed product is wet-screened to obtain ground phosphate rock for shipment to fertilizer plants. The water used in washing contains, in addition to sand, a considerable portion of finely divided phosphate particles which are too small for collection on the screens.

Discussed by Harold R. Murdock

Harold R. Murdock is a consulting chemical engineer who has been engaged in industrial research and manufacture for over thirty years. During the past sixteen years he has been director of research for one of the country's largest pulp and paper mills. He was also vice president and general manager of a company manufacturing organic mercurial compounds for use in both the medicinal and industrial fields. His experience has been diversified. His knowledge of the chemical treatment of wood, the reclamation of rubber, the manufacture of intermediates, dyestuffs, and pharmaceutical chemicals, the compounding of varnishes and lacquers, and other activities, has served as a reservoir of experience to aid him in the interpretation of problems in industrial waste, a subject in which he is now a specialist. His headquarters are at Asheville, N. C. The editors welcome him to the staff of contributing editors, and know that his monthly column on industrial wastes will be valuable to others in this field.

Waste Utilization

The spent water, containing sand and fine phosphate, is discharged to large lagoons to settle out the suspended matter so that the clarified water can be re-used. These lagoons fill up with sediment, and new lagoons are made from the pits resulting from the mining operation. Until recently this finely divided phosphate rock in the lagoons has been lost. Chemists have recovered this value by flotation of the sediment dug from the lagoons with mineral oil containing oleic acid. Cheaper substitutes which contain fatty acids related to oleic acid, such as the tallol recovered from the pulping of southern pine, have made this process economical. Now these dumps of sand and finely divided phosphate rock are being reclaimed by flotation tables and fatty-acid-containing chemicals.

The utilization of waste materials in industries other than the one which produces them has tremendous possibilities. Such opportunities are often overlooked by industry. This type of application requires a high degree of ingenuity and resourcefulness, an insatiable curiosity, and a broad understanding of the processes existing in other manufacturing establishments. The chemist can be of particular help in this method of finding an economical use for a waste material.

Some years ago the writer was associated with a wood pulp mill which was erecting a plant in a new location. The plant was to operate the so-called kraft process commonly used in pulping pines. The chemical generally utilized in the kraft process is sodium sulfate in the form of salt cake. Rather than purchase the customary chemical, it was suggested that the organization look about for substitute waste materials. Many of the dry salt lakes reasonably close to the mill site were investigated. In all of these deposits, sodium chloride was found as a contamination of the Glauber salt. A method for separating these salts was necessary, and Glauber salt had to be dehydrated to sodium sulfate in order that a suitable substitute for salt cake might be obtained. This operation required a rather substantial investment, and it was recommended that the search be continued.

It happened that this mill was also installing a chlorine plant to bleach the pulp to high whiteness. The chlorine was to be made by the electrolysis of sodium chloride in the conventional way, which yields by-product caustic soda. By the orthodox method of evaporating the cell liquor and separating sodium chloride crystals from the caustic solution as evaporation proceeded, a commercial grade of caustic soda could be produced. We learned that oil refineries used caustic soda solutions to remove hydrogen sulfide as well as other organic sulfides from the crude oil, and that the residual caustic solution was relatively concentrated. This waste product from the oil refineries was a dark tarry solution composed essentially of sodium sulfide and other sulfur-containing sodium salts. It was foul in odor. When added to the stream it created a serious problem for shipping and was a nuisance to riparian-right owners downstream for many miles. The B.O.D. value of the waste was high, and an oily tarry matter separated from the aqueous portion of the waste upon dilution with the brackish waters of the stream. The refineries were in a desperate situation. State authorities had brought suit for the abatement of the nuisance. Skimming tanks and other such procedures had only partly solved this aggravating problem. Refinery officials were only too glad to listen to the pulp mill chemist who offered to buy this stinking black tarry residue.

The processing of a kraft mill to regain the chemicals for subsequent use is essential to the economy of the process. Briefly, this recovery of chemicals consists in evaporating the spent liquors from the pulp washing step, then incinerating the concentrated solution and simultaneously adding salt cake to these liquors. The organic matter present in the black liquors reduces the sodium sulfate to sodium sulfide during incineration. The process is completed in a smelter type furnace, and molten sodium carbonate and sodium sulfide flow from the smelter into dissolving tanks. It was apparent that the oil refinery waste solution could be used in a process of this type. The refineries were asked to concentrate their waste solutions moderately to make it economical for shipment to the pulp mill. The new make-up chemical worked admirably in the pulp mill operation. Some of the advantages of the refinery product were not fully appreciated until the material was actually used in the kraft mill. This application was possible because of an understanding of the pulp mill processes. If the oil refineries had possessed such information, they could have overcome their waste disposal problem sooner and avoided litigation and other contributory nuisances. Certainly other industries and other waste materials have similar chances for utilization if their problems are studied carefully.

Current Developments in

PLANT MANAGEMENT

Time studies have merit in chemical industries for other purposes than determining incentive rates.

Discussed by Walter von Pechmann

Time study is usually regarded as a medium to determine incentive rates; its merit for other purposes is often not given sufficient consideration. More than once established rates have been rechecked without need because the time-study man who was hired to set incentive rates had nothing else to do. Management could well utilize time-study men not only as rate setters but as industrial engineers whose job is to investigate phases of the organization where the reduction of a time cycle will result in increased revenue or where time-study statistics will make it possible to conduct business in a more efficient manner. Production, which often considers time study as unrelated to its activities, should also be made to realize that the time-study man can render services which will increase the efficiency of operations.

The discussion which follows cannot cover all the possibilities of putting the time-study man to work in an organization. It is intended merely to show examples of the various ways of making improvements by the stop watch.

Job Layout

The laying out of jobs in the chemical industry is often difficult because processes do not always require an operator's continuous attention but have to be interrupted frequently. This makes it necessary to assign one man to more than one operation. The experienced foreman is usually able to schedule the work so that idle time is almost nonexistent. The fact, however, is often overlooked that the elimination of idle time does not necessarily mean the best utilization of manpower. Unnecessary movements or avoidable physical exertion is just as wasteful as idle time. By breaking down an operation into its various elements and timing each element, such shortcomings are brought to daylight. I recall one instance where the time study revealed that 22% of an operator's time was consumed in the handling of materials. He had to lift the hundreds of bottles used daily several times in order to complete his assignment. By adjusting the heights of the work benches to a common level, eliminating shelves, bridging the gaps between the benches, and sliding the bottles instead of lifting, it was possible to reduce the handling time to a fraction of the original figure. It is of interest that the stop watch not only brought out the need for improvements but also enabled us to measure the extent of our accomplishments to a point where further changes would not be practical.

Flow of Work

Arrangement of the flow of work on small operations is often left to the foreman. Surprisingly little attention is paid to the time element because of the orthodox belief that operations are best performed in the sequence in which the specifications are written. Time studies will reveal shortcomings in flow of work layouts by calling attention to the fact that employees either are not fully occupied or else have to wait for an operation to be completed before they are able to continue with a task. For example, a study reveals that operator 3 causes operators 1 and 2 to wait six times every hour for two minutes. Operator 5 is working below normal speed because insufficient work is entailed in his operation. On the basis of these findings the flow of work can be rearranged so that all employees will be kept equally busy and thus eliminate idle time. The flow of work could be arranged as follows: Operator 3 hands his surplus work to operator 5 who is able to take on additional work. Both operators pass the material to operator 4 who finishes his part of the work and then gives it to operator 5. A change in working facilities can usually be made with little effort. In this instance two work benches could be placed facing each other with a third one alongside. This would enable operator 5 to accept work from either operator 3 or operator 4. Conveyers, chutes, or trucks have to be used where operations involve equipment which cannot be moved.

Equipment Design

Equipment design plays an important part in the chemical industry because standard type equipment often cannot be used. Manufacturers who build their own machinery have to depend mainly on statistical information available in production, in order to decide whether to replace manual work by automatic equipment. Furthermore, certain time elements (such as time to drain a kettle, cleaning time, most efficient mixing speed, etc.) must be known to the designer before such decisions can be made, as to size of orifice, type of material, and kind of motors to be used. A dependence on the foreman's ability to supply these data has more than once resulted in the construction of equipment which could not be used or which had to be rebuilt before it worked satisfactorily. Time studies on hand operations or existing equipment not only facilitate the design of new machinery but also allow the construction of equipment whose capacity will fit harmoniously into the time cycle of other operations. Occasionally these studies reveal that automatic equipment is not needed at all. In one instance management was prepared to appropriate a considerable amount of money for building a device to speed up an operation. Time studies of prevailing hand operations showed that most of the operators made only partial use of their left hand. After minor changes had been made on work benches and proper instructions given to operators, output was increased to such an extent that the idea of building the automatic device was abandoned. It is evident, then, that a thorough time study should be made on existing performance before decisions are made to replace hand work by machinery.

Materials

Time studies for purchasing materials may seem to be carrying matters too far. However, since different times are required to convert identical materials in various forms, it is wise to weigh higher purchasing price against the amount of money which can be saved by using the most workable material. Purchasing agents in the chemical industry should be conscious that quantity and quality of materials are

Plant Management

not the only factors worth considering. Many a concern has saved by buying material which was more expensive but which reduced labor wherever it was used.

Industrial Relations

The merit of time study for installing job evaluation systems is generally recognized. Physical exertion, idle time, and other important factors can be evaluated in this manner. Occasionally it is possible to use time-study figures for the establishment and maintenance of merit rating systems. Employee grievances or union complaints can often be settled quickly if management is in a position to produce time-study data. In plants where ability tests are conducted before workers are hired, the time-study man can develop testing methods which are representative of actual conditions in the shop.

Accounting

Where standard cost is established on the basis of actual job performances rather than on previous average cost, time studies are essential. An accurate estimate of the cost of an anticipated product depends to a degree upon obtaining reliable labor figures. The stop watch is more dependable than the foreman's figures which may be based on personal feelings or on poor production recordings. The value of time studies on accounting job performances is not given sufficient consideration. The work of an accounting clerk does not vary in principle from the job performance found in the factory. It is reasonable to assume that more time studies on clerical operations would result in better accounting technique and less fatigue to white collar workers.

Management Information

If management is to make quick and intelligent decisions, reliable statistical information must be on hand when needed. The time-study man can accumulate these data in his spare time by observing machine speeds, the time required to set up or change over equipment, and the average job performance.

Conclusion

A particular advantage of time-study work is that the data obtained for one purpose can often be used for another. Statistical material compiled by the time-study man and made available to all sections of a plant will not only facilitate the rendering of decisions but also bring about a more thorough understanding of production problems in sales, purchasing, and personnel departments.

In closing I should like to warn against utilizing personnel inexperienced in time-study work. The technique of correctly starting and stopping the watch is only a minor problem to the qualified time-study man. He must know when his readings should be taken on an average basis and when it is better to use the so-called selective method. He must be able to break down a job into its fundamental elements before the study is made. He must have the ability to get along with workers. He must know which time factor to select and how to compensate for time lost by starting and stopping, fatigue, and minor interruptions which are beyond the control of the operator. Such work is professional and therefore should be assigned to an industrial engineer or to an employee who has taken one of the many courses in time study which are available at little or no cost in every major city.

Last-Minute Flashes
FROM THE EDITOR'S DESK

SUDDEN end of World War II frees industry of two hundred and fifty supply regulations and chemical manufacturers of over one hundred controls, sets wheels in motion for production of billions of dollars worth of consumer goods.

★ War had increased nylon production threefold, from 8,000,000 pounds in 1940 to a current capacity of 24,000,000 pounds. Stockings will have first call.

★ Controlled Materials Plan will officially end September 30.

★ Some civilian restrictions will stay for a while—tires, sugar, meats, oils and fats, Pullman travel, leather footwear.

★ Standard Oil Company of New Jersey announces it will erect two research centers, one at Linden, N. J., the other at Baton Rouge, La., at a cost of $8,000,000.

★ Hercules Powder Company and Rohm and Haas boost employees' wages 10% to compensate for reduction in work week.

★ Insufficient sugar supplies predicted by Bureau of Agricultural Economics, despite production increases in 1946 by Cuba, resumption of output by Europe and Philippines.

★ Acid plants and other sulfur consumers in Atlantic states protest rate of 9 dollars per ton proposed for coastwise shipments of sulfur from the Gulf. This rate was set by War Shipping Administration.

★ President Truman orders immediate suspension of Lend-Lease operations. Allies may acquire through purchase, if they desire, $2,000,000,000 worth of nonmunition goods still here as well as stock piles abroad worth $1,500,000,000.

★ The construction industries now await green light and materials which will permit them to go ahead with $10,000,000,000 worth of building. The federal shipbuilding program meanwhile is slashed $425,000,000 through cutbacks involving 135 vessels at sixteen shipyards.

★ Despite manpower handicaps, the potash industry delivered 434,008 short tons of salts in the first quarter of 1945 with a K_2O content of 231,200 tons. This was a gain of 2% in volume and 8% in K_2O as compared with the same period in 1944.

★ The Japanese estimate that the two atomic bombs killed 70,000 persons outright, wounded 120,000, and rendered 290,000 homeless. Many more bodies are buried in the ruins of Hiroshima and Nagasaki.

★ "Women chemists", at least, will rejoice that nylon stockings will be available shortly.

★ Du Pont Company will expand plastics activities through the construction of a new unit at Washington, near Parkersburg, W. Va., and will build new nylon capacity at Martinsville, Va.

★ Paperboard production drops 29.9% in the first postwar week, and new orders fall 39.9% below figures of a year ago.

★ Rayon production during the second quarter of 1945 was 3.4% greater due to expanding viscose yarn output for tires. Combined yarn and staple rayon production between April and June was 200,600,000 pounds.