INDUSTRIAL
EDITION
VOL. 26, No. 4

April, 1934

Industrial AND ENGINEERING Chemistry

VOL. 26, CONSECUTIVE NO. 12

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY
HARRISON E. HOWE, EDITOR

PUBLICATION OFFICE: Easton, Pa.

EDITORIAL OFFICE:
Room 706, Mills Building,
Washington, D. C.
TELEPHONE: National 0848
CABLE: Jiechem (Washington)

ADVERTISING DEPARTMENT:
332 West 42nd St.,
New York, N. Y.
TELEPHONE: Bryant 9-4430

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16,000 Copies of This Issue Printed

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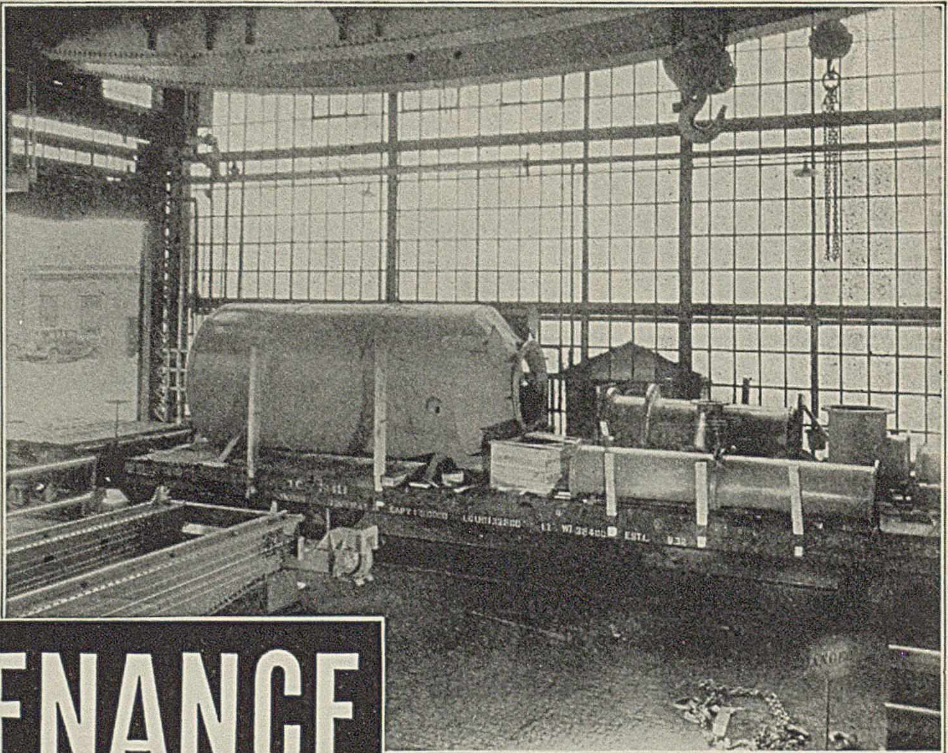
What Are Evaporation Costs?

MAINTENANCE

. . . ECONOMY DEPENDS FIRST UPON THE PROPER CHOICE OF MATERIALS



● Maintenance costs are most frequently hidden costs and rare is the superintendent that knows these costs for each piece of equipment. Maintenance can best be combated by the choice of suitable materials at the time the evaporator is purchased. The list of available materials is increasing year by year and a constant study must be made to keep in touch with developments.

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Entered as second-class matter at the Post-Office at Easton, Pa., under the Act of March 3, 1879, as 42 times a year. Industrial Edition monthly on the 1st. News Edition on the 10th and 20th; Analytical Edition bimonthly on the 15th.
Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

THE LISTENING POST

Bromine Production in the United States was multiplied more than 4.5 fold in the decade following proof of its value in motor fuels made knockless with tetraethyllead. Within the past year a single plant using new operating methods and sea water as its raw material has gone into production which increases the American supply by another 50 per cent. Nor is this the only interesting and important feature of this unique operation described in some detail by Stewart (page 361). In this account one finds described the whole history of a typical chemical engineering development from the laboratory determination of the workability of the process, pilot plant operation to learn the essentials of its engineering embodiment, the search for a proper site in relation to raw material, and finally the completion of the projected plant for commercial operation. Tapping the boundless supplies of raw material in the oceans has in it, too, an element of romance (comparable with that of utilizing the atmosphere) which cannot be entirely removed by bringing mountains of ocean to the land instead of sending a chemical-plant Mahomet to sea in a ship, as was done earlier.

Iodine Production, too, has been a child of depression in the United States with the result that brines from the California oil fields are now able to yield our full national requirements of this essential halogen, and another article is added to our declaration of economic independence of alien-controlled sources of industrial raw materials. This development, from trouble experienced in breaking up emulsions of crude oil with brine to a full-fledged national asset, is described by Robertson (page 376) who supplies another striking example of how a new process successfully applied can convert a material from one to be avoided on account of price to one seeking markets to consume potential production. A nuisance waste has been converted into a new national asset.

Aluminum Priming of wooden structures to be painted has been the subject of some disagreement among paint people. Some have vigorously held that it possesses striking utility and others have not been lacking to put forward the contrary view. Browne (page 369) gives us here the results of a long, careful series of test paintings conducted in a number of different environments which supply facts on the subject to demonstrate the value of this technic. His conclusions from a host of exposures of house paints to natural weathering are distinctly favorable to aluminum paint as a priming coat.

Clouding of Vinegar, unimportant in the days of home manufacture, is a most undesirable characteristic in the product of industry which must be in glass, without benefit of the vinegar barrel in the grocer's back room to hide its unattractiveness. Saywell (page 379) describes a successful method of making vinegar permanently clear and bright which may well find application in the clarification of other fruit products marketed in glass.

Heat Transfer, the ever present problem of plant and process design, receives important attention in several current discussions. Hebbard and Badger (page 420) develop formulas for calculating the heat transfer characteristics of vertical tubes. Kirkbride (page 425) presents another attack on the same problem. Colburn (page 432) considers the case where turbulent motion enters the condensation problem.

Absorption Tower Design has been studied by Cooper, Drew, and McAdams (page 428) from the point of view of liquid flow in wetted-wall columns.

Paint Driers have been developed to a point where their use is becoming standardized, and a great industry is busy supplying them. The characteristics of modern driers based upon the sure ground of careful research are contrasted by Elm (page 386) with the crude use of lead and umber by craftsmen of a century ago. The development of the theory of driers particularly within the past decade is outlined, and some prophecies of future trends complete the picture of this important phase of paint and varnish manufacture.

Plotting Data from a few experiments in a way that gives intermediate points without the labor of determining each separately saves much time and energy in development. Smith (page 392) describes a method of representing the data of ternary systems graphically which largely increases the value of each experiment's application. The typical case treated is that of the properties of mixed solvents, water, methyl alcohol, and isobutyl alcohol, but the utility of the method goes far beyond this series of mixtures.

Phosphoric Acid of rock phosphate has been made available to growing plants by treatment with sulfuric acid and latterly by volatilization processes. Basing their research on previous findings that reduction of the fluorine content of the raw rock increases the availability of its phosphate, Reynolds, Jacob, and Rader (page 406) have investigated the effectiveness of water vapor and silica in a calcining furnace in attaining this end. The results given form the basis of conclusions that direct calcination of rock in the presence of steam and silica will yield available phosphate and the hope that the process may become commercial.

Fractional Solution Methods based on distribution of materials between immiscible solvents have been developed and applied to the separation and concentration of vitamins. Cornish and his co-workers (page 397) describe in considerable detail the theory of such a method and its adaptation to the vitamin problem. In the course of this investigation a piece of equipment was developed capable of carrying out half a million fractionations within a two-day period. The application of the principles of the method to other materials promises interesting and important results. Its theory is also developed mathematically by Evans (page 439).

Factors Affecting the Color of Carbon Black in its various applications, particularly in inks and paints, are discussed by Wiegand and Snyder (page 413) who supply important data for users of this pigment.

Salmon Liver and Salmon Egg Oils possess vitamin potencies entitling them to definite places as sources of these dietary essentials, according to Lee and Tolle (page 446). Many fish oils are shown to be more potent than cod liver oil in this respect.

Raffinose, a sugar occurring with sucrose in beet molasses and causing much trouble in the crystallizing operations of beet sugar refineries, can become a commercial commodity if uses for it are found, according to Hungerford and Nees (page 462), who describe a method of separating it from beet molasses and the properties of the pure product.

Faced with the Necessity of correcting all boiling points for the high altitudes of Colorado, Germann and Knight (page 467) have devised a method of plotting vapor pressure–temperature relations which allows them to read correct values of either from the chart when the other is known. The method used is applicable to other similar problems.

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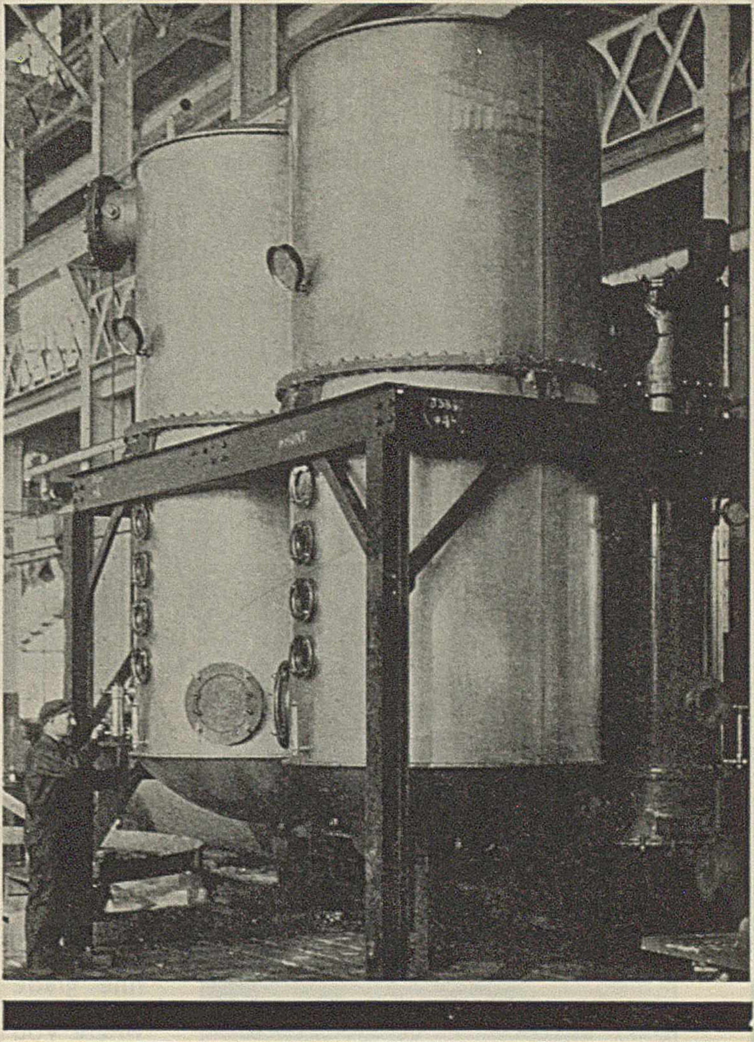

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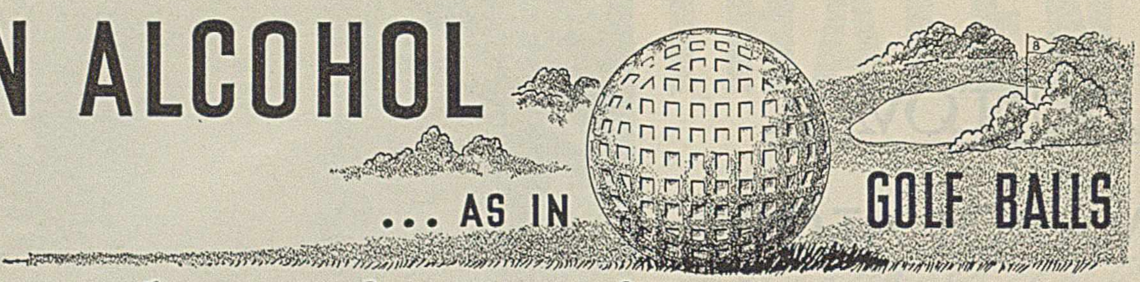

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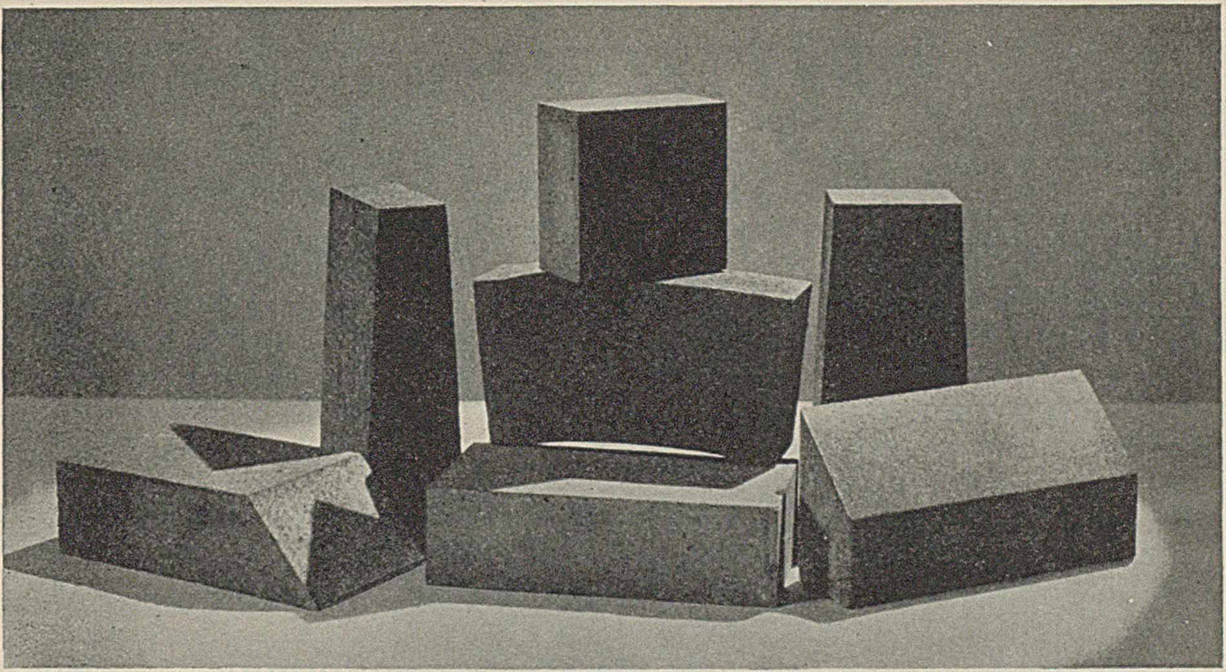

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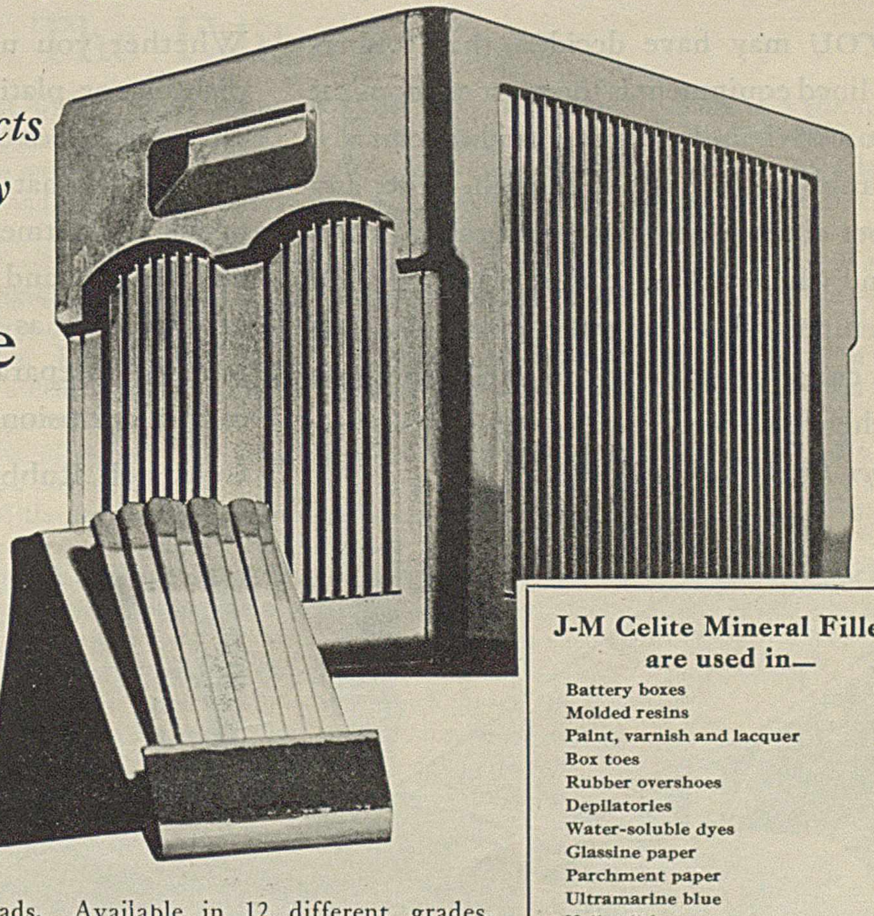

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Industrial
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VOLUME 26
NUMBER 4

APRIL
1934

HARRISON E. HOWE, EDITOR

The Editor's Page

STRIKES. At the present, when so much is being done in the interests of labor and labor is doing so much for itself, strikes seem to be more numerous than in any recent times and quite as difficult to settle as in the days when there was less machinery for that purpose.

When we read of these strikes we wonder if those engaged in promoting them have ever become familiar with the story of Sandwich glass. Here was a comfortable enterprise, conducted in a delightful little village which was supported by the glass factory. The employees achieved a high degree of skill and for their day were far better paid than any of the crafts for miles around. The owners of the factory showed no evidences of taking unreasonable profits and all this was before the day of extravagant bonuses or the introduction of some of the practices which of late have done so much toward discrediting the capital system. It seems to have been a rather ideal community enterprise with products enjoying a wide distribution.

However, in the 80's there came a time when the employees talked things over and decided that the plant could not operate without them, and even though they were well paid, here was an opportunity to obtain a larger income for themselves. The management may have been somewhat to blame for the trend things took, but at any rate a strike was called, and then the owners carefully considered their own position. They decided that the enterprise was not so profitable that they need continue with the workers in the frame of mind which was evident. In place of arbitration or strike breakers, of which we know more today, these owners decided to quit business, and this they did. The result was that the skilled workers either had to move elsewhere or seek other pursuits. Sandwich became just an interesting Cape Cod village. Even the factory burned, and there is nothing left but a scrap pile where we have helped to dig for samples of some of the glass to indicate a little more of the developments there and to find further evidence of the skill that disappeared and formulas that are no longer utilized. Sandwich glass is now an object of collectors, but the industry has long since disappeared.

THINGS. In "Boots," familiar as a poem and a favorite song, we find depicted the reaction of a soldier who was obsessed with the monotony of an object upon which his attention had become fixed. Boots too were symbolical of a routine existence, the very narrowness of which had become oppressive.

The same sort of reaction results from continuous contacts with just things—all manner of things. Material objects are necessary to our mode of living; even primitive men treasure their few possessions. When a surplus is developed and some leisure results, life grows complex, and we accumulate more things. We begin with implements necessary to an easier way of accomplishing objectives, and some of us end up with collections of historical or sentimental value. Rivalry becomes acute for the unique specimen required to complete the collection and money values soar so that the possessor must keep the thing in a safety deposit box or storage vault, enjoying only the sense of owning that which no one else may acquire. Some collections require storehouses of great capacity for their accommodation, and only an occasional specimen or two may be removed for such enjoyment as its display may bring. We are all hoarders in a sense and pity the man who has no hobby, but do we never grow tired of just things?

It all depends on whether one uses them as means to an end or allows himself to be dominated by them. The test comes when one is deprived of the things he has considered dear. Can he rise above the new condition and find the more lasting values in life?

A friend in New Zealand describes a district, almost wholly devoted to sheep farming, which was peculiarly affected by the collapse of the wool market and the low prices of lamb and mutton. After drought which continued for almost three years, conditions were just about as difficult as they could be, when an earthquake catastrophe, followed by a fire in the principal towns, not only caused great damage but a deplorable loss of life. One might have expected this succession of terrible disasters to leave the people hopeless, but on the contrary their reactions form a particularly interesting and significant study in human psychology.

The survivors were so grateful that their lives had been spared that their material losses seemed secondary, even though most of their possessions had vanished. What they prize more than anything else is the spirit in which those who have been stricken have met the situation, and the sympathy, kindness, and practical assistance shown by their more fortunate fellows in other districts. Today they see things and assign values from a different perspective. They realize that mere things have only a transient value or importance, that what they possess today may be gone tomorrow. They freely acknowledge that, like so many others, they have placed too much importance upon material success, possessions, and advantages, to the subordination or exclusion of human contacts and friendships, the simple virtues, and the eternal verities.

We all know instances of men who, beginning life with a view to accumulating things and the resources which make them possible, have placed emphasis on altogether different values as they have grown older. The depression which, praises be, seems definitely to be on its way out, has taken its toll in lives and among the living. Many a man has visibly aged and shown signs of breaking. Most such have been dominated by a single interest, and when a serious derangement of that interest has taken place there has been too little else to steady them. However, many who have not had things to share have performed a valuable service in directing attention to interests that are more lasting, in furthering friendships, and in strengthening morale.

Of course we must have things, more and better things, in the production of which chemists are directly interested. Let us retain our domination over them but fix our goal at some higher level, so that no temporary interruption may find us with a sole ambition, the thwarting of which may leave us unhappy and bitter.

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MANAGEMENT. When things go wrong or are disappointing in business enterprises, the usual practice is to displace those at whose doors the entire responsibility is laid. In occasional instances the management and the owners are identical, at least to an extent which makes it possible for those responsible to remain in charge and put into practice what their experience has taught them.

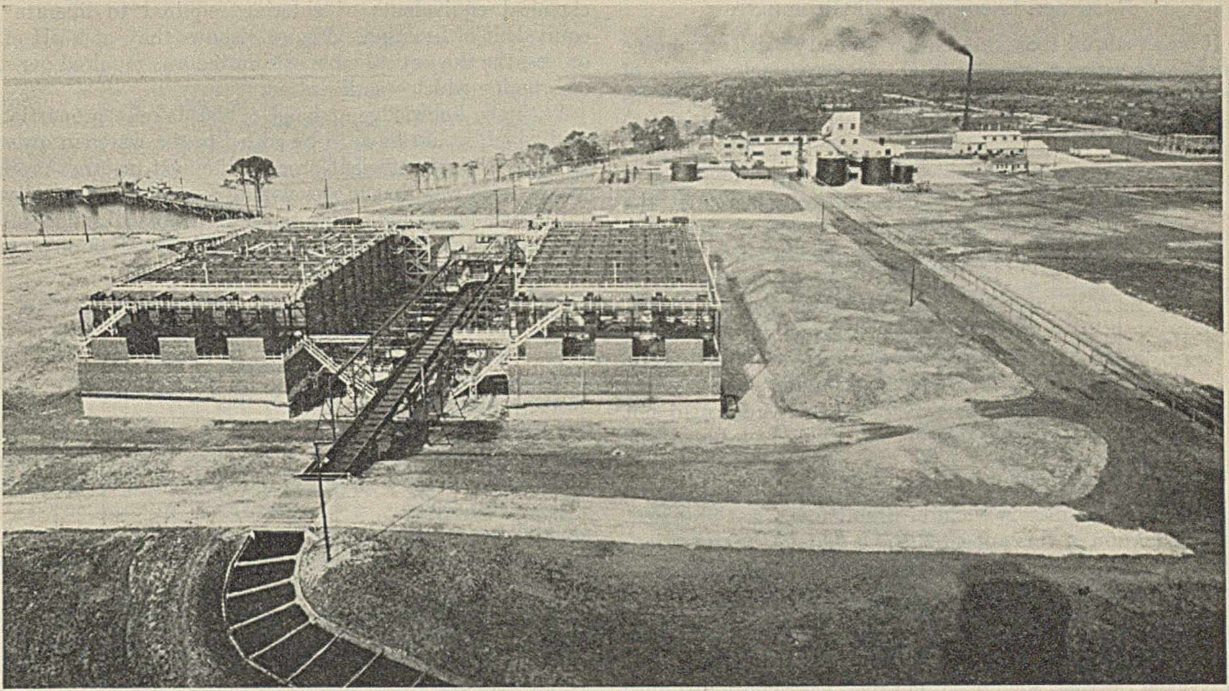
In the past four years, management, as the term is generally used, has learned much. Doubtless there are individual cases where a permanent set of mind and practice has made impossible much change in attitude, but these are the exception rather than the rule. More frequently we find greatly sobered executives who are willing to confess that the days prior to 1929 were no more normal than those that have followed. They will tell you that up to 1930 they thought themselves pretty good business men and very expert in their fields, but now they know they were neither. They have become convinced that the methods of an earlier day were unsound and wasteful almost to a criminal degree, and that half the volume they then enjoyed would now put their business on a sound profitable basis, beneficial alike to wage earners, white collar employees, and stockholders.

Unquestionably management as a whole has learned a valuable, though costly, lesson. The present question is, will it have an opportunity now to apply what has been learned? Or will some new condition, youth movement, collectivism, state socialism, fascism, communism, or what not displace it and leave us perhaps worse off than we were before? The man who can point out after it has occurred that the older generation has bungled things is not necessarily the one who can now take up the burden and carry it in a manner more satisfactory to all concerned. Sober judgment, long experience, and the skill often characteristic of maturity are still without a substitute.

∴

SERVICE AND QUALITY. We have come to consider competition as having, like Gaul, three main divisions. These have been price, service, and quality. Another important factor in many instances has been patent protection, which, in exchange for the disclosures made with the promotion of industry, grants a monopoly for a limited period to those who may have made a certain invention or improvement. The codes of fair practice, already adopted in considerable number and prescribed as a vital ingredient in the prescription to rehabilitate industry, go a long way toward changing the competitive picture. Working hours and wages, of great moment in establishing costs, are being standardized and, as they apply to raw materials as well as to finished products, very definitely promise to eliminate difference in prices from the competitive picture. This has already progressed to the point where important government contracts have been awarded by lot and has resulted in such uniform prices on cement that the Secretary of the Interior has proposed that the Government consider setting up its own plants if uniform bidding continues.

With the temptation of price differential removed, competition tends toward service and quality. The demand is for new and better products and not merely for cheaper ones, thriving under mere patent protection. Applied science under the new conditions should perform a valuable and unique service. There remains, of course, the ever-present opportunity for cost reduction through betterment of manufacturing process and waste elimination. But these seem perhaps secondary to what must be possible in improved quality and service in many industries where the scientist again has his opportunity.



Plant for Extracting Bromine from Sea Water and Manufacturing It into Ethylene Dibromide (Compare Figure 6)

Commercial Extraction of Bromine from Sea Water

Leroy C. Stewart

The Dow Chemical Company, Midland, Mich.

In 1924 the production of free and chemically combined bromine in this country amounted to approximately 2 million pounds. In 1931 this quantity had risen to about 9 million pounds, all of which was being produced from natural brines and from bitterns resulting from evaporation of sea water. This remarkable increase in consumption of bromine was due largely to the use of ethylene dibromide in conjunction with tetraethyllead in the treatment of gasoline motor fuel.

A number of years ago it became evident that the demand for bromine was becoming so great that its ordinary sources were inadequate and that new ones would have to be employed. It was logical that sea water should be considered for this purpose, in spite of the fact that its bromine content is less than 70 parts per million, since the enormous quantities of it which are available would insure an inexhaustible source of raw material. It was up to the chemist and engineer, however, to develop a practical and economical method of extracting this desirable halogen element.

The Ethyl Gasoline Corporation was one of the pioneers along this line. In 1924 they operated a small-scale plant with sea water as its source of bromine and produced tribromoaniline which can be used with tetraethyllead in the treatment of gasoline. Some months later, the same organization operated the process on board a boat, the S. S. Ethyl (*4*). Their method involved the addition of aniline to chlorinated sea water to form tribromoaniline according to the reaction:

$$3NaBr + 3Cl_2 + C_6H_5NH_2 \longrightarrow C_6H_2Br_3NH_2 + 3NaCl + 3HCl$$

A number of years ago The Dow Chemical Company likewise undertook the problem of extracting bromine from sea water but proposed to obtain it in the pure, elemental state by a process somewhat similar to that in use on natural brines at their plant in Midland, Mich. It was recognized that modifications and refinements would have to be made in the old procedure, but the basic principle was considered practical and economically sound. This process consists essentially of (*a*) oxidizing a natural bromide-containing brine with chlorine to liberate the bromine, (*b*) blowing the free bromine out of solution with air, and (*c*) absorbing the bromine from the air with an alkali carbonate solution from which it subsequently can be recovered in a commercially desirable form.

Through many years of experience and effort, the Dow process has been developed to the point where it is possible to recover, consistently, 95 per cent of the bromine content of the natural brines. The latter contain approximately 25 per cent total solids, consisting chiefly of the chlorides of sodium, calcium, and magnesium, together with approximately 1300 p. p. m. bromine. Sea water, however, contains about 3.5 per cent total solids, and only 65 to 70 p. p. m. bromine. This is approximately the same bromine content as that of the waste effluent from the commercial process just mentioned. Consequently, when laboratory work was started on the problem of removing bromine from sea water, it is not surprising that at first a low efficiency was obtained.

RESEARCH LABORATORY DEVELOPMENTS

It was realized that an addition of acid as well as chlorine would be necessary in order to obtain a satisfactory yield of bromine from sea water on account of its alkalinity, as indicated by its pH of 7.2. Otherwise, when the solution was chlorinated, neutralization would have been effected at the expense of the liberated bromine. At the same time there would have been a corresponding formation of oxidized bromine products from which bromine could not easily have been liberated again by chlorine.

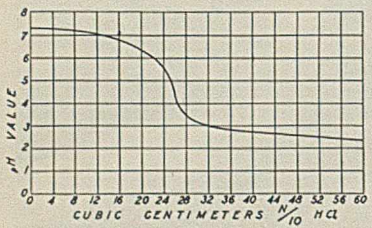


FIGURE 1. EFFECT OF ADDITION OF ACID ON pH OF SEA WATER

However, it was found that even in carefully neutralized sea water, a satisfactory yield of bromine was not obtained. An explanation of this appeared to be that in the exceptionally dilute solution the liberated bromine hydrolyzed to form bromic and hydrobromic acids according to the equation:

$$3Br_2 + 3H_2O \longrightarrow HBrO_3 + 5HBr$$

This being the case, such reaction would have continued until a sufficient concentration of hydrogen ions was obtained to suppress the hydrolysis.

In the production of bromine from Michigan brines, some hydrolysis and reabsorption of the halogen, with the attendant formation of acid, had been encountered. Because of the comparatively smaller volume handled in the case of the natural brine, it was feasible to permit such acidification by hydrolysis to take place and still to make a satisfactory recovery of the bromine. However, in the case of the enormous quantity of liquid involved with sea water as the source of bromine, such acidification by hydrolysis would be uneconomical. Careful laboratory research, involving potentiometric titration of natural sea water, showed that reabsorption of free bromine by hydrolysis ceased if the hydrogen-ion concentration were increased to a pH of 3 to 4 by the addition of acid from an outside source. This indicated, therefore, that in order to liberate bromine in sea water completely and efficiently, it would be necessary first to add sufficient acid to give a pH of approximately 3.5. This would require the use of approximately 0.27 pound of 96 per cent sulfuric acid per ton of sea water. In operation of the tribromoaniline process, already mentioned, it had also been found that it was desirable to add acid to the raw sea water before adding the chlorine, but a greater proportion was employed.

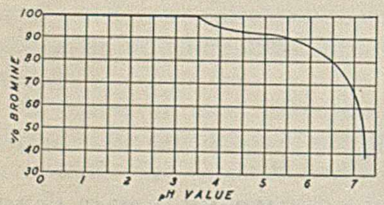


FIGURE 2. EFFECT OF pH ON PERCENTAGE OF BROMINE LIBERATED IN SEA WATER

Figure 1 shows the variation in pH of raw sea water as affected by the addition of acid. Figure 2 shows the effect of variation of pH on the percentage of total bromine that can be liberated from the sea water by chlorine oxidation. Figure 3 indicates the effect of variation of pH of sea water on the chemical equivalents of chlorine required to liberate one equivalent of bromine. Figure 3 shows that, at a pH of 3.5 or less, the theoretical mole of chlorine was required per mole of bromine which was liberated.

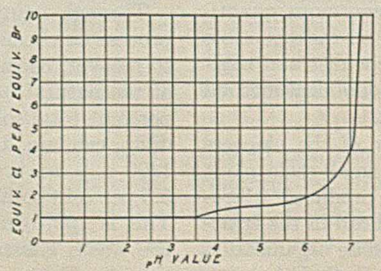


FIGURE 3. EFFECT OF pH ON CHLORINE REQUIRED TO LIBERATE BROMINE IN SEA WATER

With the knowledge at hand of the definite proportion of acid which would have to be added to sea water in order to promote a highly efficient process, the next research problem which arose was that of developing a means of immediately and continuously indicating the progress of oxidation in the chlorination step, so that the degree of liberation of bromine could be ascertained at any time.

With the use of the ocean as a source of bromine, such enormous quantities of water were involved, that, without some such control method, together with a method of continuously recording acidity, large losses of chlorine and acid would be sure to occur before the operator would realize what was happening. A method was finally developed which answered all requirements.

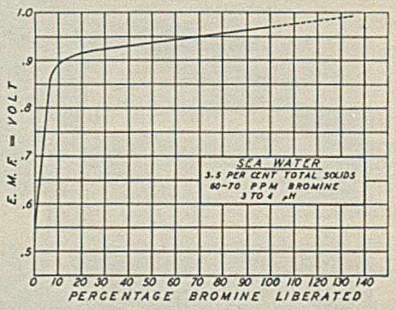


FIGURE 4. RELATIONSHIP BETWEEN OXIDATION POTENTIAL AND PERCENTAGE OF BROMINE LIBERATED IN SEA WATER

The new method of oxidation control depended on the fact that for every type of bromide-containing solution there is a characteristic range of oxidation potential values. This range depends on the initial concentration of bromine ions and also upon the collective effect of other ions present. It was found that, in acidified sea water, the first traces of free bromine in a solution that was being tested caused an immediate increase in oxidation potential. This rise was measured by the difference in voltage between a saturated calomel electrode and a platinum electrode. Figure 4 shows the relationship between the oxidation potential, expressed in volts, and the percentage of bromine liberated in sea water which contained about 3.5 per cent total solids in solution and about 60 to 70 p. p. m. bromine, and which had been acidified to a pH of 3 to 4. The characteristic potential under these conditions ranged between 0.88 and 0.97 volt. The methods of extracting bromine from sea water, involving the control of acidification and oxidation, are protected by patents (*3*).

After obtaining a clear understanding of the factors which made for the most efficient liberation of bromine from sea water and development of satisfactory control methods, the laboratory and semiplant work on the process progressed much more rapidly. This work established the fact that air, blown countercurrent through a 70 p. p. m. bromine solution, would remove the halogen sufficiently to leave a concentration as low as 5 p. p. m. It was also found that soda ash solution would effectively remove the very low concentration of bromine from the air. In these experiments, performed at Midland, Mich., synthetic sea water was used at first, and this was followed by tests made on tank car shipments of true sea water. The chief result of the small-scale work was the demonstration that more than 50 per cent of the bromine in the real sea water could be extracted and actually collected as the pure liquid. The indicated cost of operating the process seemed satisfactorily low.

Selection of Process and Plant Site

Considerable other research work was done before the final process was selected. Other natural waters, as well as sea water, were investigated as sources of bromine, and improved methods were devised for their use. More economical methods in conjunction with the liberation of bromine were studied, including the use of lime or metallic iron to remove bicarbonates from solution and thus to save acid. Many different processes for removing bromine from very dilute solutions were tried extensively in the laboratory, some on semiplant scale. These included precipitation (*1*), extraction, and vaporization of the bromine as well as its absorption and adsorption in various agents, particularly in charcoal (*2*). While some showed fair success, the technic of blowing the bromine from solutions as dilute as the tailings from previous practice was improved and developed to a sound process as already described. Various methods were devised for recovering the bromine from the blowing-out air by both physical and chemical means, including immediate reaction of the bromine with ethylene. It is possible that some such improvements may be employed in the next few years. Finally, the commercial phases of correlating this industry with others were given careful study, and publication of the more interesting and important possibilities may be expected.

A comparison of the two general methods of obtaining bromine from sea water indicated that the direct extraction process possessed several economic advantages over the tribromoaniline method:

1. The direct process requires theoretically only 1 mole of chlorine for each mole of bromine which is liberated, whereas the other scheme requires 2 moles of chlorine per mole of bromine.
2. Smaller quantities of sulfuric acid are required by the direct process than by the other method.
3. Aniline is a relatively expensive raw material and is at a further economic disadvantage as a carrier of bromine for gasoline treatment when it is considered that tribromoaniline contains only 73 per cent bromine, whereas ethylene dibromide is 85 per cent bromine.

At this point in the history of the development it was decided to build and operate a pilot plant for extracting bromine from sea water by The Dow Chemical Company's process. The site for this unit was selected after considerable careful investigation, as it was proposed to build a commercial plant in the same location if the results of this venture were satisfactory. The chief requisites for such a site were:

1. The sea water at the point selected should not be diluted by fresh water streams.

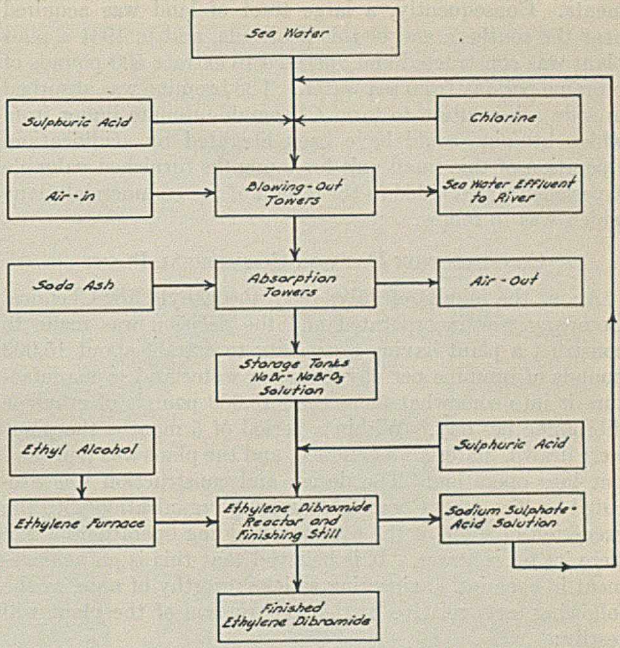


Figure 5. Manufacture of Ethylene Dibromide from Bromine Extracted from Sea Water

2. The location should be such that it would be easy to get rid of the sea water from which the bromine had been extracted, without diluting the water entering the process.
3. There should be no appreciable quantities of industrial waste present in the water entering the process.

A thorough study was made of the eastern and southern coast lines of this country. In this connection information learned from U. S. Coast and Geodetic Survey, to the effect that the water of all streams entering the Atlantic Ocean flows southward, was of considerable assistance. Many samples of sea water were analyzed, and, except where dilution with fresh water was indicated by a study of the location from which the sample was taken, the bromine content was found to be 67 p. p. m. Before construction of the commercial plant, about twenty samples were taken during a boat trip from New Orleans to Havana and then to New York. The same bromine content of the deep sea water was found throughout the entire distance.

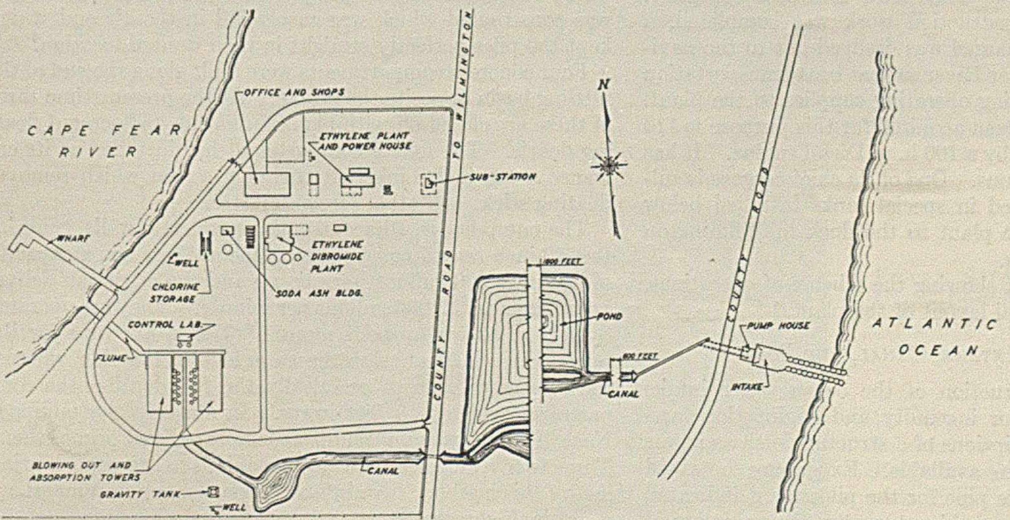


Figure 6. Layout of Plant for Extracting Bromine from Sea Water and Manufacturing It into Ethylene Dibromide

The various factors involved in the selection of the plant site all indicated that it should be located on the north shore of a river, close to the point where it entered the Atlantic Ocean, and that there should be no large river entering the ocean for a number of miles to the north of such a location. The long, narrow promontory of land in North Carolina at the mouth of the Cape Fear River, which separates the latter from the ocean, appeared to answer all the above requirements. Consequently, a large tract of land was acquired near the southern end of this peninsula, and in 1931 a pilot plant was constructed and operated to extract 500 pounds of bromine per day from sea water. The bromine was absorbed in soda ash solution to form a bromide-bromate liquor from which bromine could have been liberated by acidification. Operation of this small unit for 6 months furnished valuable experience which aided in the design of the commercial plant which was to follow.

CONSTRUCTION DATA ON COMMERCIAL PLANT

About the middle of July, 1933, the Ethyl-Dow Chemical Company was incorporated and the decision was made to construct a plant having a capacity to extract about 15,000 pounds of bromine per day from sea water and to manufacture it into somewhat more than 16,000 pounds of ethylene dibromide per day. Within a period of 5 months the plans were drawn, materials assembled, and the plant was built and put into operation. The design and construction was executed by The Dow Chemical Company organization with the exception of some of the common building operations which were let on contract. It is believed that this is an achievement in chemical engineering which is worthy of note, as the following facts relative to the construction of the plant will testify:

Clearing of ground started	July 27, 1933
Land cleared, acres	90
Ground broken for first building	Aug. 15, 1933
Production of ethylene dibromide commenced	Jan. 10, 1934
Wood piles driven (30 feet long)	1,800
Sheet steel piling (36–50 feet long), tons	750
Excavation, cubic yards	125,000
Dredging, cubic yards	100,000
Concrete, cubic yards	8,892
Reënforcing steel, tons	425
Structural steel, tons	350
Electric conduit, miles	9.5
Electric wiring, miles	38
Brick laid	3,540,764
Max. number men employed at one time, approx.	1,500
Approx. total of man-days	90,000
Building days	150
First working drawing completed	Aug. 14, 1933
Last working drawing completed	Nov. 2, 1933
No. of principal drawings (24 by 36 inches)	265

The construction facts become even more impressive when it is realized that the nearest railroad shipping point is at Wilmington, approximately 20 miles away. Consequently the large quantities of materials which were involved had to be trucked that distance to the construction site. In order that the work might proceed rapidly, a considerable number of engineers and superintendents were required. These were accommodated in a near-by fifty-room beach hotel which was leased and operated by the Ethyl-Dow Chemical Company.

Shortly before the construction work was completed, a wharf was built and a channel was dredged out to the navigable part of the Cape Fear River so that boat transportation could be used for delivering operating supplies to the plant. The boat that has since been acquired for this purpose is 116 feet long and is propelled by a 100 h. p. Diesel engine. It has a capacity of about 140 tons. One of its chief cargoes is sulfuric acid which is carried in special tanks installed below deck. The trip from the plant to the dock in Wilmington requires from 2 to 4 hours.

Figure 5 is a flow sheet showing the scheme of operations. Figure 6 shows the general layout of the plant.

OCEAN WATER INTAKE, CANAL, AND POND

The design and construction of the ocean water intake offered an opportunity for ingenuity and engineering foresight. No plans or descriptions of a structure such as it was desired to construct were available. Experience obtained in putting down an intake pipe for the pilot plant indicated that a single row of piling would not survive the pounding of the ocean waves. It had been found, however, that a row of piling on each side of the pipe remained rigid when tied together with a large number of crosspieces. In planning the intake of the new plant, it was decided, therefore, to cut a channel out into the ocean for a short distance and to protect it with a rigid wall on each side. The walls were each to consist of two parallel rows of piling tied together at suitable intervals.

In constructing the intake walls, 50-foot lengths of interlocking sheet steel piling were used. These were driven to a depth of about 42 feet below mean low-tide level. The parallel rows of piling in each wall were joined together at every tenth member by a partition of similar piles at right angles to the direction of the wall. Consequently, when completed, each wall of the intake consisted of a series of interlocked cells 21 feet long and 15 feet wide. These were built, one at a time, beginning at the shore end and were filled with sand that was dug from the channel between them.

Altogether the intake (Figure 7) is about 200 feet long. It extends approximately 30 feet out into the ocean at low tide and about the same distance on to the land at high tide. The channel between the walls is 15 feet wide and the depth is 9 feet below mean low-tide level.

The sea water flows through the intake into a settling basin which is 112 feet long, 76 feet wide, and 12 feet deep. The walls in this case were formed from a single row of 40-foot steel piles. These were left with about 14 feet exposed above mean low-tide level and are about level with the surrounding ground.

The walls of the settling basin had to be supported from the outside in order to keep them from collapsing toward the inside. This was accomplished by bolting 24-inch I-beams to every eighth piece of piling and extending 2.5-inch steel rods about 30 feet out from each I-beam to anchor into timber piling which served as "dead men" to absorb the thrust of the dirt against the piling wall.

In putting down the steel piles, considerable difficulty was experienced in driving the first few members. When these were in place, it was found expedient to use water jets to aid in sinking the subsequent units. A 0.75-inch nozzle was carried down on each side of the piles, and, by forcing the water through the nozzles at 100 pounds per square inch pressure, it was possible to drive them a considerable distance merely by raising and dropping them. When the power required to raise a pile became too great for the derrick, the jetting was continued and a hammer applied to the top of the pile until the latter was driven to the desired depth. In order to keep the piles of the intake walls in perfect alignment so that there would be no difficulty in tying-in the cross partitions, a frame was constructed which was suspended in the air and which kept the piles perfectly straight in their desired location.

Four concrete compartments were built along the end of the settling basin opposite the intake. At the present time three of these are closed off with plank bulkheads to keep out floating debris. The fourth compartment has installed at its entrance a 120-inch Link-Belt traveling screen which removes floating sticks and other foreign matter.

The pump house, adjacent to these concrete wells, contains two 30-inch centrifugal pumps. One of these has a capacity of about 26,000 gallons per minute and the other can deliver approximately 32,000 gallons per minute. They are operated by 300 h. p. synchronous motors. The intake pipe for the pumps extends 9 feet below the water level at low tide, whereas the screens operate to practically the full depth of the compartment which is 3 feet lower. In starting the pumps a Nash Hytor vacuum pump is employed to prime them. Three to five minutes are usually required to accomplish priming by this method. An interior view of the pump house appears in Figure 8.

Each of the centrifugal pumps is connected to a separate 42-inch steel pipe line which carries the water under a road

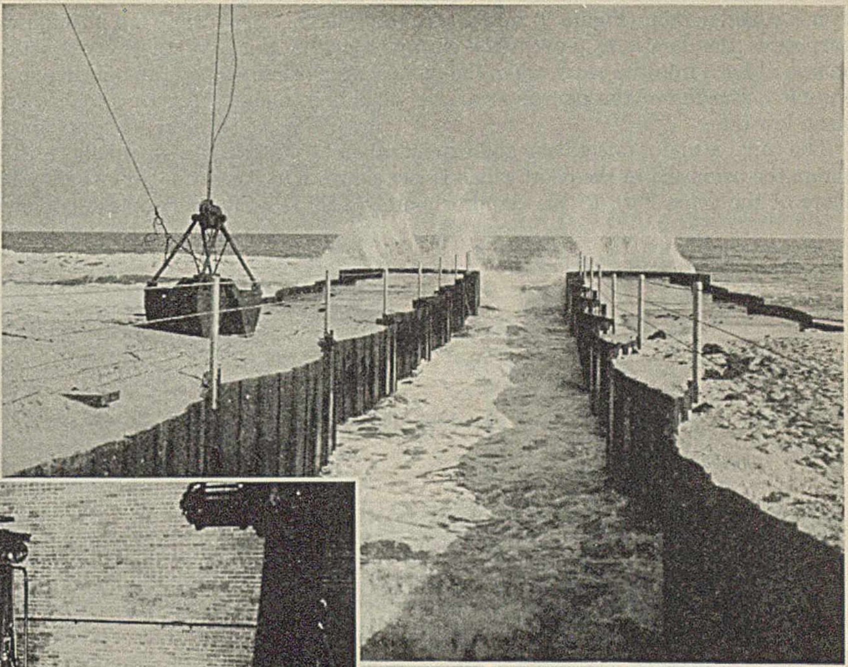
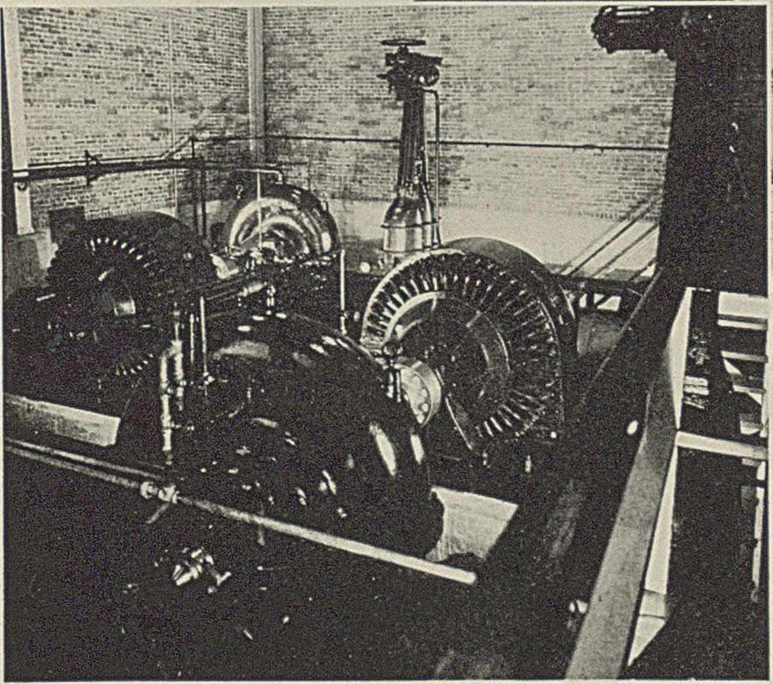


FIGURE 7 (RIGHT). SEA-WATER INTAKE

FIGURE 8 (BELOW). INTERIOR OF PUMP HOUSE AT SEA-WATER INTAKE



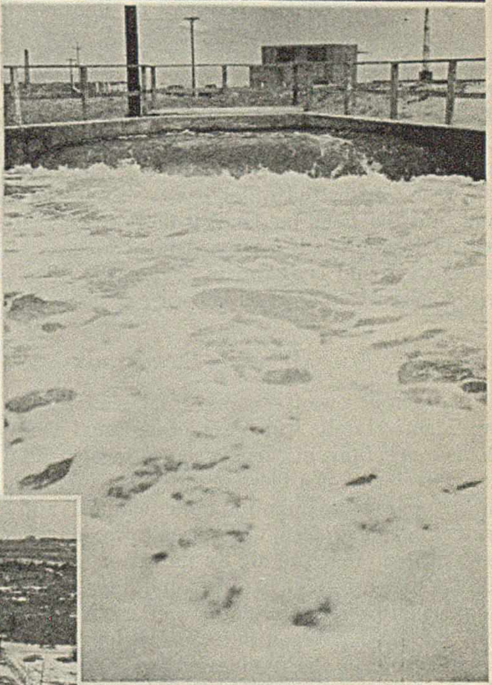


FIGURE 9 (ABOVE). SEA WATER BEING PUMPED OVER DAM AT RATE OF 58,000 GALLONS PER MINUTE

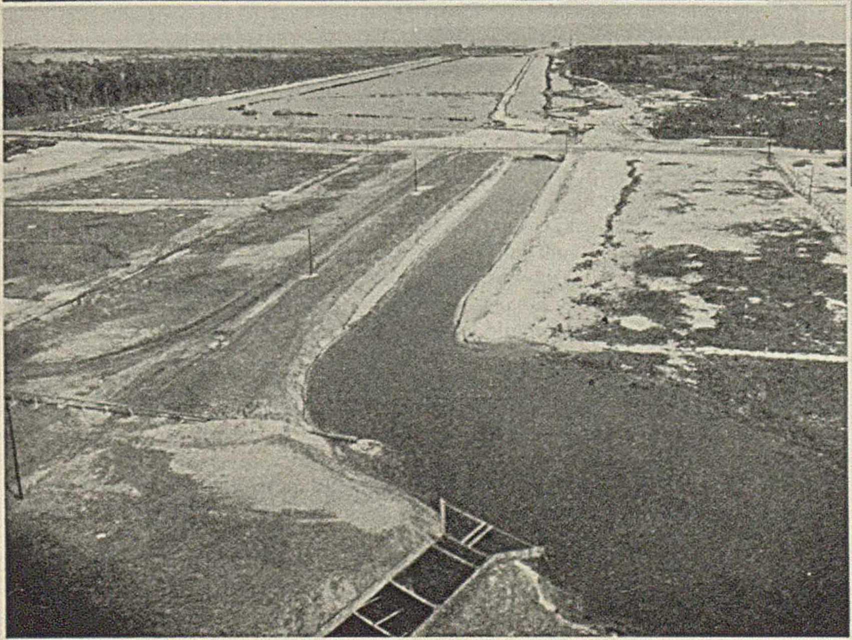


FIGURE 10 (LEFT). CANAL AND POND FOR PASSING SEA WATER TO BROMINE EXTRACTION PLANT

into a 72-inch steel pipe. The latter conducts the water up over a concrete dam (Figure 9) into a canal and pond. The purpose of the dam is to prevent the emptying of the canal and pond back into the ocean when the pumps are not in operation. The top of the dam is at a level of 23 feet above mean low tide.

The canal is about 6 feet deep and extends about 4000 feet across the peninsula to the plant which is located close to the shore of the Cape Fear River. Approximately 2200 feet of the canal are diked off from a pond through which the sea water is by-passed during the summer months. With some 900,000 square feet of exposed surface, the pond permits an increase in temperature during warm weather. This increases the efficiency of the process during several months of the year. After the water has been pumped over the dam and into the canal or pond, it flows to the extraction plant with a loss in head of only about 3 inches. A view of the canal and pond is shown in Figure 10. The pilot plant is visible near the far left-hand corner of the pond.

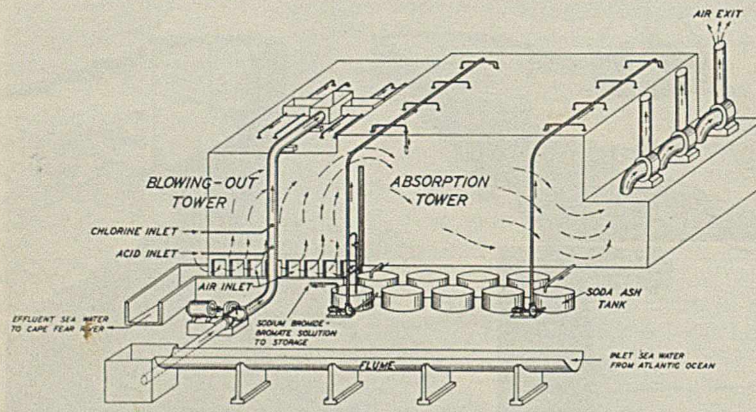


FIGURE 11. DIAGRAM OF BROMINE EXTRACTION UNIT

BROMINE EXTRACTION

The extraction of bromine from sea water takes place in two identical units which are located at the exit of the canal. A diagram of one of them is shown in Figure 11. Each unit consists chiefly of a blowing-out tower in which a current of air removes the bromine from acidified and oxidized sea water, and an adjacent absorption tower in which the bromine is extracted from the air by means of a soda ash solution. The towers are built of brick and have concrete floors and foundations. The foundations of each unit cover an area 197 × 84 feet. Wood piles 30 feet long were driven in the ground beneath the foundations to avoid any possibility of their settling.

The original ground where these structures are located was excavated to a depth of 9 feet or to a level which is about 5 feet above the river at low tide. This was done to minimize the height that the sea water would have to be pumped to the top of the blowing-out towers.

A horizontal steel flume, which is semi-circular in cross section and 10 feet in diameter, extends between the two extraction units and connects with the canal which brings in the sea water. Because the bases of the towers and the area between them are below the canal level, the flume is carried on steel supports so that it is at the same level as the canal (Figure 12). The absorption towers are located at the end of the flume which is nearest the canal. Hence, the water passes by them on its way to centrifugal pumps which elevate it to the tops of the blowing-out columns. Before entering the pumps, however, the water flows through a traveling screen at the end of the flume. This filters out any leaves or debris which may fall into the water after it enters the canal or pond.

In each extraction unit the sea water is pumped to the top of the blowing-out tower through a vertical 42-inch rubber-lined pipe. Near the bottom of this, a 10 per cent sulfuric acid solution is introduced into the water through a group of small rubber-lined pipes. A short distance higher the chlorine is introduced through similar rubber-lined pipes. At the top of the blowing-out tower the water passes through a series of large and small distributor boxes and pipes so that it eventually is divided up into about 3200 small streams. These flow down through the tower which is partitioned off into narrow chambers extending the full width of the structure. These chambers are filled with wood packing and are operated in parallel. A stream of air is sucked up through the tower countercurrent to the sea water. The bromine that has been liberated by the chlorine is thus blown out of the sea water, and the latter passes out of the bottom of the tower through exit flumes to the river and thence into the ocean about 12 miles south of the intake. Figure 13 shows a view of the exit flume.

The treatment of the sea water on its way to the blowing-out towers is regulated from the near-by control laboratory. Meters on a wall of the laboratory continuously show both the pH of the acidified sea water and its oxidation potential with respect to bromine liberation. Valves in the sulfuric acid and chlorine lines which lead to the 42-inch vertical mixing pipes are operated by hand from the control laboratory. At a later date it is probable that the control of these valves will be made automatic. Signal lights above the meters also indicate whether the condition of the treated sea water is correct for the blowing-out towers.

The chlorine which is used in oxidizing the sea water is obtained from cylinders having a capacity of one ton. A group of sixteen of these is placed in each of two wooden compartments. These are kept at a temperature of not less than 70° F. The cylinders are connected to the chlorine line and their contents, in liquid form, flow to the chlorine vaporizer. This is a steam-jacketed iron pipe and is located adjacent to the control laboratory.

The sulfuric acid is delivered to the plant in the concentrated form, but it is diluted to a 10 per cent solution before it is added to the sea water. This dilution is accomplished in two rubber-lined tanks, 16 feet in diameter and 10 feet high. These are located adjacent to the control laboratory.

In each extraction unit the air from the blowing-out tower is drawn through its adjacent absorption tower by three fans which are located on a concrete platform at the end of the unit. The air, just before entering the fans, passes through a small wood-filled chamber which catches any spray of soda ash solution that might otherwise be carried out of the system.

In the absorption tower the bromine is removed from the air by a soda ash solution to form a dissolved mixture of sodium bromide and bromate according to the formula:

$$3Na_2CO_3 + 3Br_2 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$$

The absorption towers are built on reënforced concrete arches which elevate their floors so as to permit gravity flow of the dissolving liquor into tanks which are located at their bases. This construction also makes possible the detection of any leakage which might take place in the tower bases at any future time.

Each absorption tower is divided into nine chambers which are connected in series so that the air, passing in at the end adjacent to the blowing-out tower, follows in succession

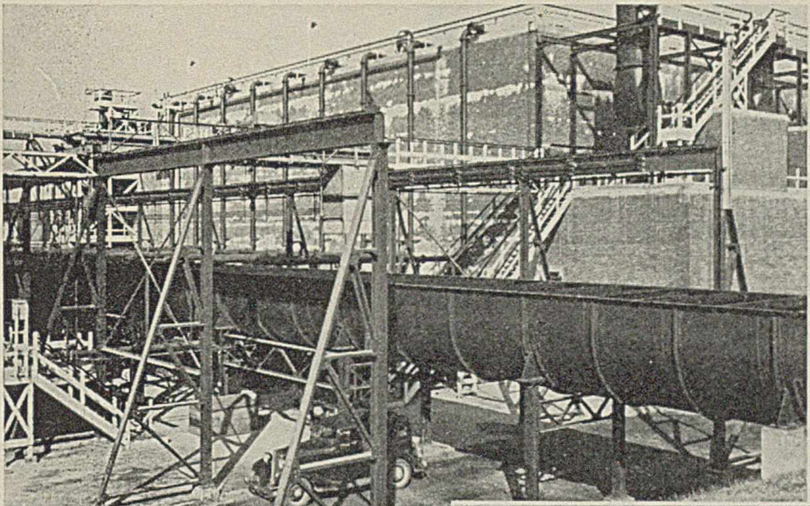


Figure 12 (Left). Flume for Conducting Sea Water to Blowing-Out Towers

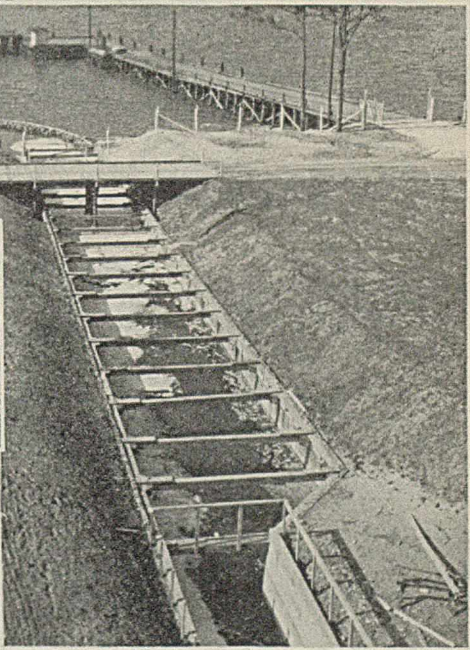


Figure 13 (Below). Effluent Sea Water Passing from Blowing-Out Towers to River

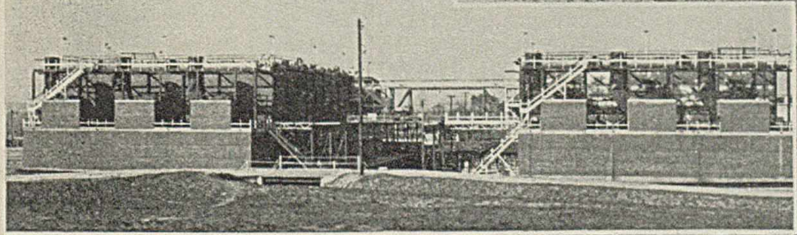


Figure 14 (Left Center). South End of Bromine Extraction Units

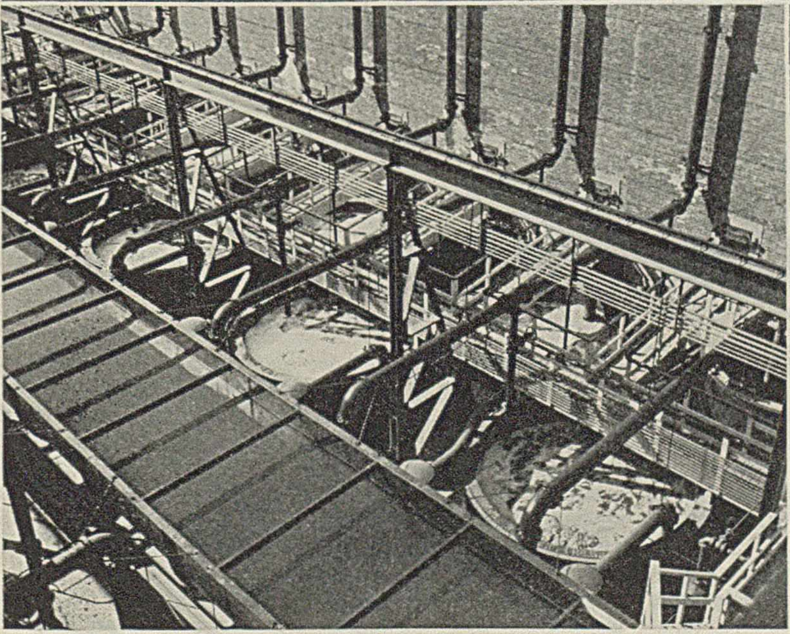


Figure 15 (Above). Looking Down on Bromine Absorption Liquor Tanks

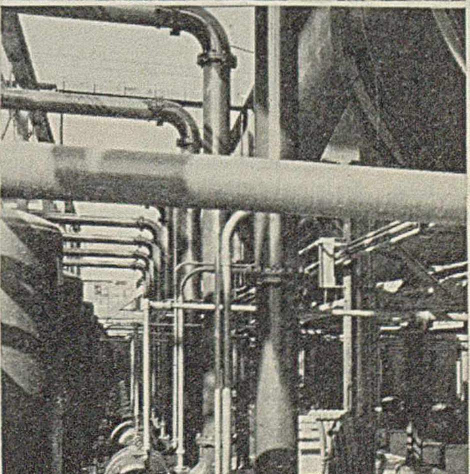


Figure 16 (Right). Battery of Pumps for Circulating Bromine Absorption Liquor

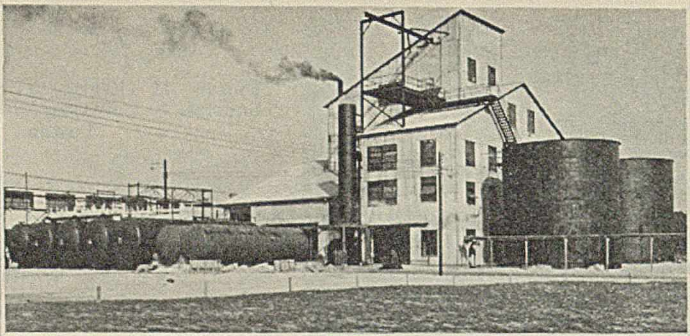


Figure 17 (Left). Bromine and Ethylene Dibromide Plant

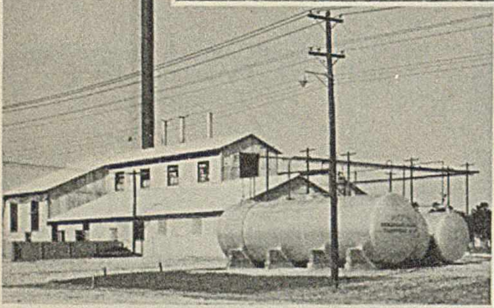


Figure 18 (Above). Ethylene Plant and Power House

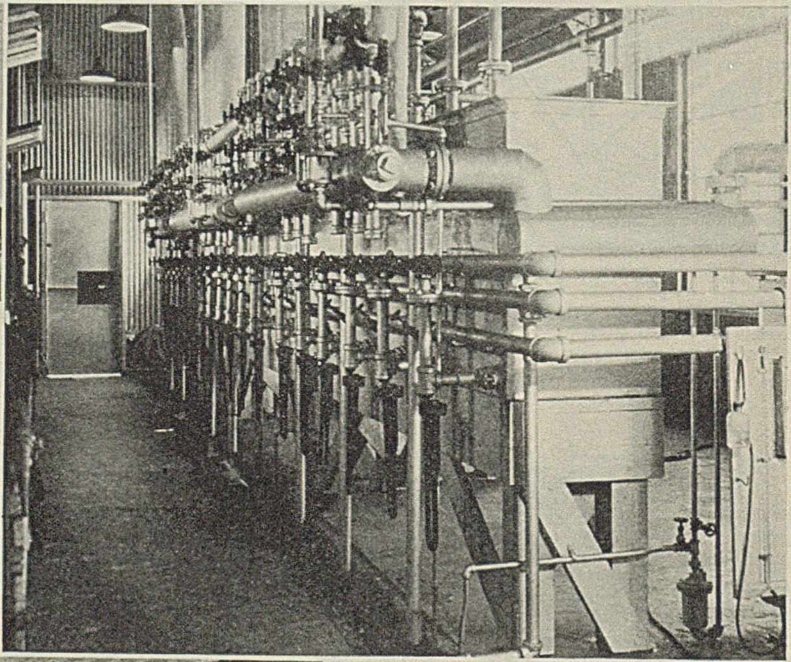


Figure 19 (Above). Battery of Valves for Controlling Ethylene Production

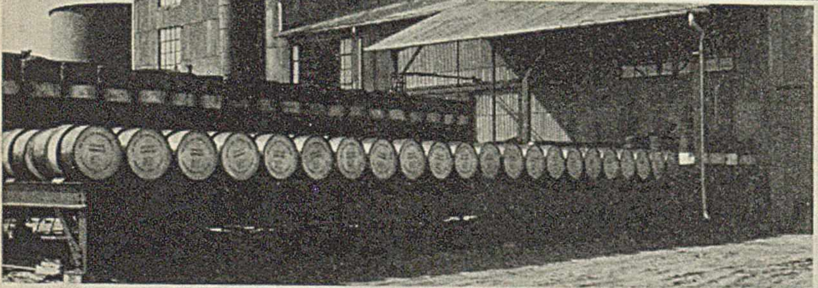


Figure 20 (Left). Shipment of Finished Ethylene Dibromide

through these absorbing chambers and out through the suction fans. Soda ash solution is circulated continuously in each chamber. This is done by pumping it from a tank at the bottom and spraying it in at the top through thirty-six nozzles from which it falls by gravity and drains again into the tank.

At proper intervals the strong bromide-bromate solution formed in the absorption chamber adjacent to the blowing-out tower is pumped to a storage tank. The charges of partially brominated soda ash liquor in the other members of the series are then pumped forward, in turn, to the next tank nearer the one which has just been emptied to storage. When the tank farthest from the blowing-out tower has been emptied, it is charged with a fresh solution of soda ash. Figure 14 shows the south end of the bromine extraction plant. Figure 15 is a view looking down on the absorption liquor tanks and Figure 16 shows the battery of pumps which circulate the soda ash solution. The inlet flume may be seen overhead.

After the bromine from the sea water has been collected in the form of a solution of sodium bromide and bromate, the remainder of the process is performed according to methods which have been previously in use in the industry. The bromide-bromate liquor is treated with sulfuric acid to liberate the bromine. The free bromine vapors are then steamed out of the acidified solution and are condensed into pure liquid bromine. Figure 17 shows the plant in which the bromine is finally obtained in liquid form. The two bromide-bromate liquor storage tanks are seen at the side of the building and the horizontal sulfuric acid storage tanks are in front of it.

The bromine is used in the manufacture of ethylene dibromide which is also made in the building shown in Figure 17. Ethylene is made by passing ethyl alcohol vapor over heated kaolin catalyst to form ethylene gas, which is in turn brominated according to the standard method to form pure ethylene dibromide. Figure 18 shows the ethylene plant and power house which are both in the same building. The battery of valves for controlling the ethylene production is shown in Figure 19. A consignment of finished product on the shipping platform of the ethylene dibromide plant is shown in Figure 20.

The power house employs hand-fired boilers and makes steam only for heating and evaporating purposes. Its capacity is about 15,000 pounds of steam per hour at a pressure of 150 pounds per square inch. Operating electric power is purchased from the Tidewater Power Company. It is delivered to the plant at 33,000 volts where it is stepped down to 2300 volts in two transformer banks.

The entire plant is functioning as anticipated and is removing about 15,000 pounds of bromine per day from sea water. This is being converted into ethylene dibromide at an efficiency somewhat over 90 per cent.

The direct recovery of minerals for industrial use from sea water has long held the attention of chemists, and it is believed that the plant which has been described is the first to accomplish this achievement on a commercial scale of operation. The extraction of gold from sea water in which it is present to the extent of but a few parts per billion has always been the investigator's most fascinating goal, but no success along this line has been reported thus far. Now that the recovery of bromine, which is present to the extent of less than 70 p. p. m., has been successfully executed, it does not seem beyond reason to expect the chemist of the next decade to extract gold from sea water commercially.

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RECEIVED February 26, 1934. Presented before the General Meeting at the 87th Meeting of the American Chemical Society, St. Petersburg, Fla., March 25 to 30, 1934.

Aluminum Priming Paint

Effect on the Durability of House Paints on Wood

F. L. BROWNE, Forest Products Laboratory, Madison, Wis.

Repeated comparisons of the durability of white paints on wood when applied over aluminum priming paint and when applied in the customary manner, using the white paint itself for the primer, consistently demonstrated a distinct superiority in service for paint applied over aluminum primer. The improvement in durability was manifested by a retardation in the rate at which paint coatings, embrittled with age, flaked from the bands of dense, horny summerwood present in softwood lumber. The benefit gained by priming with aluminum paint was greatest for woods that have much summerwood, such as southern yellow pine and Douglas fir. When repainting was neglected for some time, coatings applied over aluminum primer suffered less damage, and the surfaces were then more easily and durably repainted.

IN AN EARLIER publication (*3*) the writer reported exposure tests of special priming paints on seven species of wood. In those tests the substitution of aluminum paint for the customary white paint primer increased the durability of succeeding coats of white lead paint from 44 to 48 months, and of lead and zinc paint from 42 to 49 months on the average, although the aluminum priming paint used was seriously faulty in certain respects that will be discussed later. The increase in durability of paints applied over the aluminum primer was greatest on those woods that usually hold paint least satisfactorily and was effected by marked retardation in the flaking of the coatings from the bands of summerwood after age had made the coatings brittle (*2*, *4*). The beneficial effect of the aluminum primer became all the more marked after the coatings passed the point at which good practice calls for repainting and entered the "period of paint neglect," because the coatings over aluminum primer after such neglect offered much more satisfactory surfaces for repainting than the coatings over the white primers.

Many paint technologists have been reluctant to admit the merits of aluminum priming paint. For that reason it has been deemed necessary to repeat the earlier experiments several times and to build up unusually extensive data on the subject. The later tests thoroughly confirm the earlier findings. Nearly two hundred test areas have been primed with aluminum paint as a base for coatings of white paint in tests by the Forest Products Laboratory; almost without exception the aluminum primer materially prolonged the life of the coating and in no case did it shorten it. Similar results have been reported by other workers (*9*, *10*, *11*).

The present paper deals solely with the effect of aluminum priming paint on the durability of house paints on wood as determined by test fence exposures following in general testing methods that are described elsewhere (*6*). In all cases the test panels were rated for appearance and integrity of the coating and for maintenance of protection against wood weathering, in accordance with the general method for evaluating paint service adopted by the Forest Products Laboratory (*7*). For the present purpose, however, only the integrity and durability of the coatings need be reported. Ordinarily the appearance of coatings (largely a matter of color and cleanness) is not affected by the use of aluminum priming paint, and the contribution made by aluminum priming to the maintenance of protection against wood weathering is revealed most clearly by special tests of moisture movement that have recently been the subject of a publication by the writer (*5*).

GENERAL PROCEDURE

In tests in which comparison of aluminum priming paint with the customary white priming paint was the principal objective, the two painting procedures were followed on neighboring areas of the same test panel so that the comparison could be made on identical boards. As a further precaution each test panel was made of three, four, or five boards. In certain other experiments for which pertinent

TABLE I. COMPOSITION OF SPECIAL PRIMERS

(Composition in per cent of primer by weight)

	PIGMENTS				LIQUIDS						
SYMBOL	Aluminum powder[a]	Zinc dust	Red lead	White lead[b]	Raw linseed oil[c]	Boiled linseed oil	Bodied linseed oil[d]	Varnish[e]	Synthetic drying oil[f]	Turpentine	Liquid paint drier
A_1	21.4	...	..	..	..	...	...	78.6	..	...	...
A_2	21.0	...	..	..	..	...	79.0	...	..	...	...
A_3	17.0	...	..	..	..	...	...	83.0	..	...	...
A_4	20.7	...	..	..	..	...	...	...	79.3	...	...
SP_1	4.8	9.6	52.9	..	22.7	4.7	...	...	..	4.3	1.0
SP_2	5.9	...	68.9	..	15.2	...	...	...	..	9.3	0.7
SP_3	2.3	...	..	64.7	27.7	...	...	...	..	4.6	0.7
SP_4	..	...	..	..	..	...	100.0	...	..	...	...
SP_5	..	...	..	..	..	...	...	100.0	..	...	...

[a] Standard varnish grade.
[b] Basic carbonate.
[c] Examination of a typical shipment revealed an acid number of 5.5 mg. potassium hydroxide per gram and an iodine number (Wijs) of 178.0.
[d] Made by heating varnish makers' linseed oil at 300° C. for 2.5 hours, adding lead and manganese paint drier, continuing the heating for 0.5 hour longer cooling, and thinning with mineral spirits until the nonvolatile content of the mixture was 60 per cent by weight.
[e] A commercial aluminum vehicle of 80-gallon (302-liter) length in oil and presumably made chiefly of ester gum, tung oil, and thinners. It contained 52 per cent nonvolatile by weight.
[f] A commercial aluminum vehicle of the glycerol–phthalic acid type, "for use under U. S. Patents 1,108,329–30 and 1,119,592."

TABLE II. COMPOSITION OF WHITE PAINTS

(Composition in per cent of paint by weight)

	PIGMENTS				LIQUIDS				UNIT WEIGHT OF PAINT FOR MAKING MIXES IN TABLE III	
SYMBOL	White lead[a]	Zinc oxide[b]	Titanox B	Magnesium silicate	Linseed oil	Turpentine	Mineral spirits	Liquid paint drier	*Pounds*	*Kg*
L_1	92.0	..	..	..	8.0	...	...	...	100	45.4
L_2	85.0	..	..	..	15.0	...	...	...	100	45.4
LZ_1	45.0	22.5	..	7.5	25.0	...	...	...	100	45.4
LZ_2	49.5	24.8	..	8.3	17.4	...	...	...	86	39.0
LZ_3	38.4	19.2	..	6.4	32.4	1.8	...	1.8	16.6[c]	7.53
LZ_4	39.6	19.8	..	6.6	30.6	1.7	...	1.7	17.2[c]	7.80
LZ_5	36.3	23.1	..	6.6	30.6	...	1.7	1.7	16.8[c]	7.62
LZ_6	29.7	26.4	..	9.9	30.6	1.7	...	1.7	16.9[c]	7.65
TZ_1	..	23.4	43.0	11.7	21.9	...	...	...	68.4	31.0
TZ_2	..	23.6	47.1	7.9	21.4	...	...	...	70.0	31.7
TZ_3	..	23.1	36.3	6.6	30.6	...	1.7	1.7	16.1[c]	7.3

[a] Basic carbonate. [b] Lead-free.
[c] Prepared paints for which the unit weight for mixing is the weight of 1 gallon (3.78 liters).

TABLE III. MIXES OF WHITE PAINTS FOR APPLICATION

(The liquids are those bearing similar designations in Tables I and II.)

	VOLUME OF LIQUIDS IN GALLONS[a] ADDED TO UNIT WEIGHT OF PAINT RECORDED IN LAST COLUMN OF TABLE II					
SYMBOL	Raw linseed oil	Bodied linseed oil	Varnish	Turpentine	Mineral spirits	Liquid paint drier
			MIXES FOR PRIMING COAT			
a_0	4.0	...	...	2.0	..	0.125
a_1	3.5	...	...	2.0	..	0.25
a_2	3.0	...	...	2.0	..	0.125
a_3	2.75	...	...	1.85	..	0.125
a_4	2.0	...	...	..	2.0	0.125
a_5	1.5	...	...	2.0	..	0.125
a_6	0.125	...	...	0.25	..	...
a_7	...	...	...	0.5	..	...
a_8	...	...	...	0.25	..	...
a_9	...	...	...	..	0.31	...
av_1	...	4.0	...	2.0	..	0.125
av_2	...	3.5	...	2.0	..	0.25
av_3	...	...	1.5	2.0	..	0.125
av_4	1.5	...	0.5	2.0	..	0.125
av_5	...	...	0.16	1.85	..	0.125
av_6	2.75	...	16.0	1.86	..	0.125
av_7	0.125	...	2.0	0.25	..	...
ar_1	1.6	...	...	2.0	..	0.125
ar_2	1.25	...	...	2.0	..	0.125
ar_3	0.125	...	...	..	..	0.25
			MIXES FOR INTERMEDIATE COAT			
b_0	1.5	...	...	1.5	..	0.125
b_1	2.62	...	...	1.25	..	0.125
b_2	0.5	...	...	1.5	..	0.125
b_3	0.41	...	...	1.39	..	0.125
b_4	...	...	...	0.125	..	...
b_5	...	...	...	0.2	..	..
			MIXES FOR FINAL COAT			
c_0	3.5	...	...	0.125	..	0.125
c_1	3.0	...	...	..	0.125	0.125
c_2	2.62	...	...	0.22	..	0.22
c_3	2.5	...	...	0.125	..	0.125
c_4	2.25	...	...	0.125	..	0.125
c_5	...	...	...	..	..	...

[a] One gallon = 3.78 liters.

data are shown, the principle of "matched specimens" does not apply, but the number of boards painted was large enough to accomplish fair comparison through the principle of averages.

Some technologists have attributed the beneficial effect of aluminum priming paint to the varnish or bodied oil vehicle with which aluminum paint is made rather than to the aluminum pigment (*15*, *16*). For that reason some of the experiments included tests in which these vehicles were used with the white paints as primers or in which the clear vehicles without any pigment were applied as primers. Some tests also included special priming paints in which aluminum powder was used in admixture with other pigments.

All test panels were exposed facing south. Some were placed on the test fences in the vertical position, as on the side of a house, others were placed at a slope of 45°. Paint fails more rapidly on inclined than on vertical panels (*17*); the degree to which failure is accelerated by the inclined position can be gaged from tests involving concurrent exposure in both positions.

Most of the tests were made at Madison, Wis., but some were repeated at stations representing distinctly different climatic conditions.

COMPOSITION OF PAINTS

The paints and their various mixes are listed in Tables I, II, and III with a system of symbols that will represent them in the subsequent discussion.

TESTS ON WESTERN LARCH

A series of tests was begun in 1927 at Madison, Wis., to study the painting characteristics of western larch, a heavy softwood which contains much summerwood and is therefore difficult to paint durably (*2*). For that reason some of the painting procedures tested were based on aluminum priming paint. Each panel contained five boards of commercial 4-inch (actual width, 9 cm.) strip flooring. Tests on panels of flat-grain boards and on panels of edge-grain boards were made in duplicate with panels in the vertical and inclined positions. After 26 months and again after 52 months of exposure most of the inclined panels were repainted with white paints.

In Table IV the painting procedures tested are indicated, together with the durability of the resulting coatings.

In this series of tests, coatings over aluminum primer always proved distinctly more durable than the corresponding coatings over a white primer, whether the white primer was mixed with linseed oil in the customary manner or with a vehicle containing some of the varnish used in the aluminum paint (*13*, *16*). The increase in durability caused by aluminum primer was greatest for lead and zinc paint LZ_6, which proved very low in durability when applied in the customary manner. On flat-grain inclined panels three coats of paint LZ_6 lasted only 9 months, but substitution of aluminum for white priming paint increased the durability to 23 months.

The beneficial effect of initial aluminum priming continued after the inclined panels were repainted twice. At the time this is written, by far the best panels of the series are those initially primed with aluminum paint. Presumably the continued good effect is due to the fact that aluminum priming not only prolongs the serviceable life of coatings but retards the flaking from summerwood if the surfaces become paint-neglected.

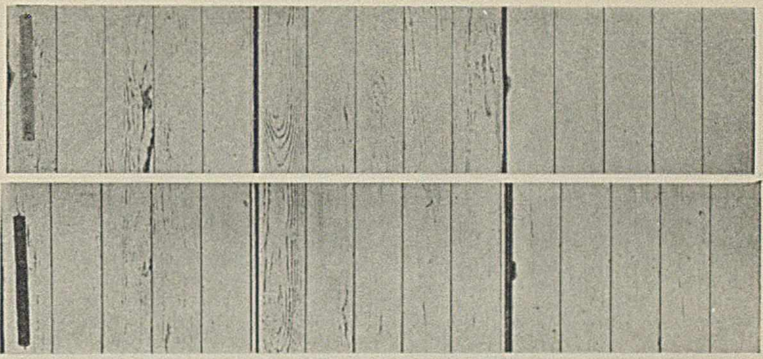


FIGURE 1. EFFECT OF ALUMINUM PRIMING IN RETARDING CRUMBLING OF WHITE LEAD PAINT ON WESTERN LARCH

The three panels in the upper row were primed, respectively (from left to right), with white lead paint, white lead paint containing varnish, and aluminum paint, and then finished with two coats of white lead paint. The photographs were taken after 25 months of exposure in the inclined position at Madison, Wis. At 26 months all three panels were repainted with two coats of white lead paint; the photographs in the lower row show the repainted coatings after 24 months of additional exposure.

TABLE IV. PAINTING PROCEDURES AND DURABILITY OF THE COATINGS TESTED ON WESTERN LARCH

INITIAL PAINTING PROCEDURE			DURABILITY OF INITIAL COATING ON:		REPAINTING PROCEDURE AT 26 MONTHS AND 52 MONTHS		DURABILITY OF REPAINTED COATING APPLIED AT:	
Priming coat	Second coat	Third coat	Vertical panels	Inclined panels	First coat	Second coat	26 months	52 months
			Months	*Months*			*Months*	*Months*
ON FLAT-GRAIN BOARDS								
L_1a_5	L_1b_9	L_1c_9	31	21	L_1ar_1	L_1c_9	19	20
L_1av_3	L_1b_9	L_1c_9	31	19	L_1ar_1	L_1c_9	20	20
A_1	L_1b_9	L_1c_9	35+[a]	26+	L_1ar_1	L_1c_9	26+	21+
L_1a_5	L_1c_9	...	28	16	L_1ar_1	L_1c_9	21	20
L_1av_3	L_1c_9	...	25	16	L_1ar_1	L_1c_9	21	21+
A_1	L_1c_9	...	35+	25	L_1ar_1	L_1c_9	26+	21+
LZ_6a_7	LZ_6b_5	LZ_6c_5	19	9	...	...	..	..
A_1	LZ_6b_5	LZ_6c_5	35+	23	LZ_4ar_3	LZ_4c_5	26+	21+
LZ_6a_7	LZ_6c_5	...	13	9	...	...	..	..
L_1a_5	LZ_6c_5	...	31	13	...	...	..	..
L_1av_3	LZ_6c_5	...	19	13	...	...	..	..
A_1	LZ_6c_5	...	35	23	LZ_4ar_3	LZ_4c_5	26+	21+
LZ_4a_8	LZ_4b_4	LZ_4c_5	35+	19	LZ_4ar_3	LZ_4c_5	19	21+
LZ_4a_8	LZ_4c_5	...	31	16	LZ_4ar_3	Lz_4c_5	19	21+
ON EDGE-GRAIN BOARDS								
L_1a_5	L_1b_9	L_1c_9	35+	25	L_1ar_1	L_1c_9	26+	21+
L_1av_3	L_1b_9	L_1c_9	31	25	L_1ar_1	L_1c_9	24	21+
A_1	L_1b_9	L_1c_9	35+	25	L_1ar_1	L_1c_9	26+	21+
L_1a_5	L_1c_9	...	31	19	L_1ar_1	L_1c_9	26+	21+
L_1av_3	L_1c_9	...	25	13	L_1ar_1	L_1c_9	26+	21+
A_1	L_1c_9	...	35	23	L_1ar_1	L_1c_9	26+	21+
LZ_6a_7	LZ_6b_5	LZ_6c_5	25	13	...	...	..	..
A_1	LZ_6b_5	LZ_6c_5	35+	23	LZ_4ar_3	LZ_4c_5	26+	21+
LZ_6a_7	LZ_6c_5	...	19	9	...	...	..	..
L_1a_5	LZ_6c_5	...	35	19	...	...	..	..
L_1av_3	LZ_6c_5	...	31	13	...	...	..	..
A_1	LZ_6c_5	...	35+	23	LZ_4ar_3	LZ_4c_5	26+	21+
LZ_4a_8	LZ_4b_4	LZ_4c_5	35+	20	LZ_4ar_3	LZ_4c_5	26+	18
LZ_4a_8	LZ_4c_5	...	35	19	LZ_4ar_3	LZ_4c_5	26+	21+

[a] + following a rating for durability indicates that the coating was still considered serviceable when the panel was either repainted or removed from the test at the age indicated; coatings on inclined panels for which the durability is rated less than 26 months passed through a period of "paint neglect" represented by the difference between 26 months and the recorded durability in months.

These experiments do not offer a fair comparison of the merits of two-coat and three-coat work for the initial painting of wood. Later experience has proved that two-coat work in which the priming and final coats are mixed richer in pigments compares much more favorably in durability with conventional three-coat painting. Two-coat painting in which the priming coat is aluminum paint and the final coat is white or tinted white paint is often impracticable because one coat of white paint usually fails to hide the color of the aluminum primer satisfactorily. If the final coat is gray, however, or a tint in which a component of gray is desirable, two-coat painting over aluminum primer may give good results in the hands of a skillful painter.

TESTS ON SOUTHERN YELLOW PINE

A series of tests begun in 1928 had for its primary object the study of the effect on paint maintenance of impregnation of wood with zinc chloride wood preservative, but incidentally the tests provided data on aluminum priming paint under three kinds of white paint on southern yellow pine, both with and without zinc chloride. There were ninety test panels, each panel made up of three boards. The panels were divided into nine groups of ten panels each, one group for each of nine paints or painting procedures. Of the ten panels in each group, two were made of boards containing no injected chemical, three with boards impregnated with approximately 0.75 pound of zinc chloride per cubic foot (12 kg. per cubic meter), three with 1.5 pounds of zinc chloride per cubic foot (24 kg. per cubic meter), and two with 1.5 pounds per cubic foot of a mixture of two parts of zinc chloride and one part sodium dichromate.

All of the painting was done in two-coat work following procedures indicated in Table V. Each of the three white paints was applied according to the customary practice (using the white paint for the priming coat), each paint was applied over aluminum primer, and each paint was applied over a white paint priming coat in which some varnish had been mixed.

The panels were exposed at Madison, Wis., late in October, 1928. In January, 1931, many of the panels were repainted with two coats of white paint as indicated in Table V.

Table V reports average results. All coatings failed more rapidly on wood containing zinc chloride than they did on untreated wood but not sufficiently to preclude the use of wood treated with zinc chloride where painting is required. The relative durability of the different coatings was much the same on treated and untreated wood. On wood impregnated with the mixture of zinc chloride and sodium dichromate (not reported in Table V) the coatings proved at least as durable as they did on untreated wood, the relative durability of the different coatings again falling in the same order.

As in the tests on western larch, aluminum priming-coat paint added materially to the durability of white lead paint and of lead and zinc paint, and the benefit of the aluminum

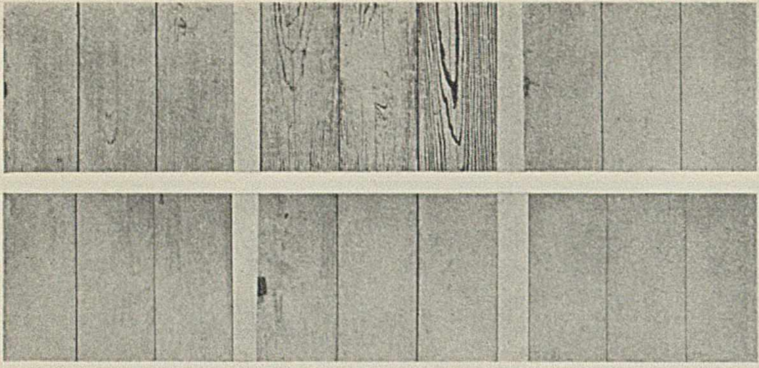


FIGURE 2. EFFECT OF ALUMINUM PRIMING IN RETARDING CRUMBLING OF WHITE LEAD PAINT ON SOUTHERN YELLOW PINE

The panels in the upper row were painted with two coats of white lead paint, those in the lower row with one coat of aluminum paint and one coat of white lead paint. In each row the left-hand panel was made of untreated wood, the middle panel of wood treated with zinc chloride, and the right-hand panel of wood treated with a mixture of zinc chloride and sodium dichromate. They were exposed in the inclined position at Madison, Wis. The coatings were 26 months old when photographed.

primer continued after the panels had been repainted with white paints. When first painted, one final coat of the white paints failed to hide the color of the aluminum completely; as time passed, however, the coatings began to chalk, and their opacity increased enough to hide the aluminum color satisfactorily. The repainted coatings showed no sign of the aluminum color at any time.

TABLE V. PAINTING PROCEDURES AND DURABILITY OF THE COATINGS TESTED ON SOUTHERN YELLOW PINE

INITIAL PAINTING PROCEDURE		INITIAL COATING		REPAINTING PROCEDURE		REPAINTED COATING	
Priming coat	Second coat	Durability	Rating for integrity at 26 months	Priming coat	Second coat	Durability	Rating for integrity at 58 months
		Months				*Months*	
ON UNTREATED SOUTHERN YELLOW PINE							
L_1a_4	L_1c_1	23	Bad	L_2ar_2	L_2c_4	32+[a]	Poor+
L_1av_4	L_1c_1	24	Bad	L_2ar_2	L_2c_4	27	Poor
A_3	L_1c_1	..	Good	L_2ar_2	L_2c_4	32+	Fair
A_3	L_1c_1	42	Good	Not repainted			
LZ_5a_9	LZ_5c_5	26	Poor	LZ_2ar_2	LZ_2c_4	32	Poor
LZ_5av_5	LZ_5c_5	23	Bad	LZ_2ar_2	LZ_2c_4	20	Bad
A_3	LZ_5c_5	..	Fair	LZ_2ar_2	LZ_2c_4	32+	Poor+
A_3	LZ_5c_5	35	Fair	Not repainted			
TZ_3a_9	TZ_3c_5	..	Good	TZ_2ar_2	TZ_2c_4	32+	Poor+
TZ_3a_9	TZ_3c_5	46	Good	Not repainted			
TZ_3av_5	TZ_3c_5	..	Good	TZ_2ar_2	TZ_2c_4	32+	Poor+
A_3	TZ_3c_5	..	Fair	TZ_2ar_2	TZ_2c_4	32+	Poor+
A_3	TZ_3c_5	46	Fair	...	...	...	...
ON SOUTHERN YELLOW PINE IMPREGNATED WITH ZINC CHLORIDE							
L_1a_4	L_1c_1	18	Bad	L_2ar_2	L_2c_4	16	Bad
L_1av_4	L_1c_1	16	Bad	L_2ar_2	L_2c_4	12	Bad
A_3	L_1c_1	30	Good	Not repainted			
A_3	L_1c_1	..	Good	L_2ar_2	L_2c_4	29	Poor
LZ_5a_9	LZ_5c_5	23	Bad	LZ_2ar_2	LZ_2c_4	17	Bad
LZ_5av_5	LZ_5c_5	19	Bad	LZ_2ar_2	LZ_2c_4	16	Bad
A_3	LZ_5c_5	28	Fair	Not repainted			
A_3	LZ_5c_5	..	Fair	LZ_2ar_2	LZ_2c_4	19	Poor
TZ_3a_9	TZ_3c_5	43	Fair	Not repainted			
TZ_3a_9	TZ_3c_5	..	Fair	TZ_2ar_2	TZ_2c_4	29	Poor
TZ_3av_5	TZ_3c_5	..	Fair	TZ_2ar_2	TZ_2c_4	27	Poor
A_3	TZ_3c_5	41	Fair	Not repainted			
A_3	TZ_3c_5	..	Fair	TZ_2ar_2	TZ_2c_4	31	Poor

[a] + following a rating for durability indicates that the coating was still considered serviceable when last inspected; the rating "poor +" means that the integrity was not considered quite poor enough at the last inspection to require repainting.

Addition of varnish to the priming coat of the white paints proved slightly deleterious on the whole (*13*, *16*), just as was the case in the tests on western larch.

Titanox and zinc paint TZ_3 proved outstandingly durable, so much so that it made little difference whether it was applied over aluminum or over white priming paint. Paint TZ_2 applied in repainting did not last quite as long as in first painting but proved more durable than either repainted white lead or lead and zinc. The outstandingly good results with paint TZ_3 are attributed to the high volume of pigment, 31 per cent, in the coating after evaporation of the volatile thinner, and to the moderate addition of liquid in the priming-coat mixture. Paints that contain no white lead, however, are subject to serious disadvantages that make it unwise to recommend them for general use by painters. Paints containing titanium pigment, white lead, and zinc oxide in suitable proportions prove nearly as satisfactory as properly applied titanium and zinc paints and are much less subject to damage from painters' blunders.

TESTS ON DOUGLAS FIR

A detailed study of the painting characteristics of Douglas fir was begun at Madison, Wis., in June, 1929, from which data on aluminum priming paint have been obtained as a secondary objective. Five types of commercial Douglas fir lumber were tested, each type in flat-grain and in edge-grain boards, making in all ten classifications of wood. Seven test panels for vertical exposure and seven for inclined exposure were made from boards of each of the ten classes. Each panel contained three boards. Vertical panels were divided into two test areas, inclined panels provided only one test area each.

The painting procedures and the results appear in Table VI. By far the most durable coatings were obtained when the priming coat was aluminum paint, whether A_1 or A_2. After 47 months the coatings over aluminum primer on most of the vertical panels were still serviceable and rated "fair" in integrity. The improvement in durability must be attributed chiefly to the action of the aluminum pigment in the primer. The white primers containing bodied linseed oil and the clear bodied oil primer, although superior to the ordinary white paint primers, proved much less satisfactory than the aluminum primers.

TABLE VI. PAINTING PROCEDURES AND DURABILITY OF THE COATINGS TESTED ON DOUGLAS FIR

PAINTING PROCEDURE				DURABILITY OF COATINGS	
PRIMING COAT ON ONE AREA OF VERTICAL PANELS OR ON ENTIRE AREA OF INCLINED PANELS					
Left-hand area	Right-hand area	SECOND COAT	THIRD COAT	Av. for 10 vertical panels	Av. for 10 inclined panels
				Months	*Months*
L_1a_0	...	L_1b_0	L_1c_0	38	30
...	A_2	L_1b_0	L_1c_0	47+[a]	..
L_1a_6	...	L_1b_0	L_1c_0	35	26
...	L_1av_1	L_1b_0	L_1c_0	39	..
L_1a_0	...	L_1b_0	L_1c_0	38	31
...	SP_4	L_1b_0	L_1c_0	40	..
A_1	...	L_1b_0	L_1c_0	47+	..
LZ_1a_1	...	LZ_1b_1	LZ_1c_2	42	28
...	A_2	LZ_1b_1	LZ_1c_2	47+	..
LZ_1a_1	...	LZ_1b_1	LZ_1c_2	38	25
...	LZ_1av_2	LZ_1b_1	LZ_1c_2	43	..
LZ_1a_1	...	LZ_1b_1	LZ_1c_2	41	29
...	SP_4	LZ_1b_1	LZ_1c_2	42	..
...	A_1	LZ_1b_1	LZ_1c_2	47	35

[a] + following a rating for durability indicates that the coatings were still considered serviceable when last inspected.

TESTS ON PONDEROSA PINE AT TUCSON AND FRESNO

Aluminum priming paint was included in some tests of painting ponderosa pine started at Fresno, Calif., and at Tucson, Ariz., in 1929. The test panels consisted of three boards of commercial 6-inch (actual width, 14 cm.) bevel siding forming a panel area of 16 by 72 inches (41 by 180 cm.), which was marked off into three test areas of 16 by 24 inches (41 by 60 cm.). Only those test areas that were primed with aluminum paint and the neighboring areas on which a white paint primer was applied are considered here.

The painting procedures and results appear in Table VII. In every case the use of aluminum priming paint materially increased the durability of the coating.

Table VII. Painting Procedures and Durability of the Coatings Tested on Ponderosa Pine

Painting Procedure			Durability of Coatings at:		
				Fresno, Calif.	
Priming coat	Second coat	Third coat	Tucson, Ariz.	Vertical panels	Inclined panels
			Months	*Months*	*Months*
L_2a_2	L_2b_2	L_2c_3	30	28	21
A_1	L_2b_2	L_2c_3	46	36+[a]	29
LZ_2a_2	LZ_2b_2	LZ_2c_3	25	28	23
A_1	LZ_2b_2	LZ_2c_3	46	36+	29
TZ_1a_2	TZ_1b_2	TZ_1c_3	24	25	23
A_1	TZ_1b_2	TZ_1c_3	46	46	26

[a] + following a rating for durability indicates that the coating was still considered serviceable when the panel was removed from the fence.

Tests Begun in 1930 at Five Stations

In 1930 a series of tests of special priming paints was begun at Madison, Wis., Sayville, N. Y., Washington, D. C., Fargo, N. D., and Fresno, Calif. Present concern is only with those primers that contained aluminum or the varnish vehicle used with aluminum.

The test panels were made of four boards of commercial 6-inch (actual width, 14 cm.) bevel siding, comprising one board each of redwood, northern white pine, Douglas fir, and southern yellow pine. The panels were 18 by 72 inches (46 by 180 cm.) in size and were marked off into three test areas each 18 by 24 inches (46 by 60 cm.). The middle area was primed in each case with a white paint, and the end areas with special priming paints, after which two coats of white paint were applied over the entire panel. The value of a special primer is therefore determined by comparing the coating on the appropriate end area with the coating on the middle area of the same panel. The panels were exposed in the vertical position facing south. For the most part the coatings on boards of redwood and northern white pine were still in serviceable condition at the last inspection, so that significant comparisons could not be drawn as to those woods, but failure by flaking of the coatings from summerwood was progressing on boards of Douglas fir and southern yellow pine. For that reason the results reported in Table VIII refer only to the latter woods. The data for the three areas of each panel appear consecutively in Table VIII.

Of the special priming procedures reported in Table VIII only the aluminum priming consistently proved superior to the customary white priming paints. Of the three primers containing aluminum in conjunction with granular pigments (SP_1, SP_2, and SP_3), the two in which red lead was the principal pigment (SP_1 and SP_2) usually proved inferior to the customary white primer. Primer SP_3, in which white lead was the principal pigment, usually proved somewhat better than the customary white primer but not as consistently or as markedly superior as did the aluminum primer (A_1). The primer of clear varnish (SP_5) and the white primers containing varnish usually proved superior to the customary white primers from the point of view of coating integrity, but they were not as consistently or as markedly so as the aluminum primer (*13*, *16*); and in addition they led to coarse and conspicuous fissures in the coatings. Over the primer of clear varnish the fissures in the coating of lead and zinc paint were strikingly apparent at a distance of 50 feet (15.2 meters). Even these fissures were not considered sufficient cause for judging the coatings unserviceable, although such large ones might well be so regarded. The fissures that developed in the different coatings over aluminum primer, on the other hand, were similar in all respects and were no more conspicuous than the fissures in the coatings over the customary white primers.

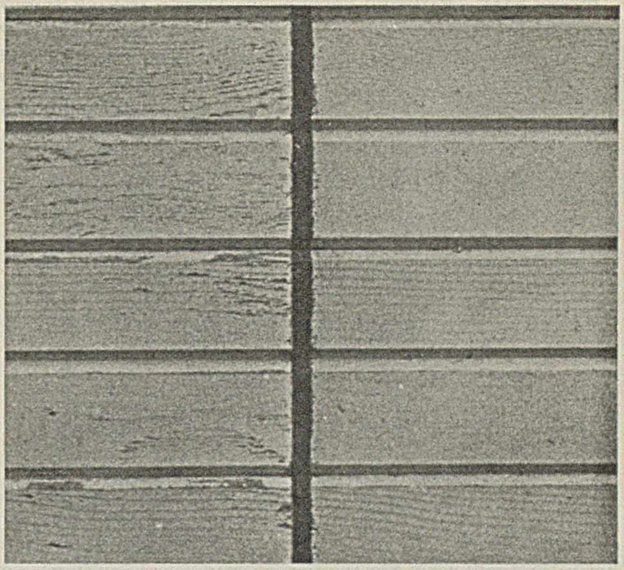


Figure 3. Effect of Aluminum Priming in Retarding Flaking of Lead and Zinc Paint on Douglas Fir

The left-hand area was painted with three coats of lead and zinc paint, the right-hand area with one coat of aluminum paint made with bodied linseed oil vehicle and two coats of lead and zinc paint. The panel was exposed in the vertical position at Madison, Wis., and was photographed when the coatings were 46 months old.

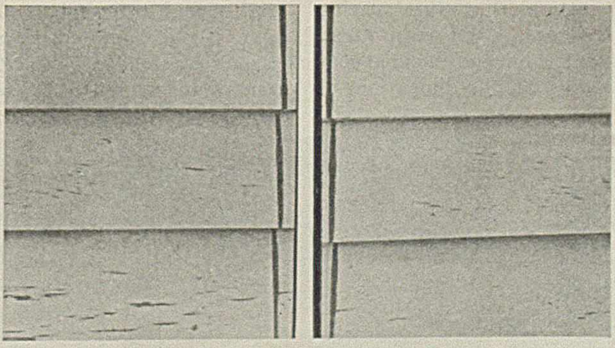


Figure 4. Effect of Aluminum Priming in Retarding Flaking of Titanox and Zinc Paint on Ponderosa Pine

The left-hand area was painted with three coats of Titanox and zinc paint, the right-hand area with one coat of aluminum paint and two coats of Titanox and zinc paint. The two areas are neighboring parts of the same boards. The panel was exposed in the vertical position at Fresno, Calif., and was photographed when the coatings were 34 months old. At 46 months the bands of summerwood in the two lower boards of the left-hand area were almost entirely bare while the right-hand area showed only slightly more flaking of the coating than appears here.

Glycerol–Phthalic Acid Vehicle for Aluminum Primer

One test was begun in 1930 with an aluminum priming paint made with a commercial synthetic drying oil of the glycerol–phthalic acid type. One panel of the four woods chosen for the tests described in the preceding section was exposed at Madison in the inclined position. The aluminum primer, A_4, was applied on one area of this panel, and a white priming paint very similar in composition to paint TZ_3a_3 was applied on the neighboring area. Subsequent coats of white paints similar to TZ_3b_2 and TZ_3c_4 were applied over both primers. The durability of the coating over the aluminum primer was 31 months as compared with 20 months over the white primer. The durability of three coats of a commercial white paint made with glycerol–phthalic acid drying oil vehicle by the manufacturer of the aluminum paint, A_4, was also tested on a third area of the same test panel and found to be 20 months.

Fissures in White Paints over Aluminum Primer

Coatings of white paint on wood eventually develop fissures after the coatings become brittle with age. The significance

Table VIII. Painting Procedures Tested at Five Stations, Starting in 1930, and Results Obtained by 1933 on Boards of Douglas Fir and Southern Yellow Pine

(In each group of three lines, compare the top and bottom lines with the middle line.)

	Painting Procedure			Madison, Wis.		Sayville, N. Y.		Washington D. C.		Fargo, N. D.		Fresno, Calif.	
Panel	Priming coat	Second coat	Third coat	Durability	Integrity at 35 months	Durability	Integrity at 30 months	Durability	Integrity at 29 months	Durability	Integrity at 32 months	Durability	Integrity at 33 months
				Months		*Months*		*Months*		*Months*		*Months*	
1	SP_1	L_2b_3	L_2c_4	28	Bad	..	Fair −	22	Bad	27	Bad	16	Bad
	L_2a_3	L_2b_3	L_2c_4	..	Fair	..	Fair	..	Poor +	..	Fair −	24	Bad
	A_1	L_2b_3	L_2c_4	..	Fair +[a]	..	Fair	..	Poor +	..	Fair	..	Fair −
2	SP_3	L_2b_3	L_2c_4	..	Fair +	..	Fair −	..	Fair −	..	Fair	..	Fair
	L_2a_3	L_2b_3	L_2c_4	35	Poor	..	Fair	..	Poor +	..	Fair	33	Poor
	SP_2	L_2b_3	L_2c_4	16	Bad	..	Fair −	29	Poor	..	Fair	30	Poor
3	SP_5	L_2b_3	L_2c_4	29	Bad	..	Fair	..	Poor +	32	Poor	24	Bad
	L_2a_3	L_2b_3	L_2c_4	30	Poor −[b]	..	Poor +	..	Poor +	32	Poor	29	Bad
	L_2av_6	L_2b_3	L_2c_4	30	Poor −	..	Fair	..	Poor +	32	Poor	21	Bad
4	SP_1	LZ_3b_4	LZ_3c_5	30	Bad	..	Fair −	29	Poor	27	Bad	19	Poor
	LZ_3a_6	LZ_3b_4	LZ_3c_5	30	Bad	30	Poor	26	Poor −	27	Bad	16	Bad
	A_1	LZ_3b_4	LZ_3c_5	..	Fair −	..	Fair	..	Poor +	..	Fair +	33	Poor −
5	SP_3	LZ_3b_4	LZ_3c_5	..	Fair −	..	Fair −	29	Poor	..	Fair −	33	Poor
	LZ_3a_6	LZ_3b_4	LZ_3c_5	25	Bad	..	Poor +	29	Poor	..	Fair −	21	Bad
	SP_2	LZ_3b_4	LZ_3c_5	31	Poor	..	Poor +	29	Poor	..	Fair +	26	Poor
6	SP_5	LZ_3b_4	LZ_3c_5	24	Bad	18	Bad	24	Poor −	18	Bad	19	Poor
	LZ_3a_6	LZ_3b_4	LZ_3c_5	25	Bad	..	Fair −	24	Poor −	18	Bad	19	Bad
	LZ_3av_7	LZ_3b_4	LZ_3c_5	35	Poor	..	Poor +	29	Poor	..	Fair −	21	Bad

[a] + following a rating for integrity means that deterioration had not quite attained the rating named.

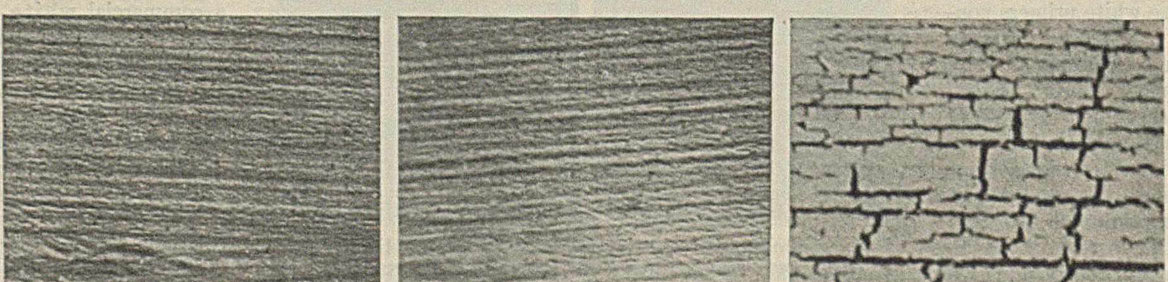
[b] − means that deterioration had passed slightly beyond the rating named.

of fissures is not yet fully understood. They give no reliable basis for predicting the relative durability of coatings, because some very durable paints exhibit well-defined fissures relatively early in service, whereas other paints show no fissures until they are on the verge of rapid failure. In linseed oil paints the development of fissures is markedly affected by the nature of the white pigments. Pure white lead paint, for example, displays fissures that have a characteristically reticulate pattern. Addition of zinc oxide to white lead paint changes the pattern; the fissures appear first as lines parallel to the direction of the last strokes of the paint brush; later the pattern becomes reticulate but remains easily distinguishable from the fissures in pure white lead paint. The development of fissures of these kinds, which are presumed to be superficial until late in the life of the coating, is commonly called "checking" (*1*, *12*). The writer distinguishes between reticulate and parallel checking as to form and believes that both types result from internal stresses within the coating that are not affected in any way by expansion and contraction of the wood under the coating. Fissures of another kind, however, probably result from stresses applied to the coating by movement of the wood beneath it. Such fissures are usually relatively long openings that pass entirely through the coating at their first appearance. Development of such fissures is called "cracking." Cracking rarely occurs in a pattern that is uniformly characteristic of the pigment composition of the paint.

The checking fissures in coatings of any given pigment composition form characteristic patterns, but their spacing varies widely according to circumstances. With white lead paint, for example, when the pigment volume in the final coat is less than that in the intermediate coat, the dimensions of the reticulate meshes are small, and the checking is inconspicuous; but if final and intermediate coats are reversed, the dimensions of the meshes become larger and the checking more conspicuous.

In tests started in 1925 and previously reported (*3*), coatings of white lead paint and of a lead and zinc paint developed coarser checking when applied over aluminum primer than when applied over white priming paint. The checking was sufficiently pronounced to make the coatings appear grayish during much of the life in service. On the other hand, in all the tests so far reported in this paper, fissures in the coatings of white paint were essentially equivalent in all respects, whether the paints were applied over aluminum primer or over customary white primers. The coarse and conspicuous checking and the tendency to give white paints a gray color over aluminum primer in the 1925 tests did not appear in any of the later tests. This difference in behavior was attributed mainly to the fact that the aluminum primer used in the earlier test was not entirely hardened when the next coat of paint was applied.

To determine the validity of this explanation, a series of tests was started in 1931. The test panels, which were of the kind used for the tests noticed in the preceding section, were exposed in the inclined position at Madison. Four test areas were primed with aluminum paint A_1 and covered by coats of white lead paint L_2b_3 and L_2c_4; the time intervals between application of A_1 and L_2b_3 were 6, 12, 24, and 336 hours, respectively, for the four areas. In 6 hours the primer was barely hard enough to permit application of more paint, but in 24 hours it was thoroughly hard. The interval between applications L_2c_4 and L_2b_3 was 72 hours in all cases. Four more areas were painted in the same way except that primer A



A, three coats of lead and zinc paint. *B*, aluminum primer and two coats of lead and zinc paint. *C*, bodied linseed oil (without pigment) and two coats of lead and zinc paint.

Figure 5. Checking of Lead and Zinc Paint over Three Different Primers

A and *B* were taken at Fargo, N. D., on vertical panels at age 32 months, and *C* at Fresno, Calif., at the same age, but they are all representative of the results obtained at all stations and on all woods on which the tests were made.

was used instead of A_1. Eight more areas were painted in the same way as the first eight, except that lead and zinc paint LZ_2 replaced white lead paint L_2, and a further group of eight areas were similarly painted with paint TZ_2. Finally, three areas were painted, respectively, with each of the three white paints over white primers L_2a_3, LZ_2a_3, and TZ_2a_3.

In the coatings of white lead paint, finely reticulate checking was first observed at 10 months of exposure and was then well developed on all areas, whether primed with white or with aluminum paint and regardless of the time allowed for the aluminum primer to harden. The subsequent development of the checking was the same on all white lead areas.

In the coatings of lead and zinc paint, parallel checking was observed at 10 months over the white primer in an early stage of development. At 17 months parallel checking was well developed in LZ coatings over both white and aluminum primers, but it was inconspicuous and similar on all areas, and it did not seriously affect the appearance of the coatings. At still later stages the checking gradually became coarsely reticulate in pattern, until at 29 months it was as conspicuous as it had been in the 1925 tests, and the white paint appeared gray over the aluminum primers. The checking became conspicuous slightly faster over primer A_2, made with bodied oil, than over A_1, made with varnish, but the time allowed for the primers to harden had no effect on the conspicuousness of the checking. Since the coating over the white primer was judged unserviceable because of flaking from summerwood after 18 months, whereas the coatings were still rated as serviceable over the aluminum primers after 31 months, despite the checking, the aluminum primers had already contributed notably to the durability of the coatings before the checking became conspicuous. In the 1925 tests such was not the case, the checking over aluminum primer having become conspicuous at much earlier stages.

In the coatings of Titanox and zinc paint, checking never appeared, but cracking was observed at 17 months. At that time it was well developed over aluminum primer A_2 (made with bodied oil), partially developed over the white primer, and barely started over primer A_1, made with varnish. It became well developed over the white primer at 22 months and over primer A_1 at 29 months. Even when well developed, however, the cracking did not cause the white paint to appear gray. There was no relation between cracking and the time allowed for the primers to harden.

The durability of the white paints over white primers in these tests was 22 months for white lead paint, 18 months for lead and zinc paint, and 20 months for Titanox and zinc paint. Over aluminum primers the coatings of all three paints were still serviceable after 31 months, although disintegration over the bands of the summerwood had begun.

These experiments make it necessary to find some other explanation for the early appearance of conspicuous checking over aluminum primer in the 1925 tests. Reconsideration suggests that it may have resulted from the use of an excessive amount of aluminum powder in the aluminum primer in 1925, when the amount was 2.43 pounds per gallon (0.29 kg. per liter). The current recommendation of 2 pounds of aluminum powder per gallon of vehicle (0.24 kg. per liter) may be regarded as the maximum permissible.

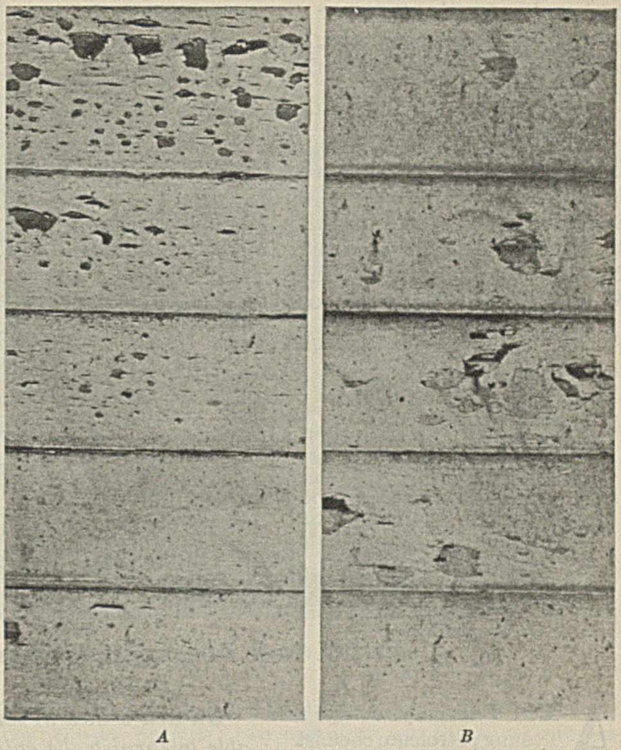


FIGURE 6. MOISTURE FAILURE OVER ALUMINUM AND OVER A WHITE PRIMER

These coatings were only 9 months old when photographed. After 6 weeks' initial exposure the panels had been placed on a laboratory "blistering box" for 3 weeks, after which they were exposed again on the test fence. *A* was primed with aluminum primer and *B* with a commercial white primer advertised as particularly resistant to failure under these conditions. Both panels were finished with two coats of a lead and zinc paint. The cure for paint failure of this kind lies in keeping the side walls of houses dry, not in the application of special primers.

ALUMINUM PRIMER AND PAINT SCALING

Confusion has arisen about the bearing of aluminum priming upon the moisture-blistering and subsequent scaling (*1A*, *14*) of house paints (*8*). The fact that aluminum primers increase the resistance of coatings to moisture movement has led painters and house owners to assume that it should prove helpful in minimizing the defects in question. On the other hand, many paint technologists assume that coatings are more susceptible to moisture-blistering the greater their resistance to moisture movement, inasmuch as the harmful moisture nearly always operates from the back of the painted boards. The mechanism of moisture-blistering, however, is by no means completely understood, nor do the facts thus far available permit acceptance of either of the above assumptions.

Tests by a method recently described by the writer (*6*) indicate that white lead paint applied with a priming coat also of white lead is more resistant to peeling and scaling as a result of moisture-blistering than other kinds of house paint. If the white lead paint is applied over aluminum primer instead of white lead primer, the danger of serious damage by moisture acting behind the boards is undoubtedly increased. Lead and zinc paints applied in the customary manner are more sensitive than white lead paint to scaling following blistering, and substitution of ordinary aluminum primer for white primer does not materially improve their behavior under the conditions in question. On the other hand, the writer finds that aluminum primer made with aluminum powder of standard lining grade instead of standard varnish grade makes lead and zinc paints somewhat more resistant to faulty moisture conditions.

White paints of the classification containing no white lead at all are the most sensitive to scaling following moisture blistering. The resistance of such paints is found to be definitely increased by applying them over ordinary aluminum primer.

The writer's experiments also indicate that back-priming of exterior woodwork with aluminum paint does not reduce the chances of blistering and scaling when moisture penetrates behind the boards. Back-priming may, however, protect woods that contain water-soluble colored materials against discoloration by water that temporarily finds its way behind bevel siding and then seeps out between the overlapping boards to run down over the paint.

ACKNOWLEDGMENT

Acknowledgment is made of assistance of C. E. Hrubesky in supervision of the tests on western larch, of Don Brouse in supervision of the tests on Douglas fir and in the making of inspections, and of the following organizations in providing test fences for some of the experiments: Bureau of Standards, North Dakota Agricultural College, National Lead Company, W. P. Fuller Company, and Southern Pacific Railroad.

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RECEIVED October 24, 1933.

New American Iodine Industry

G. ROSS ROBERTSON, University of California at Los Angeles

Oil-well brines in southern California are now able to furnish the entire iodine requirements of the United States at present business levels, with some possibility for expansion when needed.

The iodine present in very dilute solution as iodide is separated either as the free element, adsorbed in charcoal, or in the form of silver iodide, from which the desired element may readily be obtained.

ABOUT seven years ago a young petroleum chemist of Signal Hill, Long Beach, Calif., was struggling with the problem of separating emulsified brine from the native crude oil of the local field. The great resistance of this mixture to conventional demulsification technic led him to look for disturbing substances among the ionic components of the aqueous phase. It was soon noted that the addition of an acidic oxidizing agent, such as nitrous acid, turned the brine slightly yellow, and considerable quantities of iodine were revealed.

Although iodine has been observed in oil-well brines of other districts, such as Louisiana, the high content in the California wells was particularly encouraging. Later surveys have shown, however, that only a few petroleum zones of the Far West have enough iodine content to warrant development. These lie in and near Long Beach, Calif., and include not only Signal Hill, of the 1922 boom-time oil fame, but the near-by Dominguez and Seal Beach fields which are not far from the city limits of Los Angeles. In these districts the day of flush oil production is long past, and the current flow from wells shows a high percentage of saline water. These facts are to the advantage of the iodine producer.

The brines in question, aside from iodine content, approximate sea water in general composition. The usual high percentage of sodium chloride, and substantial calcium and magnesium content, are found. Iodide ion, in amounts ranging from 30 to 70 parts per million, is the unique feature.

A reasonable explanation pictures a vast forest of seaweed in some past geological epoch in the southern part of what is now Los Angeles County. It is known that the whole southern coast, running for many miles on either side of Long Beach, has had comparatively recent elevation from submarine levels. The entire lowland section adjacent to Los Angeles was under water during the Tertiary geological period. Not only ordinary kelpweed, but possibly deposits of diatoms and similar small plants may have accumulated. Presumably the decomposition of huge quantities of the marine vegetation yielded first petroleum as an organic residue and iodide as an aqueous extract. Districts lying outside the supposed seaweed zone, such as at Santa Fe Springs, of great oil fame, do not show such high iodine content; the large oil fields to the north are not promising, both from lack of water and distance from the marine location. The bromide content is not high, so that no special concentration of a prehistoric sea water is indicated.

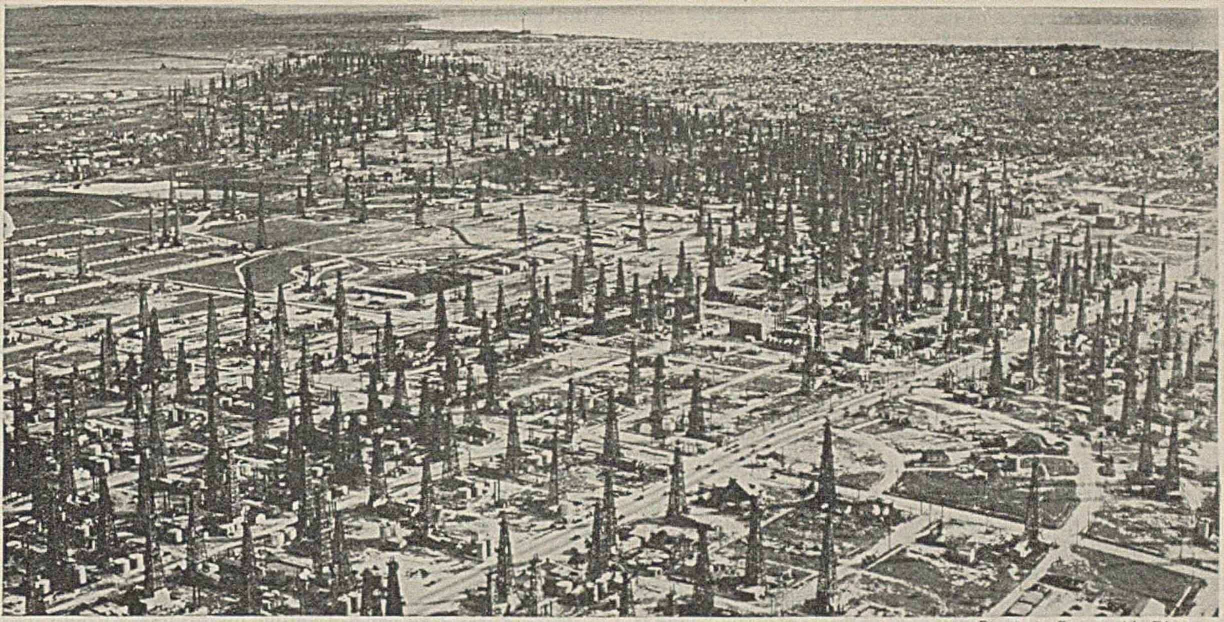
The iodine industry, always something of an uncertain commercial quantity, is no more of a bonanza here than in Chile, Japan, or other foreign production center. Production costs are always substantial. Since Los Angeles County's three iodine producers are now meeting the equivalent of the entire United States' demand for iodine, a future potential resource is recognized. At the present writing approximately one-half ton per day of so-called "crude" iodine, of purity above 99 per cent, is being manufactured.

Even the high figure of 70 parts per million, while favorable, naturally requires plant processes suited to huge flows of brine. If the raw material were clean, one might hope to pay the expenses of concentration by running an adjunct salt business. The contamination of oil and mud, however, introduces serious difficulties.

Fortunately there are several characteristic properties of iodine which offer aid in reclamation from extremely dilute solution. Chief among these are the ease of oxidation of iodide to volatile iodine, and the readiness and completeness of precipitation as silver iodide. These two fundamental reactions are the basis of the present California processes and are discussed in detail below.

MINOR PROCESSES

The classical experiment of extracting iodine from solution with the aid of chloroform or similar oil solvent led to considerable investigation of the application of the cheaper kerosene to a large-scale method. Emulsion difficulties and fire haz-



Courtesy, Spence Air Photos

DERRICKS AT SIGNAL HILL OIL FIELD FROM WHICH IODINE IS NOW BEING OBTAINED

ards, among other factors, have led to the abandonment of the plan, at least temporarily.

The blowing-out process, sometimes known as the Turrentine process, has been used in Louisiana (*2*) but has been shelved there and in California. By this scheme the iodide is first oxidized to the free state with any cheap oxidizing agent. The pH is necessarily adjusted, according to the patent claim, to a value not greater than 3.5. Air is now blown through the resulting dilute iodine solution. The effluent air, laden with the halogen, passes into bubble towers where iodine is extracted with aqueous caustic alkali. Final isolation of the product may then proceed as discussed later.

Precipitation of the native iodide as the cuprous salt seems feasible and has been tried. Unfortunately the necessary reduction or splitting of the cuprous iodide is not so readily accomplished as the like procedure for silver iodide, presumably because of the higher position of copper in the electromotive series. Oxidation of the cuprous ion may offer difficulty as well. Similarly the mercurous iodide process has not come into favor.

PRACTICAL METHODS

Before any chemical process is started, a clean-up of the brines is an obvious necessity. Some of the unattractive raw material comes from oil traps, settling tanks, and other containers where the petroleum was supposed to have been separated from the water. Other fractions come from rotary drill operations (during prosperous times when wells are being drilled) and still others from petroleum dehydration plants. The combined flow runs to several million gallons daily.

The huge flow means the exclusion of such filter aids as charcoal or diatomaceous earth as being too expensive. Sand filters are employed. By a system of ponds, each emptying into the next through a submerged spillway, much of the gross accumulation of crude oil is left behind. Where rotary drill mud has entered, colloidal clay persists even in the presence of the salts and makes some trouble in later operations. Peculiarly, the effluent of the iodine plant is more attractive than its raw material, and hence cannot but be a benefit rather than a nuisance to the adjacent beaches.

The clarified brine is now subjected either to the silver iodide or the charcoal process, the two plans at present favored. The latter method accounts for more than half of the recent Los Angeles output; two operators use the silver process. The following descriptions are representative of California technic, subject to interchange of operations and modification with rapidly changing conditions.

SILVER IODIDE PROCESS

To the clarified brine, in a wooden tank, is added the exact theoretical requirement of silver nitrate in a 1 to 2 per cent solution. Mechanical stirring facilitates the immediate and complete precipitation of silver iodide without trouble from localized formation of silver chloride. A small quantity of ferric chloride is added, and this hastens the subsidence of the desired silver precipitate. Within 2 to 4 hours the settling is complete, and most of the supernatant liquid is run out to waste.

The mixed silver iodide–ferric hydroxide precipitate, with some residual brine, is pumped out as a thin sludge. A second settling and further elimination of brine may take place in a second tank. Concentrated hydrochloric acid is now added; this of course dissolves the ferric hydroxide. The resulting acidic slurry of silver iodide is now mixed with clean new steel scrap (punchings, wire, etc.). If the brine is clean, transformation to metallic silver and ferrous iodide is complete in an hour. With oil contamination, several hours may be required. The material for the container in this reaction has been something of a problem, neither wood nor iron being entirely satisfactory.

The reclaimed silver, in a finely divided state, is readily converted into silver nitrate and sent back for repeated duty. The ferrous iodide filtrate is now treated with whatever oxidizing agent is favored by the manufacturer or the market. Chlorine, or sodium dichromate and sulfuric acid, or nitrite and acid, are employed. Granular iodine is at once precipitated. This is melted, while still wet and fresh from filtration, under concentrated sulfuric acid. The resulting slightly diluted acid is of such high boiling point that iodine can be directly melted under its surface. The liquid iodine phase can be tapped off or otherwise separated in a condition relatively free from acid. After the material has cooled, the cake of iodine is cracked up, washed free of acid, and dried over calcium chloride in drying chambers. The product, while termed "crude" iodine, is often of 99.8 per cent purity and has been purer than much of the more beautiful resublimed iodine known in ordinary commerce. The final product is shipped in 200-pound kegs. No attempt is made in California to prepare either the resublimed flake iodine or any of the salts. Further details of this method are discussed in the patent literature (*3*).

Carbon Process

The brine, partially cleansed of its oil and mud, is treated with the amount of sulfuric acid needed for the oxidation reaction which soon follows. The change in acidity causes some further clarification, and accordingly this operation is conducted in a pond where deposition of solids offers no complications.

Just as the acidified water is about to reach the main tank, the proper quantity of sodium nitrite solution is added. Iodide is oxidized to iodine, and presumably the nitrite is reduced to nitric oxide. In view of the exposed condition of the solution, we may also presume that atmospheric oxygen may cause the formation in turn of nitrogen dioxide, fresh nitrous acid, and thus start a new cycle in reduced quantity.

The resulting yellow solution, carrying free iodine, is treated with Nuchar or equivalent activated carbon, and the whole is thoroughly stirred with a battery of vertical-shaft individually motored agitators. Iodine and some clay and oil are caught in the carbon.

After the carbon has settled in the reaction tank, most of the clear mother liquor is run to waste. Successive batches, up to twelve or fifteen in number, of new oxidized brine are introduced, and the charcoal is eventually loaded with iodine to the limit of efficiency. The mixture is then thickened to a sludge with appropriate drainage of the worthless mother liquor.

Extraction of Iodine

The sludge passes to a large rectangular vacuum filter, suggestive of an immense Büchner funnel, with a canvas filter bed. The residue from filtration is treated with caustic soda solution until the latter acquires about 3 per cent of sodium iodide. Apparently the iodate, which should appear in the familiar ratio of 1 iodate to 5 iodide, is at least partially reduced. Possibly the carbon catalyzes the reduction. This is of course a disadvantage in view of the oxidizing agent required soon thereafter.

The iodide solution is now treated in a conical precipitating vessel with chromic-sulfuric acid mixture. Iodine collects as a dull granular lumpy mass. It is either melted under sulfuric acid, as previously described in the other process, or steam-sublimed. By the latter procedure the crude iodine is melted in a large metal vessel. Steam is blown through the material, and the vapors pass to a long vitrified stoneware pipe line wrapped in cloth over which water constantly pours. Since the steam is completely condensed, less loss of iodine is experienced than would occur in a conventional air-sublimation process. The latter technic, however, yields a more beautiful product.

The wet iodine sublimate is dried on trays in the presence of calcium chloride in a heated room. Fortunately this place which is thoroughly saturated with iodine can be out of doors.

Iodine Market

Thanks both to the California producers and the Japanese kelp iodine industry, the old pegged price level of $4.65 per pound seems to have been abandoned indefinitely. This question has been taken up in detail by Holstein (*1*) who discusses in particular the Chilean situation. Roman (*4*) has given an elaborate review of the economics of iodine over a period of several decades, with world-wide consideration. An extended bibliography is given with his paper.

The old standard price of iodine, maintained without regard to general business conditions, apparently was based to some extent on the observation that no one person or company seems to need a large quantity of the material. Iodine does not make up a large part of the cost of any major world product. At the same time a great many customers need small amounts. In cases where iodine would seem to be requisite in quantity, usually its brother bromine, or perhaps chlorine, can be drafted into service without serious difficulty. Accordingly the traffic in iodine, like that in diamonds, has been able to bear a price not directly related to production costs.

Under present-day competitive conditions, however, the price of iodine is approaching manufacturing costs, or does so in regions of respectable living standards. Unless some new and important use for iodine is discovered, we may expect comparatively little expansion of the California industry.

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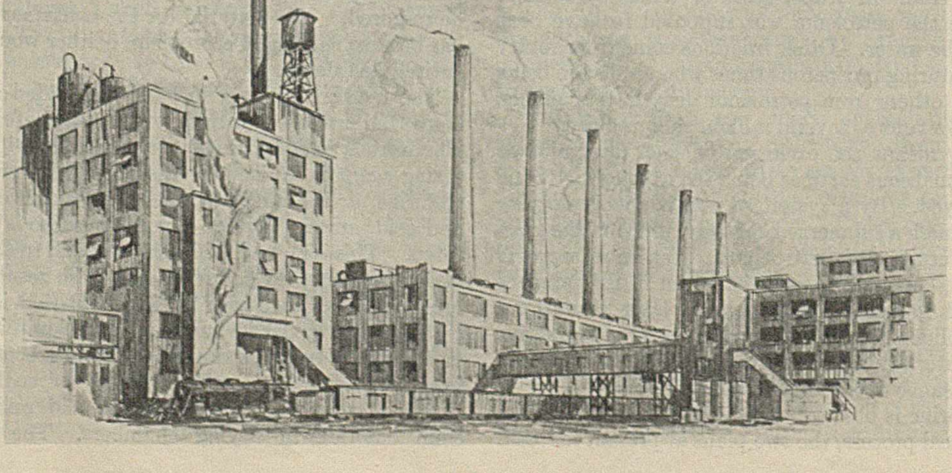

Clarification of Vinegar

Lawrence G. Saywell, University of California, Berkeley, Calif.

The data obtained in these studies indicate that certain of the properties of wine and cider vinegars are related to the presence of colloidal material. It has been found that many of the earlier methods of clarification of vinegars were unsatisfactory because of a lack of consideration of their colloidal properties. On the basis of this work, three methods of clarification have been devised involving the use of casein and tannin, casein and bentonite, and potassium ferrocyanide and a protein such as gelatin or albumin. These methods have resulted in satisfactory clarification of vinegars as evidenced by the fact that vinegars so treated have remained brilliantly clear for 2 years or more. It has been found that heating in a closed system facilitates clarification.

VINEGAR prepared from grape musts or wines, as well as cider vinegar, often becomes cloudy or hazy on standing. This objectionable property may become apparent within 30 or 60 days or may be delayed for periods up to 12 and 15 months or more. The clouding has been observed to occur in both pasteurized and unpasteurized vinegars, in sealed bottles as well as in those exposed to the air through cotton plugs.

Often an attempt to clarify the vinegar is based on methods used for fruit juices or for wines and beer, without considering the properties and composition of vinegar. In juices and beverages, clouding or turbidity is more generally ascribed to the systems involving the proteins, pectins and gums, tannins and heavy metals present. The methods of clarification of fruit juices (*2, 3, 5, 8, 23*) usually involve clarification by means of enzymatic changes, by the formation of a precipitate on the addition of tannin and gelatin, by the use of inert absorbing agents such as the carbons, and by the use of diatomaceous-earth filter aids in direct filtration. In addition, use is made of special procedures such as the coagulation of the protein by heating at an optimum pH. For the individual juices and beverages the general conditions as well as the details of the respective clarifications are known and generally available. However, the situation with regard to vinegars, particularly wine vinegar, is somewhat unsatisfactory.

Preliminary Experiments

Commercial vinegars from both red and white wines were employed in these studies. A few observations were also made on cider vinegars. The effectiveness of the methods has been judged by the color and stability (nonclouding) of samples held for 22 to 26 months at room temperature. Stability over a shorter period has been considered inadequate as a measure of the success of clarification.

Experiments were conducted in order to observe the effect of added tannin, citric acid, sulfur dioxide, gelatin, hydrogen peroxide, dipotassium hydrogen phosphate, potassium dihydrogen phosphate, pectin hydrolyzing enzymes, and two carbon blacks. These materials were added singly, as well as in combination; they are often used for fining, clarifying, or decolorizing purposes.

Three tests with tannin were made. Vinegar solutions containing 0.2 gram tannin per 100 cc. red vinegar were treated, respectively, as follows: (1) no further treatment; (2) heated at 70° C. for 10 minutes; (3) not treated and 50 p. p. m. sulfur dioxide added. After standing for 10 days, all three samples had a heavy black sediment at the bottom of the flasks. The pasteurized sample had somewhat more than the unheated sample, while the sample with the added sulfur dioxide had about twice the sediment of either of the others. The three samples were filtered through a cellulose or paper pulp filter, the resulting filtrates being reddish black. To these filtrates were added 0.1 per cent diatomaceous earth and 2.0 per cent activated carbon. The sample that had previously been heated to 70° C. was then heated at 65° C.; the other two samples were not heated. All three were filtered. All filtrates were much lighter in color; the one heated at 65° C. was a light amber. On storage the first sample clouded within 30 days, the third within 45 days, and the second remained sterile and clear for 80 to 90 days. The heavy precipitate with the added tannin resembled that of a pyrocatechol tannin with ferric iron. The heating at 70° C. apparently coagulated or in some other manner removed from the vinegar substances which would later contribute to clouding. The tannin treatment alone or with heating or added sulfur dioxide appeared inadequate for complete clarification. Likewise, the activated carbon did not appear to remove all the constituents responsible for clouding.

The effect of adding citric acid in the proportions of 0.05 to 1.00 gram per 100 cc. of vinegar was also noted. Three similar sets of such samples were prepared in duplicate. The first received no further treatment; the second was heated at 60° C. for 10 minutes; the third was heated at 70° C. for 10 minutes, cooled, and, after one week, reheated at 70° C. for 10 minutes, cooled, and again filtered. It was observed that such heating, in a closed system, followed by rapid cooling, tended to reduce the harshness of some vinegars and was therefore desirable. Those samples with the larger amounts of citric acid had larger quantities of precipitate. All samples were cloudy at the end of 100 days. The samples with the higher amounts of citric acid were slightly less cloudy than the others of the same set. Clouding occurred in both the set exposed to air and in the one not exposed. For duplicate samples the amount of clouding apparently decreased with the increase of heating employed. Sediment on the bottoms of the flasks was also observed, in all cases being greater than with controls containing no added citric acid.

In two similar sets of experiments the effect of citric acid and tannin, or of citric acid, tannin, and sulfur dioxide was also studied. All treatments were the same as those with the previous set which used only added citric acid. Observations showed that, although all the samples filtered clearly to brilliantly, those with added tannin were blackish red in color, while those with added sulfur dioxide were somewhat lighter. All samples became cloudy within 90 to 120 days.

Samples were also clarified by the use of gelatin and gelatin plus tannin. It was found that there was an optimum for the quantity (from 0.05 to 0.2 gram per 100 cc.) of gelatin added in relation to the maximum clarification effected. However, these samples reclouded in 75 to 100 days. Samples containing added gelatin and tannin were somewhat darker than with equal amounts of gelatin alone, and remained unclouded for as much as 30 to 45 days longer. The added tannin presumably reduced the quantity of gelatin finally remaining in the vinegar. These results are similar to those reported by LaMarca (*9*) on the clarification of wines.

An additional observation was made on duplicates of the samples treated with the optimum amounts of both gelatin and tannin which were then also heated at 70° C. for 10 minutes and cooled, etc., as above. These samples remained clear for about 5.5 to 6 months. These results also would indicate that the heat coagulation removed some of the substances which were involved in the clouding of the vinegar. In any event it would appear that the use of gelatin introduces a soluble material into the vinegar which is not entirely removed during clarification as above described—e. g., with tannin—and which may be involved in later reclouding. The use of gelatin or gelatin plus tannin does not result in a clarified vinegar which remains brilliantly clear on continued storage.

Samples treated similarly to those showing the greatest stability in the above tests were given either an additional treatment of aëration for 24 hours or were subjected to the direct addition of 0.1, 0.3, and 0.5 per cent hydrogen peroxide at the time of addition of gelatin and tannin. This treatment did not appear to affect the period of stability greatly, such samples clouding after about the same time of holding as those without aëration or hydrogen peroxide. The increased quantities of hydrogen peroxide produced a decrease in color of the vinegar.

Both potassium dihydrogen phosphate and dipotassium hydrogen phosphate were added to vinegars in concentrations of 0.05 to 1.0 per cent. Concentrations of both salts of 0.5 and 1.0 per cent produced clear to brilliant vinegars. Slight precipitates which occurred on the bottoms of the flasks of both series were found to consist largely of the insoluble phosphate. On standing 135 days, all samples became cloudy.

Experiments using varying proportions of two different carbon blacks yielded brilliant filtrates which, however, clouded on standing from 60 to 120 days. With the larger proportions marked decolorization was observed.

ENZYMATIC CLARIFICATION

A study of the hydrolysis of the pectin in apple juice by the enzymes of several organisms has been reported by Pitman and Cruess (*15*). They have shown that the enzymes of a type elaborated by *Penicillium glaucum* have a marked ability to hydrolyze the pectin of apple juice, over 75 per cent of the pectin being hydrolyzed in one case. Later Kertész (*8*) adapted this property of this organism to the clarification of apple juice. Experiments were completed using commercial preparations of these enzymes for the purpose of clarification of wine vinegars. In most cases even an initial clarification was not obtained, and in all cases the clarified products clouded in 60 to 120 days. The results of Marsh and Pitman (*12*) indicate that the pectin content of grape juice is from 0.1 to 0.3 per cent. The lower value is somewhat below 0.12 per cent pectin obtained on a grape juice sample clarified in this manner and reported by Willaman and Kertész (*20*). These combined results suggested that the pectin content of the vinegar would be quite low, perhaps below a concentration at which the enzymatic method would be effective. Analysis of several vinegars for pectin by the Wichmann method (*19*) indicated initial pectin contents of 0.048, 0.073, 0.053, 0.038, 0.040, 0.048, 0.052, and 0.032 per cent. These values, with the exception of 0.073 per cent, are all lower than the reported minimum values of 0.056 for enzymatically clarified apple cider (*8*) and 0.061 for grape juice (*20*) similarly treated. As a result of the observed reclouding of such clarified samples and the demonstrated low original pectin contents, it was concluded that such an enzymatic method of clarification was not satisfactory. Parallel observations (unpublished) on the clarification of apple cider and Muscat, Pierce Isabella, Carignane, and Tokay grape juices confirmed this conclusion, for all such clarified samples reclouded within 45 to 120 days. Recently this reclouding of previously enzymatically clarified ciders also has been confirmed by Diehm (*6*) and by Carpenter and Walsh (*3*).

However, Diehm also reports (*6*) that in collected samples of reclouded ciders, invariably the clouding was found to be due to the growth of organisms. In this respect the present author's results with wine and cider vinegars and those of Carpenter and Walsh (*3*) with apple juice do not confirm Diehm's. It has been found here that previously clarified samples, even though pasteurized, have developed a heavy cloud after storage for 8 or 9 months. Diehm has reported that samples containing 0.1 per cent sodium metadisulfite, which is equivalent to 0.067 per cent available sulfur dioxide, were effectively preserved in a sterile condition and presumably did not recloud during his period of observation. On the contrary, it has been observed in this laboratory that clarified commercial samples containing as much as 0.20 per cent liquid sulfur dioxide were sterile, and yet they all developed a heavy cloud in 8 to 12 months. The results of these two investigations may not be entirely contradictory but are perhaps largely supplementary. Diehm's reported observations are over comparatively short periods, up to 15 days and to 3 and 4 months. Observations here have been over 2-year intervals. Consequently, the difference may be explained by the fact that samples which appear to be perfectly clarified and remain brilliant for several weeks or 3 and 4 months will gradually develop a heavy cloud after 8 to 15 months. Furthermore, pasteurized samples and those sterilized by the use of chemical preservatives, such as sulfur dioxide, may also cloud.

The above several experiments suggest the conclusion that the reclouding of previously clarified juice or vinegar is due to two causes: In one instance the clouding is the result of an interaction of the organic and inorganic constituents of a sterile heterogeneous system; in the second, such interactions or others are affected by the presence of bacterial action. In general it is evident that any clarified sample will cloud if subjected to sufficient bacterial action, that some clarified sterile vinegars will cloud, and that other clarified sterile vinegars will not cloud on prolonged storage. Hence, sterility as such is not the criterion of stability. Rather, it is the type of clarification to which the sterile vinegar is subjected that appears to be the controlling factor.

COLLOIDAL PROPERTIES OF VINEGAR

The results of these experiments indicated that clarification and the removal of certain constituents from clouded vinegars involved substances which were probably in the colloidal state, or were at least affected by added materials exhibiting an oppositely charged particle. The constituents of the vinegar likely to possess colloidal properties were considered to be the proteins, tannin, and pectin. In addition, qualitative analyses of clouded vinegars often indicated relatively high iron concentrations. Such iron contents were generally accounted for by the contact of the original juice with iron parts of presses, pipes, and other containers where special precautions had not been followed by the processor. The pH range for most of the vinegars observed was 3.2 to 3.5, and in this range the protein should exhibit a positive charge (*21*), tannin negative (*21*), pectin negative (*13*), and iron a positive charge.

Considering the vinegar as a colloidal system, many of the results of the above experiments offer new suggestions. Oppositely charged constituents would have a tendency to neturalize each other electrically with an eventual precipitation of the neutral particles. Also, the rate of clouding and precipitation should be greatly decreased after the first precipitation and filtration (clarification), since the concentration of the reacting substances will have been relatively greatly decreased. In the experiments with the added tannin, a mutual precipitation with positively charged particles, including those of protein and iron, was probable. This was found to be the case. Using heat coagulation as an indication of the protein content, it was found that samples of vinegar, treated with tannin and filtered, yielded (on equal centrifuging) a smaller quantity of heat-coagulated material than did those not treated with tannin. Similarly it was found that tannin treatment decreased the iron content. In a typical sample the iron content was reduced from 2–3 mg. per 100 cc. to 1.0–1.5 mg. per 100 cc. The effect of the added citric acid in increasing the quantity of precipitate formed suggests the occurrence of a Hofmeister series of ions where the citrate ion possesses a greater ability to flocculate the sol than do either the tartrate or acetate ions. This agrees with the general arrangement of citrate > tartrate > acetate for, at least, protein systems (*7*).

The effect of added carbon black should be quite different from that of added tannin. In the acid vinegar the electronegative constituents and, to a certain extent, the amphoteric protein substances will be strongly adsorbed (the former increasingly so with decreasing pH, and the latter increasingly so as the pH approaches the isoelectric point of the amphoteric substance). Inasmuch as the pH range was relatively limited, a wide variation of effect was not noted. However, the actual decolorizing effect was very marked. Presumably this paralleled the decrease of tannin and pigment content and would also be similar to the decrease in other negatively charged constituents, such as pectin, which were present. The effect of added protein was similar to that of the carbon black, though probably to a smaller extent, as evidenced by only a slight decolorization of the vinegar. With both gelatin and the carbons, reclouding occurred and was the result of electropositive constituents remaining in the vinegar. A portion of these could be coagulated or precipitated by heating at 70° C. or by the further addition of electronegative substances. Apparently the use singly of any of the above positively or negatively charged agents was unsatisfactory.

Casein-Tannin Clarification

While the results with gelatin had not been entirely satisfactory, it seemed worth while to attempt the use of some similar material which would be positively charged, would have known capacities for combining with tannin, might possibly form an insoluble iron compound, and would be much less soluble in the vinegar, thus avoiding a marked fault of gelatin. The properties of casein (*14, 18*) coincide closely with the above demands. It is positively charged at pH values below 4.0, it precipitates tannins from solutions (particularly between pH 2.7 and 4.0), it apparently forms insoluble iron compounds at this pH range, and its solubility in vinegar is very low.

The solubility of the casein in acid solutions was first investigated. Sutermeister (*18*) gives some data on the solubility of casein in hydrochloric acid solutions of various acidities. His data show that, after 22 hours in the acid solution, casein is soluble to the extent of 0.10 to 0.16 per cent in solutions of pH 4.36 and 3.11, respectively. The solubility of casein in acetic, tartaric, and citric acid solutions, both without and with 0.1 per cent added tannin, was then determined. The method was similar to that of Sutermeister (*18*). The results are given in Figure 1.

The data show that for the pH range studied there are considerable differences of solubility of the casein in the acid solutions employed. The solubilities increase with the acids in the order: citric, tartaric, acetic, hydrochloric. These results would confirm and explain the observation that the citrate ion possesses a greater ability to flocculate the sol than do either the tartrate or acetate ions. It is important to observe further that the presence of 0.1 per cent added tannin also decreases the apparent solubility of casein in either citric, tartaric, or acetic acid solutions of pH 2.0 to 3.5. For example, at a pH of 3.3, corresponding to that of a vinegar, tannin decreased the apparent solubility of casein in tartaric acid solution from 0.13 to 0.065 gram per 100 cc. of solution, and similarly in citric acid from 0.10 to 0.06 gram per 100 cc. of solution.

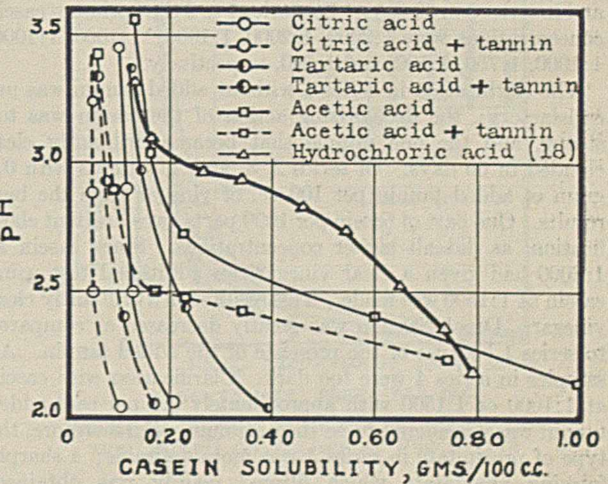

Figure 1. Effect of pH and Tannin on Solubility of Casein in Various Organic Acids

These data show that the individual constituents (acetic acid, tartaric acid, and tannin) of the wine vinegar at a given pH cause a decreased solubility of casein. Further, in vinegar there are other constituents such as pectin which are electronegative and therefore also react with the electropositive casein. Casein also reacts with the iron, forming an apparently insoluble, complex compound. This latter would not be the result of the colloidal behavior of two oppositely charged particles, for in this pH range both the casein and iron are electropositive. It has been suggested (*18*) that such casein-iron compounds are of a purely physical nature. Quantitative tests showed that with a typical sample of vinegar the iron was reduced from 2.5–3.0 mg. per 100 cc. to 1.0 mg. per 100 cc. The casein, therefore, appeared to be quite as effective as tannin in this respect.

On the basis of the above observations, several series of experiments were prepared. To nine samples in each series casein was added in the proportions of one part of casein to 125, 250, 500, 1000, 2000, 5000, 10,000, 20,000, 50,000, 100,000, 200,000, and 500,000 parts of vinegar. The following series was prepared:

1. Natural vinegar (pH 3.35).
2. Vinegar + 0.05 gram added tannin per 100 cc. vinegar.
3. Vinegar + 0.10 gram added tannin per 100 cc. vinegar.
4. Vinegar + 0.20 gram added tannin per 100 cc. vinegar.

5, 6, 7. In series 2, 3, and 4 the casein was added 5 hours after the tannin; series 5, 6, and 7 were duplicates of series 2, 3, and 4, respectively, except that casein was added 15 hours after the tannin.

8. Vinegar + 0.10 gram added tannin per 100 cc. vinegar, heated at 70° C. for 10 minutes, cooled, and filtered after one hour.
9. Same as 8 except that the sample was filtered after 15 hours.

The casein was dissolved in an ammoniacal solution, the ammonia was removed by aëration under a vacuum, and suitable amounts of this 4 per cent stock solution were added to the vinegar samples. All samples were filtered and stored in stoppered flasks, observations being taken at 10-day intervals.

With both the natural vinegar and the vinegar plus added tannin there was an optimum and variable quantity of casein required for clarification. Less than this quantity did not produce a brilliantly clear vinegar; progressively more than this amount produced clear or brilliantly clear vinegar that, however, was increasingly decolorized. In series 5, 6, and 7 with the added tannin present for 15 hours before the casein was added, satisfactory clarification was not obtained. Clouding occurred within 60 days. Series 8 and 9 were also unsatisfactory; too high concentrations were required for clarification, and subsequent clouding occurred in series 8 in 60 days and in series 9 in 30 days. For series 1 to 9 the optimum casein concentrations were 1:2000, 1:2000, 1:1000; 1:1000, 1:1000, 1:1000, 1:750, 1:500, and 1:500, respectively.

The clarification in series 1 without added tannin was unsatisfactory; the decolorizing action of the casein was too strong, and the one sample that became brilliantly clear clouded in 60 days. Of series 2, 3, and 4, series 3 with 0.1 gram of added tannin per 100 cc. of vinegar gave the best results. One part of casein per 1000 parts gave brilliant clarification, as did all higher concentrations. Since casein at 1:2000 had given a clear vinegar, an additional test using casein at 1:1500 was made. This resulted in a brilliantly clear vinegar. Decolorization was greatly decreased as compared to series 1 because of the presence of the added tannin. All samples in series 4 were too dark. Clarification with casein at 1:1000 or 1:1500 with approximately 0.1 per cent added tannin was considered to be the optimum. Furthermore, the type of precipitate in series 3 was more desirable; a sharply forming precipitate which filtered readily was obtained. The samples of series 3 clarified with casein at 1:1500 or higher concentration kept without clouding for 11 to 12 months.

A marked relation between the volume of the precipitate and the degree of clarification was observed in both series 3 and 4. Twenty-cc. portions of the vinegar were taken immediately after adding casein in the twelve proportions from 1:125 to 1:100,000 parts, inclusive, and centrifuged in graduated tubes at 2000 r. p. m. for 10 minutes; the volumes of the separated precipitates were then noted. These volumes are given in Table I.

Table I. Volumes of Casein Precipitate from 20 cc. of Vinegar

(In cubic centimeters)

Casein concn.:	1:125	1:250	1:500	1:1000	1:2000	1:5000	1:10,000	1:20,000	1:50,000	1:100,000
Series 3	1.70	1.55	1.35	0.80	0.40	0.30	0.16	0.14	0.13	0.10
Series 4	1.98	1.80	1.60	0.95	0.70	0.35	0.27	0.19	0.17	0.14

It is notable that in series 3 the volumes of the precipitate from the sample with casein at 1:2000 is half that of the sample with casein at 1:1000, and that this sharp difference in relative volumes (which is not so marked with other similar differences of casein concentrations) coincides closely with the difference between the casein concentration effecting brilliant clarification and that insufficient for this purpose. With series 4 this change was noted between casein concentrations of 1:2000 and 1:5000, the former being clear but not brilliant, and the latter hazy. A comparison of the volumes of series 3 and 4 given in Table I indicates that the increase of the added tannin from 0.10 to 0.20 gram per 100 cc. of vinegar increases the volume of the precipitate.

A similar variation of the volume of precipitate with the varying tannin contents of the natural vinegars was also noted. While the tannin contents of many of the vinegars of a given type may not vary greatly, nevertheless it was found necessary to make a limited series of tests for each vinegar. Usually a series with 0.10 gram added tannin per 100 cc. vinegar and casein at 1:750, 1:1000, 1:1500, and 1:2000 or 1:4000 was found sufficient. For many commercial wine vinegars casein at 1:1000 to 1:2000 was found satisfactory.

Of the methods investigated, the casein method appeared to offer the greatest possibilities, as evidenced by the longer periods during which clarified samples remained brilliantly clear. However, there appeared to be certain disadvantages: A still longer period of stability was desirable; the decolorizing property of higher concentrations, while an advantage with very dark vinegars, was not always wanted; and the preparation of the stock casein solution was somewhat bothersome. In an attempt to eliminate this latter disadvantage, skim milk was used as a source of casein. Brilliantly clear samples were obtained which, however, clouded in 4 to 6 months. The difference between the observations with the two casein preparations was presumably the result of the added milk solids, not casein in the skim milk.

Bentonite Clarification

Studies of the effect of other colloidal substances were also made. Among these substances were suspensions of bentonite. Lothrop and Paine (*11*) have reported the use of bentonite in the removal of the colloids from honey, and certain of their observations have been paralleled in these studies. Bentonite differs from casein in many respects, including that of particle charge, bentonite being electronegative. Typical vinegars were treated with varying amounts of a 5 per cent fresh stock bentonite suspension such that bentonite was added in the proportion of one part to 100, 200, 400, 800, 1000, 1500, 2000, 5000, and 10,000 parts of vinegar. From the standpoint of volume of precipitate formed and effected clarification, the proportion of 1:1500 was found most satisfactory. At higher concentrations of bentonite the volume of the precipitate was progressively greater, until at a concentration of 1:100 the precipitates occupied 75 to 90 per cent of the total volume of the vinegar. With concentrations lower than 1:2000, clarification was not complete, progressively decreasing to 1:10,000 parts. An estimate of the desirability of the precipitation was obtained by centrifuging 20-cc. portions of vinegar with each of the concentrations of bentonite at 2000 r. p. m. for 10 minutes in graduated tubes. The volumes of the collected precipitates from vinegars with pH values of 2.85, 3.30, 3.80, and 4.30 were determined. The curves given in Figure 2 were constructed from these data. It is apparent that there is a sharp increase of volume of precipitate with increase of bentonite concentration above that required for satisfactory clarification. The change in pH of the vinegar effects a considerable relative change of volume for bentonite concentrations of 1:2000 to 1:1000, but this difference is also very small in relation to increased volume resulting from bentonite concentrations above 1:1000.

Several series of experiments were thus arranged in which bentonite was used in different ways. Having observed that bentonite at 1:1500 appeared to be the optimum, this concentration was employed in subsequent experiments, unless otherwise noted. It has also been observed that the bentonite precipitate was quite heavy and firm, and filtration was often retarded. Accordingly, a combination of the flocculating and filter-aid principles was secured by adding 0.1, 0.2, and 0.4 per cent filter aid with the bentonite. The flocculation and settling occurred in these samples in 30, 15, and 28 minutes, respectively. The samples filtered clearly, that with 0.1 per cent being the best in appearance. However, on standing 30 days, the samples became hazy, and light sediments which increased with the quantity of filter aid added, appeared on the bottoms of the flasks. Control samples with only added bentonite remained clear for the same length of time. Two tests were made on heated vinegars. The vinegar was heated at 70° C. for 10 minutes and bentonite was added to one portion. Flocculation occurred within 30 seconds and settling within one minute with only bentonite present. In the second portion with the filter aid also present, flocculation required about 5 minutes but was not sharply apparent, and settling required 15 to 20 minutes. The presence of the filter aid greatly retarded the precipitation. The samples were both filtered after complete settling and cooling, and portions of the filtrate were centrifuged. The filtrate from the first sample was brilliantly clear and gave no detectable precipitate on centrifuging, while the second filtrate was clear and yielded a slight sediment on centrifuging. The noticeable difference in these samples in comparison with those of the previous tests was in the effect of heating on the character and rate of flocculation. There was a distinct and marked improvement in the rate of floccuation and in the subsequent rate of filtration. It was also found better to add the bentonite to the hot vinegar rather than to the vinegar after cooling, and such procedure was followed in all subsequent experiments. The results of similar experiments (a total of fourteen) with different vinegars indicated that, in general, while the use of 0.1 per cent filter aid with or without bentonite gave a more desirable precipitate than with 0.2 per cent, the samples did not remain clear for more than 90 days and were often hazy within 20 to 30 days after filtration. On the other hand, samples clarified with bentonite possessed their original color and remained brilliantly clear for more than 22 months, and the accumulated sediment on the bottom of the containers was at a minimum even on prolonged storage.

Bentonite-Casein Clarification

The results with casein clarification were again considered. It seemed possible that the use of a minimum amount of casein with or without filter aid would not greatly affect the color of the vinegar and that the later addition of the electronegative bentonite would serve to remove any remaining positive colloidal material, including possible dissolved casein, which might be responsible for the clouding or sedimentation observed after 11 or 12 months of storage. Accordingly, several series of tests were made, varying the sequence and manner in which the casein and bentonite were added. The effect of the temperature of the vinegar at the time of their addition was also observed.

It was found that samples simultaneously treated with 0.1 per cent filter aid and one part of casein to 2000 parts of vinegar (1:2000) gave a good clarification when they were added to a cold vinegar. Such samples remained clear for over 12 months and did not exhibit the heavy haze observed when the filter aid was used with bentonite. The sediments that accumulated on the bottoms of the flask were likewise very light. However, clouding of many of the samples occurred within 15 months, indicating that the addition of the filter aid did not complete the clarification process. Samples heated at 70° C. for 10 minutes just before the addition of casein and filter aid did not filter clearly even when as many as 16 hours were allowed for coagulation and settling.

The nature of these hazy to cloudy vinegars indicated a stabilization of a certain amount of casein in the vinegar. Accordingly, two tests using bentonite were devised. A quantity of vinegar was heated at 70° C. for 10 minutes and casein at 1:2000 was added. After standing for 16 hours the vinegar was filtered (filtrate not clear) and divided into two portions. To the first portion 0.1 per cent bentonite was added, and after coagulation the vinegar was filtered. The filtrate was clear but clouded within 9 months. The second portion was heated at 70° C. for 10 minutes, 0.1 per cent bentonite was added, and the sample was filtered after coagulation and cooling. The filtrate was brilliantly clear. At the end of 32 months this sample was still brilliantly clear, was of excellent color, and exhibited no observable precipitate on the bottom of the flask. Similar observations on other samples have shown the same results over an equal length of time. These samples have been retained for observation and have shown no indication of clouding. It would therefore appear that the combination of heating in a closed system and the use of casein and bentonite, as above described, constitutes a satisfactory method for clarifying wine and grape vinegars.

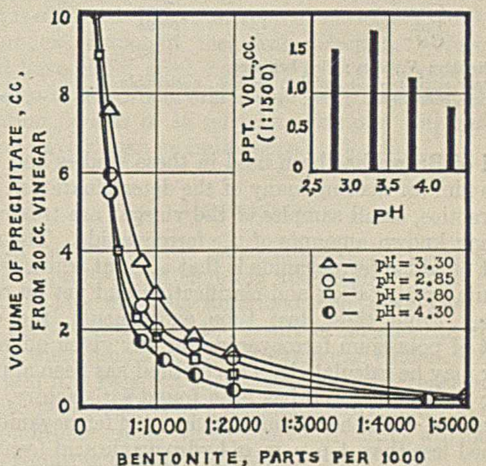

Figure 2. Effect of Bentonite Concentration and pH on Volume of Precipitate

Samples of cider vinegars also have been clarified in this manner, remaining clear for 8 to 12 months, during which time they were observed. With some cider vinegars a somewhat higher casein concentration (up to 1:1000) was required for effective clarification.

Potassium Ferrocyanide–Protein Clarification

In addition to the above experiments with casein and bentonite, similar tests were made using potassium ferrocyanide as the clarifying agent. It has been observed that probably a part of the clarifying effect of casein is due to its reduction of the iron content of vinegars. This supposition was strengthened by dividing a quantity of vinegar so clarified into two portions. The first portion was untreated, but 50 p. p. m. of ferric iron were added to the second portion. Both samples were then stored at room temperature. The first sample remained clear over an observation period of 6 months while the second sample formed a heavy cloud within 60 days. It therefore seemed probable that in certain vinegars of known high-iron content (over 30 to 100 or more p. p. m.) the clouding was primarily the result of the presence of the iron. In such cases, while the casein-bentonite method had been satisfactory, it also seemed desirable to test the adaptability of the ferrocyanide method.

The use of potassium ferrocyanide in the clarification of wines is practiced in some European countries, and methods for its use have been developed. Brown (*1*), working in this laboratory, has studied this method in its use with grape juices and has also modified the method for the determination of residual cyanide. This determination is important because with each clarification it is essential with the present method of use that an excess of the ferrocyanide must be carefully avoided; otherwise a varying amount of hydrocyanic acid will be formed and such formation must be ascertained. The

Table II. Clarification of Vinegar with Potassium Ferrocyanide

Series	$K_4FeC_6N_6$ added, p. p. m.:	15 Days after Clarification				6 Months after Clarification			
		200	350	500	650	200	350	500	650
A	Clearness[a]	S. cloudy	S. hazy	Cloudy	V. cloudy	V. clear	Br.	Br.	Br.
	Ppt.[b]	None	+	+ +	+ + +	+	+ +	+ + +	+ + +
	CN⁻[c]	Nil	+	+ +	+ + +	Nil	+	+ +	+ + +
B	Clearness	Clear	Br.	Clear	S. hazy	Br.	Br.	Br.	Br.
	Ppt.	None	+	+	+ +	+	+	+	+ + +
	CN⁻	Nil	Nil	Nil	+	Nil	Nil	Nil	+
C	Clearness	V. clear	Br.	V. clear	V. S. hazy	V. Br.	V. Br.	Br.	Br.
	Ppt.	None	None	+	+ +	+	None	+	+ +
	CN⁻	Nil	Nil	Nil	+	Nil	Nil	Nil	+
D	Clearness	Clear	Br.	V. clear	S. hazy	Br.	Br.	Br.	Clear
	Ppt.	None	+	+	+ +	+	+	+ +	+ + +
	CN⁻	Nil	+	+ +	+ +	Nil	+	+ +	+ +

[a] S., slightly; V., very; Br., brilliant.

[b] +, very slight; + +, slight; +++, noticeable.

[c] Nil, less than 2–3 p. p. m.; +, less than 10 p. p. m.; + +, less than 20 p. p. m.; + + +, less than 40 p. p. m.

method of Brown has been used in these studies and thanks are due him for making many of the determinations.

In practice, small samples of the vinegar are treated with increasing known amounts of the ferrocyanide. The correct amount of added ferrocyanide is that amount which will give maximum precipitation and clarification and yet no residual cyanide. From these test tube experiments, the correct amount of potassium ferrocyanide for any given quantity of vinegar may be calculated. This method has been applied to vinegar clarification and has been found satisfactory. Vinegars clarified with the optimum amount of ferrocyanide have contained less than 1 p. p. m. of hydrocyanic acid (sensitivity of test) and have remained clear over observation periods up to 18 months.

With a typical vinegar, test tube experiments using potassium ferrocyanide concentrations of 100 to 500 p. p. m. indicated that approximately 350 p. p. m. were required to clear the vinegar. Four series of experiments were then arranged, in each of which the potassium ferrocyanide ($K_4FeC_6N_6 \cdot 3H_2O$) was added in the proportions of 200, 350, 500, and 650 p. p. m. This relatively wide range of added ferrocyanide, both above and below the optimum amount, was used in order to study the nature of the reaction in this system. The treatment of the samples in each of the four series was as follows:

A. Vinegar + added ferrocyanide (200, 350, 500, or 650 p. p. m.); stir mechanically; let stand 48 hours; filter.

B. Same as A, but add 36 mg. egg albumin per 100 cc. vinegar after filtration; let stand 5 hours and again filter.

C. Same as B, but heat and add bentonite at concentration of 1:1500 parts vinegar at 60° C. after filtering albumin precipitate; decant or refilter.

D. Same as B, but stir for 30 minutes by vigorously bubbling air through vinegar after adding albumin.

After final filtration all samples were observed for color, effectiveness of clarification (clearness), and cyanide content. In general, the samples with only 200 p. p. m. added ferrocyanide were hazy to slightly cloudy, those with 350 p. p. m. were clear to brilliant, and those with 500 and 650 p. p. m. were very clear to brilliant. Very slight reduction of color was observed with only the higher concentrations of ferrocyanide.

Observations of the samples were made at 15-day intervals for several months, then at monthly intervals. During the first 6 months there was a slight but noticeable clearing of all of the hazy samples. This is apparent from a comparison of the above observations made immediately with those made after 45 days as well as after 18 months. The least change appeared in the samples with 350 and 500 p. p. m. ferrocyanide. In Table II are given the data from the observations after the 15-day and 6-month intervals for series A, B, C, and D.

From the results with series A it would appear that treatment of the vinegar with potassium ferrocyanide alone did not produce an entirely satisfactory product because clarification was not complete and there was a small residual cyanide content. The difference between the results with series A and B was marked. The addition of the gelatin greatly facilitated clarification, reduced the quantity of residual cyanide, and brought about a more effective precipitation as evidenced by the observation that the volume of precipitate for the optimum quantity of added ferrocyanide (350 p. p. m.) did not increase appreciably between 14 days and 6 months after clarification. The point that there was practically complete removal of residual cyanide even up to 500 p. p. m. is particularly satisfactory and will be discussed later. The fact that, while there was a discernible sediment on the bottom of the container, there was no increase after the 15-day interval suggests that the final filtration should have been delayed. With series C, the further addition of bentonite effected a more rapid clarification, as indicated by the decreased sedimentation between 15 days and 6 months after final filtration. It was also observed that the two samples in this series with 350 and 500 p. p. m., respectively, were slightly lighter than the corresponding samples in series A or B. Aside from the extra heating and filtration, the use of the bentonite appeared desirable. Inasmuch as the samples with the optimum quantity of potassium ferrocyanide (300 to 350 p. p. m.) were held after the final filtration without any sediment forming within the first 15 days or at any later time, its use would be recommended. In these experiments, the 30-minute aëration after the addition of the gelatin (series D) did not materially improve the gelatin treatment. In fact, the removal of the excess ferrocyanide by the gelatin appeared to be considerably reduced. Since this method of mixing the gelatin with the vinegar is practiced at present in some plants, it is suggested that mixing by pumping over would be more desirable.

It has been indicated that the use of gelatin with the potassium ferrocyanide is particularly desirable both from the consideration of effectiveness of clarification and of the relatively great reduction of residual cyanide in the vinegar. In general, any use of potassium ferrocyanide must be only with and under the direction of a competent technician or chemist. However, a more detailed discussion of this phase of the problem is desirable. Aside from the effectiveness of the clarification, the residual ferrocyanide is an important factor in this method of clarification. While in commercial practice no more potassium ferrocyanide is employed than is just sufficient to effect brilliant clarification, and under these conditions the above results show that a very small quantity of ferrocyanide (less than 2 to 3 p. p. m.) may remain in the vinegar, additional information may be obtained by experimentally using the larger quantities of 500 and 650 p. p. m. of ferrocyanide. With 500 p. p. m. no residual ferrocyanide was observed when gelatin was added as in series B and C. Even with 650 p. p. m. of added potassium ferrocyanide, which was practically twice the optimum quantity of 300 to 350 p. p. m., less than 10 p. p. m. residual ferrocyanide were found. Hence a method such as was employed in series B or C appears to be capable of practically entirely eliminating the factor of residual ferrocyanide in the vinegar when even more than optimum quantities for satisfactory precipitation and clarification are employed.

A consideration of the residual total cyanide in relation to the known toxic action of cyanides is also important. This residual cyanide has been calculated as the total cyanide present. However, at most, only half of it is present as hydrocyanic acid because acids liberate only one-half of the total cyanide of potassium ferrocyanide as the acid (*1*). Nevertheless, we may assume, as a maximum precaution, that the entire cyanide is present as a very dilute solution of hydrocyanic acid. With dilute solutions it is stated (*17*) that the fatal dose of the acid would be about 2.5 grams. Assuming that as much as twice the required amount of potassium ferrocyanide for clarification had been used and that as much as 10 p. p. m. total cyanide remained in the vinegar, it is evident that approximately 250 liters of the vinegar would be required to give a fatal dose. With the suggested use of potassium ferrocyanide and gelatin resulting in less than 2 p. p. m. total cyanide, it would require about 1200 liters of vinegar to produce fatal effects. It is obvious that a few drops to a few cubic centimeters of such vinegar normally consumed would have no toxic effects. On the contrary, the use of a dilute solution (0.1 per cent) as a stimulant may be considered. In such cases (*17*, *22*) from 1 to 6 mg. are given in a dose. It is stated (*17*) that the ordinary dosage for man is 1.0 cc. of a 0.1 per cent solution of hydrocyanic acid. This may be repeated as needed, at intervals not shorter than 30 to 15 seconds. Such a single dose of 1 cc. would contain 1.0 mg. of the acid. With vinegar of 2 p. p. m. it would require 500 cc. to give such a single dose. That is, such vinegar would contain one five-hundredth of the prescribed amount. Consequently, the residual cyanide concentration is negligible in effect if the proper methods for use of the potassium ferrocyanide and gelatin are strictly followed.

The complete removal of the lower concentrations of ferrocyanide ion by gelatin, as evidenced by the negative test for cyanide in series B and C (Table II), suggested that a quantitative relationship might be involved. As a matter of fact, Loeb (*10*) has shown that, when gelatin was treated with potassium ferrocyanide and other salts on the acid side of the isoelectric point, the protein combined with the anion of the salt. It was suggested that the combination between the gelatin and the ferrocyanide would be similar to that between certain acid dyes and proteins (*4*). A study of this relation has been made with a modified technic, and it has been found (*16*) that there is a quantitative relationship between the protein, gelatin, or albumin and ferrocyanide which is a function of the pH. It has been found possible quantitatively to precipitate a given amount of ferrocyanide from solution, the ensuing tests for residual cyanide being negative.

In practice the determination of the amount of protein (gelatin or albumin) solution required to remove an excess of ferrocyanide was made in a manner similar to that for determining the quantity of ferrocyanide required for clarification of the vinegar. Increasing amounts of a standard protein solution were added to aliquots of the vinegar until ferric chloride added to the filtrates, after coagulation and filtration, no longer produced the Prussian blue color of ferroferricyanide. The calculated amount of protein was then added to the larger quantity or tank of vinegar. The importance of this new procedure is in the fact that, while the small quantities of gelatin often added simply to facilitate clearing of the vinegar also incidentally aid to a varying degree in preventing excess or residual ferrocyanide, it is now possible to judge accurately and uniformly the quantity of protein needed for both clearing or fining and for removal of any excess ferrocyanide. Furthermore, an additional control of the cyanide content is obtained so that an appreciable excess should never occur under competent technical direction. Vinegars so clarified have either given negative tests or have shown less than 2 p. p. m. residual cyanide and have remained clear for observation periods of 18 months. Samples still under observation have shown no indications of clouding.

APPLICATION

Several factories in the grape industry have encountered the serious problems of clouding and sedimentation in their products. The methods described and developed in the studies here reported are the result of an attempt to solve certain of these problems. All experimental evidence has been stated, and it is believed that satisfactory alternate methods have been presented. The final choice of method will depend upon conditions under which the clarification will be made and the resulting product utilized.

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RECEIVED September 12, 1933.

INCREASED GOVERNMENT CONTROL IN GERMAN POTASH INDUSTRY. After extensive study, the Reich Government has formulated a new law drastically reorganizing the potash industry and placing it upon a quite different foundation, in keeping with national socialistic principles. The main effects of the new law will be to restrain the independence of the industry and place it more completely under government control, ministerial decrees replacing the hitherto determining decisions of elective representative bodies regarding fundamental questions concerning the conduct of the industry.

The most important feature of the new law is the abolition of the Reich Potash Council, which was formed in 1919, when the socialization of German industries was planned on a comprehensive scale, the council in question consisting of 30 members representative of the various groups interested in the potash industry.

A Century of Progress in Driers

A. C. Elm, The New Jersey Zinc Company, Palmerton, Pa.

The use of litharge or red lead and possibly umber for the purpose of accelerating the drying of oil paints or glazes is almost as old as the use of linseed oil itself. Varnish formulas described by Jacobus de Tholeto (1440), Joseph Petitot (1644), and Alberti of Magdeburg (1750) are among the first written records to contain references to the use of metallic oxides for this purpose. It is highly probable, however, that these formulas were several hundred years old when they were published and that the accelerating effect of litharge, at least, was known to the Egyptians who made use of it in the preparation of the oil employed in the mummification of their dead. These formulas were handed down through the ages as carefully guarded trade secrets, and thus litharge and umber remained the only driers for centuries.

Beginning of Drier Research

It is doubtful that anything was known about the nature of the action of the driers until 1835 to 1850 when the efforts of the French zinc oxide manufacturers to substitute zinc white for white lead in paints started a search for compounds which would improve the drying of zinc oxide paints. This was the beginning of the science and the industry of driers.

The results of the first few years of drier research were critically reviewed and briefly summarized by J. S. Stas in a report presented at the International Exposition at Paris in 1855 on the value of zinc white as a substitute for white lead.

Although there is no definite statement to this effect in the literature, it may be assumed that litharge was the first metallic oxide to be incorporated into oil by heating. Stas says: "It is also well known that lead oxide in very large quantities can dissolve in linseed oil . . . The famous Liebig was the first to show this. Linseed oil thus acquires high drying power. The ancient use of lead oxide to render this oil more siccative is abundant proof of this fact."

Leclair, in his studies to substitute zinc oxide for white lead (1835–1850), found that heating linseed oil for a long time with manganese dioxide makes it drying in the presence of zinc oxide.

These observations led to the theory that metallic oxides high in oxygen yielded their oxygen to the oil, making it more siccative. The observation that, when heating oil with litharge or red lead, the solid residue sometimes contains metallic lead seemed to substantiate this theory.

Sorel's observation, about 1840, that anhydrous manganous chloride, and M. E. Barruel's discovery (about 1845) that manganese borate are very effective driers could not be readily reconciled with this theory. Stas, then, pointed out that on this basis zinc oxide should be an excellent drier. Based on these facts and the results of his own investigation conducted with M. W. de la Rue, Stas concludes that "every metal, of which the oxide, linoleate, and margarate are soluble in a siccative oil," possesses drying properties. To explain the nondrying properties of zinc oxide, he states: "although zinc oxide in the presence of moisture may react with linseed oil to form soaps, they never remain in solution upon cooling, the cooled and separated clear oil scarcely retaining more than 0.2 per cent zinc oxide. Thus zinc linoleate may be said to be insoluble in oil and therefore have no drying action."

Thus, by emphasizing the necessity of solubility of a drier, Stas laid the foundation for the modern theories of the effect of driers on drying oils and paved the way for the next important development in the history of driers—the soluble drier.

Development of a Theory of Driers

The develpment of a theory for the action of driers on drying oils followed closely the knowledge of these oils and their chemical and physical changes when exposed to air in thin films. Until a few years ago the drying of oils was thought to be an oxidation of the liquid unsaturated glycerides to solid oxyglycerides, and the action of the driers was assumed to be merely an acceleration of the rate of oxidation. The original picture in which the metallic oxide furnished the oxygen for the oxidation of the glycerides was changed to an improved picture in which the dissolved metal atoms, while oscillating between two stages of oxidation, activated the oxygen of the air and passed it on to the oil molecules. This "bucket elevator theory," as Long called it, was quite satisfactory as long as the colloid-chemical aspect of the drying of oils was not fully recognized.

More recent investigations made it evident that the presence of a drier not only accelerates the rate but also modifies the course of the oxidation, because the total amount of oxygen absorbed up to the time the film solidifies is lower than that absorbed when no drier is present. Furthermore, in the presence of a drier the amount of carbon dioxide evolved during the oxidation is approximately the same as for the oil alone, whereas the evolution of hydrogen peroxide is suppressed entirely. In the light of this evidence it is obvious that the drier does not act as a catalyst in the strictest sense of the term, because there is no doubt that it changes the course of the reaction.

With the development of the modern combined chemical and colloidal theory of oil drying came a new and improved theory of the action of driers. The principal points of the modern theory of the drying of oils are as follows:

During the transition of the liquid into the solid oil film, there are taking place three primary reactions:

1. Oxidation of the unsaturated compounds to oxyns.
2. Association or polymerization of the oxidized oil molecules to colloidal dimensions.
3. Gelation or coagulation of the colloidal system.

The rate of oxidation of the oil is very low at the beginning of the exposure. This period, which passes before the rate of oxidation becomes perceptible, is called the "induction period" and may be caused by the presence in the oil of natural antioxidants.

Oxidation results in the formation of highly polar compounds which, in their desire to satisfy as far as possible their free energy, associate or polymerize, yielding colloidal systems which eventually gel and solidify.

As the concentration of oxidized oil molecules increases, the rate of association increases; and with increasing concentration of particles of colloidal dimensions the rate of gelation increases. Thus, these three primary reactions overlap, each in turn being the predominant reaction.

The modern theory of the action of driers attempts to answer the question: Which one of these three basic reactions is influenced by the drying metal and what is the mechanism of its action? In 1932 the Philadelphia Paint

Superintendents' Club reviewed and analyzed this subject and came to the following conclusions:

1. The driers are primarily accelerators of the oxidation reaction, neutralizing antioxidants and increasing the rate of oxidation.
2. To a lesser degree the driers accelerate association or polymerization of the oxidized oil molecules by increasing the concentration of the polar compounds and by exerting an orienting influence upon them.
3. It is undecided but it is quite conceivable that the driers accelerate gelation by serving as coagulation centers or nuclei.
4. In order to be able to act in this threefold manner, the drying metal must be in an "available" form and occur in two stages of oxidation of which the higher one is stable in air but unstable in a drying oil, and the lower one is stable in oil but unstable in air.

The Philadelphia Club, using tetraethyllead as an example, points out that solubility of the metallic compound is of no avail unless the metal is "available." It is difficult to define clearly this term "availability," but an idea of what it seeks to describe might be obtained from its analogy to ionization in aqueous solutions.

Although the theories on the action of the driers on the solidification of drying oils have not yet been developed to an entirely satisfactory end, they should, in their present form, prove of considerable help in future developments in the field of metallic driers. Modern drier research which dates from the introduction of the so-called soluble driers has slowly recognized the two main requirements—solubility and availability of the metal—and has been guided by them.

The Soluble Driers (About 1885)

Strictly adhering to every detail of his secret formulas, the varnish maker of the nineteenth century incorporated lead and manganese oxides, acetates, and borates into his boiled oils and varnishes much in the same way as it is still practiced today. The secrecy surrounding all operations in the varnish industry prevented an exchange of ideas which, together with the antipathy of the old-time varnish maker to deviate even the slightest degree from his secret formulas, retarded progress in driers as much as in the other branches of the paint and varnish industry.

It is not at all surprising therefore that it took about thirty years before Stas' ideas on the relation between solubility of a metallic compound and its effectiveness as a drier were applied. Stas, in 1855, had pointed out that a metal, in order to act as a drier, must be soluble in oil in the form of its linoleate or margarate. The varnish maker was slow in realizing that, when boiling oils with litharge or manganese dioxide, he was converting the metallic oxides into the soaps by a slow and wasteful process yielding dark colored products. Nevertheless, when in 1885 the so-called soluble driers (the fused and precipitated linoleates and resinates of lead and manganese) made their appearance, the industry was very slow in accepting them in spite of their easily recognizable advantages. This may have been caused partly by the difficulty of manufacturing entirely satisfactory soluble driers of this type. Although in the course of the years the basic principles involved in these manufacturing processes did not change appreciably, the introduction of more scientific methods and equipment and a thorough control of the individual manufacturing stages resulted in products improved as to purity, uniformity, and solubility. Nevertheless, they never entirely replaced the oxides, acetates, and borates.

Introduction of Cobalt

For a long time lead and manganese remained the only driers. The writer was unable to locate in the literature a definite reference as to the discovery of the drying action of cobalt, but the indications are that it took place about 1901. The Russian chemist Fokin, who in 1907 published the first series of metals in the order of their ability of accelerating the drying of oils, treats cobalt in a way which leads one to believe that it was an old acquaintance and not a new discovery of his own. Earlier publications on the drying of oils—for instance, Livache's articles in 1901—contain references to lead and manganese only. A report by H. T. Vulte and H. W. Gibson on their studies of the solubilities of linseed oil soaps in certain hydrocarbons, published in 1902,[1] contains the first reference to cobalt linoleate the writer was able to find. It is therefore permissible to assume that the discovery of cobalt as one of the most efficient metallic driers was made in 1901. In spite of their advantages over lead and manganese in color and effectiveness, cobalt driers, on account of their high price, were not used commercially until about 1911.

Iron as a Drier

The only other metallic drier of importance is iron. This was included in Fokin's series (1907), but it is difficult to establish the date of its first commercial application. Because of its comparatively low acceleration effect and the extremely dark color it imparts to oils and varnishes, it has found only limited application, especially in dark colored products. In the form of Prussian blue it is incorporated into asphalt-base black baking enamels and into dark colored oilcloth and patent leather oils, and it is supposed to be largely responsible for the beautiful gloss and luster of these products.

Other Metals

Cerium, vanadium, thorium, and nickel compounds have been suggested and offered as driers during the last two decades. Since, however, they do not offer any advantages over lead, cobalt, and manganese, and did not induce properties which would not be obtained with the three established drying metals, they found only limited use in a few specialties. Lead, cobalt, and manganese still are the common driers and the indications are that they will retain this position for some time to come.

Most Recent Developments

The last ten years have seen an unusual activity in drier research. The recognition of the importance of solubility and of the fact that fused and precipitated linoleates, tungates, and resinates are at best only colloidally dissolved in the vehicles and thinners and are, therefore, subject to flocculation and coagulation caused some drier chemists to resort to the use of solubilizing agents, mostly of an acidic nature. When it was realized that the tendency of the linoleate and resinate driers to oxidize spontaneously on exposure to air during storage is, to a large degree, responsible for the unsatisfactory solubility characteristics, a search was made for bases which would yield more soluble and stable metallic salts. Drying metals were combined with more saturated organic acid radicals to yield salts of solubilities approaching molecular solution in the usual paint oils and thinners. Thus lead, cobalt, and manganese were combined with naphthenic acids, acidic oxidation products of crude and refined waxes and petroleum fractions, sulfonic acids, and other organic acids especially synthesized for this purpose. Thus a radical departure from ancient practices and the adoption of sound scientific reasoning resulted in the development of drying compounds of superior solubility and stability, improved color, and a higher concentration of

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[1] *J. Am. Chem. Soc.*, 24, 215 (1902).

active metal which permits an accurate control of the metal content and a reduction of the total amount of drying compound necessary to obtain the desired drying properties.

The many advantages offered by the soluble driers are so striking that it is not difficult to visualize the time when varnishes and paints free from driers will be tanked, stored, and even sold in order to prevent such common troubles as skinning. The proper type and correct amount of drier will then be added just before the paint or varnish is used and will make it possible to adjust the amount of drying metal to the individual requirements. Excess and misuse of drier can thus be avoided, and paints and varnishes will be greatly improved.

During the past century the drier industry has progressed from the empirical use of litharge and umber by a few craftsmen or artists, who had neither knowledge nor theory to explain the results, to a great industry well founded on scientific knowledge and research. The scientific approach to the drier problems is, to a large degree, responsible for the advances made during the last twenty-five years. It is to be expected that a careful study and intelligent application of the modern theory of the action of driers and especially the laws governing the solubility of organic compounds will result in still further improvements.

Acknowledgment

The author wishes to acknowledge the suggestions and criticisms offered by Nelson and Werthan of the Research Division of The New Jersey Zinc Company.

Received October 4, 1933. Presented before the Division of Paint and Varnish Chemistry at the 86th Meeting of the American Chemical Society Chicago, Ill., September 10 to 15, 1933.

Aërogel Catalysts

Thoria: Preparation of Catalyst and Conversions of Organic Acids to Ketones

S. S. Kistler, Sherlock Swann, Jr., and E. G. Appel, University of Illinois, Urbana, Ill.

The conversion of aliphatic acids to ketones has been studied over thoria aërogel. It has been found that the aërogel catalyst is distinctly superior to thoria hydrogel, thoria prepared from the oxalate, and thoria on pumice for this purpose. The yields of ketones compare favorably with the best reported in the chemical literature.

In view of the unique physical properties of the aërogels, it has seemed desirable to study them as catalysts. The extent of their surface per unit mass is probably greater than that of any other form of solid available for catalysis. In addition, the structure is such that the accessibility of the surface is a maximum. The ratio of free space to volume of the solid is so great that diffusion through the structure occurs rapidly, while the diameter of the capillaries is so large that capillary condensation is negligible, a factor that seriously reduces the efficiency of the usual gel type of catalyst under certain circumstances. On the other hand, unpublished measurements made in this laboratory show that the average distance between surfaces in the aërogels is smaller than the mean free path of a gas at atmospheric pressure, so that under normal operating conditions a molecule will bound from surface to surface and experience a maximum number of collisions.

The methods of preparation of the aërogels are so versatile that it may be possible to prepare gels of a given material which will show marked differences in activity. It is possible to support films of substances that do not form gels, such as the metals, on aërogels and thus obtain added versatility.

The selection of the first catalyst for investigation was more or less fortuitous. One of the authors needed certain ketones, and the catalytic decomposition of aliphatic acids was therefore investigated. Thorium dioxide is one of the preferred catalysts for this reaction, according to Sabatier.

Preparation of Catalyst

The general method for the preparation of aërogels has been given in detail in a former publication (8). In the preparation of the catalyst a transparent jelly of thorium dioxide was desired, since the gelatinous precipitate usually used in the preparation of gel catalysts would not have the desired mechanical strength, and since there is possibly better and more uniform subdivision in the clear jellies. No satisfactory method was found in the literature. Eventually two methods were devised that gave products of excellent catalytic activity. With the present data it is impossible to discriminate between the products.

In the first method 50 grams of c. p. thorium nitrate in solution were treated in the cold with an excess of ammonia, and the precipitate was washed repeatedly by decantation with distilled water until free of ammonia. It was then made up to a volume of 600 cc. with distilled water, heated to 90° C., and peptized by the addition of 5 grams of thorium nitrate with rapid stirring. Stirring was continued at 90° C. for one hour, after which the material was cooled to 60–70° C. and the peptization continued with stirring until complete (about 1 hour). The sol was yellow-orange and transparent. It was then dialyzed for 24 hours in a Cellophane bag, concentrated to 33–35 per cent thorium dioxide (by ignition of a sample) by evaporation under vacuum on a steam bath, and cooled. A 10 per cent solution of citric acid in alcohol was added dropwise with stirring until the viscosity had risen to a point where by experience it was known that, on standing, the sol would set to a gel. An alcoholic solution was used to prevent precipitation before the drop was dispersed. The amount of citric acid used will depend largely upon the extent of dialysis.

The gel was cast in a beaker and, when thoroughly set, was covered with acetone in which it was allowed to stand for 4 days. Care was taken not to disturb the gel. The acetone was changed daily. The gel was then loosened from the beaker by a wire inserted at the edges. After about 5 days the gel was transferred to another beaker in as large lumps as possible. It was again allowed to stand in acetone for 24 hours. The acetone was then exchanged for methanol by allowing the gel to stand in the latter for 12 hours. The gel was carefully removed to an autoclave. The autoclave was nearly filled with methanol, closed, and heated to a point above the critical temperature of the alcohol (usually to about 250° C.). While it is heating the alcohol will expand and completely fill the autoclave. It may then produce excessive pressures because of the liquid expansion so that it is necessary to bleed some out, maintaining a pressure at all times in excess of the critical pressure until the critical temperature is passed, when the methanol may be released. The gel may have shrunk to some extent, but will be transparent in thin sections and of a very low density compared with massive thorium dioxide.

In the second method 53 grams of thorium nitrate were dissolved in 35 cc. of methanol. When solution was complete, 50 cc. of aniline were added. The solution was placed in a beaker, and 9 cc. of water were added quickly with rapid stirring. It was then poured with as little delay as possible into a wide evaporating dish and allowed to stand until it set to a firm jelly. The time required for setting depends upon several factors not thoroughly understood and may vary from a few seconds to hours. It is most critical with respect to the water. Much over 10 cc. will cause it to stiffen so rapidly that it cannot be poured from the beaker; with too little water no jelly will form at all.

The jelly was loosened from the evaporating dish with a spatula, broken into pieces about lump-sugar size and placed in a mixture of 90 per cent methanol and 10 per cent concentrated ammonia. This solution was replaced from time to time until it no longer contained aniline. The last time or two that exchange is made it is preferable to use pure methanol, and to use methanol in the autoclave with the gel. The gel was put through the autoclave in the same manner as in the first method.

To prepare the aërogel for use, the large pieces were broken up and all fine particles smaller than 20 mesh screened out. It naturally contained some organic matter, and therefore before use it was heated slowly in a tube with a current of air (not over 3 liters per minute) passing through until the temperature reached about 430° C. where it was held until clear. The whole oxidation operation lasted about 4 hours. The gel was then ready for use. Since no other metallic ions except thorium and no negative ions that are not readily destroyed were used in the preparation of the aërogel, it was of excellent purity.

The physical state of the thorium dioxide aërogel is a matter of interest. Freundlich (*5*) reports that sols of thorium dioxide are amorphous, and it is therefore to be expected that the aërogel is also noncrystalline. Three x-ray photographs taken of thin fragments with copper radiation showed no signs of crystallinity, even in the sample that had been used as a catalyst many hours at temperatures up to and exceeding 500° C.

In order to compare the efficiency of the aërogel with thoria catalysts made by other means, three other preparations were made and studied. The first was a gel prepared exactly according to the first method for the aërogel except that instead of replacing the water with acetone and methanol, and then autoclaving, the hydrogel was broken up and dried in an oven set at 140° C. In 6 hours it shrank to a hard, glassy, transparent mass. The second catalyst for comparison was made by igniting thorium oxalate at 400° to 425° C. and pelleting the oxide. The third was made by soaking pumice in thorium nitrate solution, drying at 150° C., and passing air over it at 450° C. in the catalyst chamber until decomposition was complete.

APPARATUS AND PROCEDURE

The design of the apparatus used is shown in Figure 1.

In runs at atmospheric pressure the acid sample was placed in a flask and distilled into the catalyst chamber. When more than one acid was used, the sample was placed in a constant-flow apparatus and allowed to drop into a heated distillation flask which caused it to flash into the catalyst chamber.

For runs at subatmospheric pressures the acid was placed in a Claisen flask and distilled into the catalyst chamber.

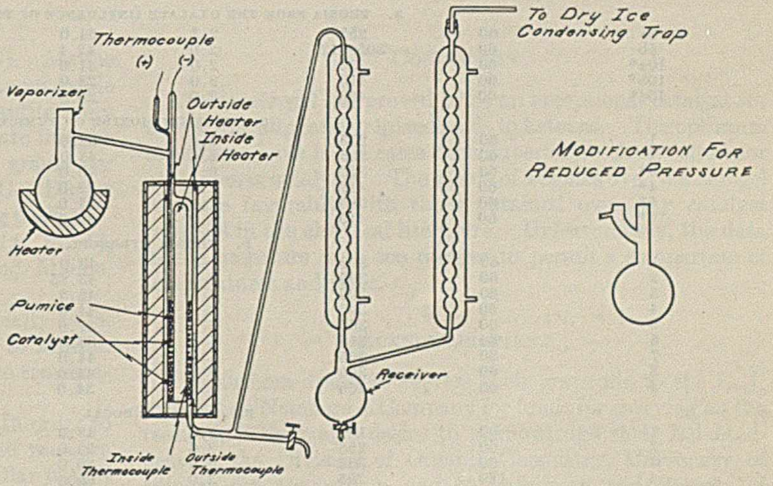

FIGURE 1. DIAGRAM OF APPARATUS

The catalyst chamber consisted of two concentric Pyrex glass tubes sealed at the ends so that a 4-mm. annular space was formed between them. The lower 5 cm. of the annular space was filled with broken pumice; on this were carefully placed 25 cc. of the catalyst (about 18 grams of thoria aërogel) screened to pass a 10-mesh but not a 20-mesh screen. The space above the catalyst was usually filled with pumice merely to aid in bringing the entering gases to the required temperature before reaching the catalyst. A condenser and solid carbon dioxide trap were sealed to the lower end.

Since high rates of flow were studied, a heater was placed inside as well as outside of the catalyst chamber so that a maximum heating surface was obtained. These two heaters were controlled by a galvanometer relay and Thyratron tube, and there was also a thermocouple embedded in the catalyst as a check on the temperature. The sensitive galvanometer relays worked very well for a short time after cleaning, but the contact surfaces showed a discouraging tendency to foul in the laboratory air. In the future the galvanometer relays will be replaced with photoelectric relays.

The usual experimental procedure was to bring the chamber up to temperature, pass through at the predetermined rate the gas or vapor to be studied until constant conditions were attained, and then run several samples through in succession, collecting the products separately for analysis.

A fresh catalyst was always activated by passing acetic acid over it at a rate of 3 grams per minute at 300° C., until the odor of acetic acid could not be detected.

The factors varied in this investigation were the temperature of the catalyst and the rate of flow of vapors over it.

ANALYTICAL PROCEDURE

Several methods were used for analyzing the products. The lower ketones, acetone, and diethyl ketone were first analyzed by the hydroxylamine sulfate method (*2*) with dimethylaminoazobenzene[1] as indicator after the unchanged acid had been determined by titration with standard alkali. It was found later that the determination of the residual acid was sufficient, since the estimation of ketone by difference checked closely enough with the values obtained by the

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[1] The discovery that this indicator was superior to the customary methyl orange for the determination is due to W. H. B. Howard at the Johns Hopkins University in 1926.

Table I. Conversion of Acetic Acid to Acetone over Thoria Aërogel and Other Thoria Catalysts

Run	Acetic Acid	Temp. of Catalyst	Rate over Catalyst	Distillate	Acetic Acid Recovered	Conversion Based on Acid Titration	Yield Based on Ketone Titration
	Grams	° *C.*	*G./min.*	*Grams*	*Grams*	%	%
			A. Thoria from the oxalate (influence of rate)				
5b	60	305–312	2	42.4	17.4	71.1	70.6
4a	60	303–	2.8	45.0	25.2	57.0	59.8
2b	60	305–317	4	43.8	20.2	66.4	69.1
1a	60	295–312	5.5	43.7	20.6	65.7	...
9a	30	295–317	8	25.0	18.0	40.0	..
7b	30	305–320	10.0	24.5	34.5	42.5	39.9
6b	30	290–326	12	24.0	38.4	36.0	29.5
			B. Thoria from the oxalate (influence of temperature)				
8a	60	255	2.3	54.0	46.8	22.0	
5b	60	305–312	2.0	42.4	17.4	71.1	
10a*	60	355	2.0	31.0	0.95	98.5	
10b*	60	410	2.0	28.0	0.168	99.7	
10c*	60	450	2.0	28.0	0.14	99.8	
			C. Thorium dioxide on pumice				
1	60	255	2.4	52.0	47.4	21.0	
2	60	305	2.4	48.0	42.6	28.9	
3*	60	350	2.4	40.0	17.8	70.3	
4*	60	412	2.4	32.0	0.704	98.8	
5*	60	305	1.0	41.0	22.6	62.5	
6*	60	415	4.0	35.0	0.95	98.4	
			D. Thoria hydrogel				
1	60	300	1.6	43.0	19.7	67.0	
2	60	300	3	43.85	19.2	62.1	
3	60	300	4	46.5	26.2	56.3	
4	60	340	3	41.0	10.2	83.0†	
5	60	365	3	37.0	3.03	95.0†	
6	60	365	4	38.0	3.15	94.7†	
7	60	365	5	44.0	14.7	75.5	
8	60	365	8	44.0	22.1	63.1	
9	60	400	8	34.0	6.66	88.9†	
			E. Thoria aërogel				
1	60	180	2.6	43.0	31.1	48.2	
2	60	255	2.6	32.0	9.54	84.3	
3	60	303	2.6	30.0	0.1857	99.7	
4	180	295	3.0	89.0	0.297	99.84	
5	60	305	3.0	31.0	0.085	99.86	
6	60	300	3.2	31.0	0.0094	99.98	
7	60	310	4.0	37.0	1.02	98.3	
8	120	293–300	4.8	75.0	3.86	96.78	
9	60	295–326	6.0	37.0	3.415	94.5	
10	60	293–352	8.57	37.0	10.0	83.33	
11	60	352–380	12.0	40.0	24.64	58.9	

* Odor of mesityl oxide in sample.
† Mesityl oxide in product.

hydroxylamine sulfate method. The higher ketones, which are insoluble in water, were determined by weight after purification either by distillation or crystallization. The mixed ketones were determined by weight after fractionation in a high-precision column.

Results of Experiments

Acetic Acid to Acetone (*1, 3, 4, 6, 7, 9, 11, 12, 16, 17, 18, 20*). The best yield reported in the literature of acetone from acetic acid was obtained by Sabatier and Mailhe over manganous oxide. They found that the conversion was 100 per cent at 400° to 450° C.

Table IA shows that the percentage conversion of acetic acid to acetone at a given temperature with thoria prepared from the oxalate does not change very much until a rate of 10 grams per minute is reached. At this point the conversion is appreciably lowered. It was difficult to obtain consistent results with this catalyst. The lowest temperature at which the thoria from the oxalate was at maximum activity was about 350° C. (Table IB). A temperature of about 400° C. was necessary before good conversions were possible with thoria on pumice (Table IC). In the results with the thoria hydrogel (Table ID) good conversions were not obtained until temperatures of 365° C. were reached. With the thoria aërogel catalyst, quantitative yields were obtained at about 300° C. at rates as high as 4 grams per minute; increasing the temperature permitted higher rates to be used (Table IE).

Table IIA shows that thoria aërogel will operate at a temperature about 50° C. lower than any other catalyst studied. Table IIB shows that the three other catalysts do not compare with the aërogel in efficiency at the same temperature, even when the acid is allowed to pass over the catalyst at much lower rates.

Table II. Comparison of Catalysts in Conversion of Acetic Acid to Acetone

Catalyst	A. Optimum Temperatures at Constant Rate			B. Optimum Rates at Constant Temperature		
	Temp.	Rate	Conversion	Rate	Temp.	Conversion
	° *C.*	*G./min.*	%	*G./min.*	° *C.*	%
Thoria aërogel	300–310	2.6–4.0	100.0	3.2	300	100.0
Thoria hydrogel	365	3.0–4.0	94.8	1.6	300	68.0
Thoria from the oxalate	355–450	2.0–5.5	100.0	2.0	293–310	64.6
Thoria on pumice	412	2.0–4.0	98.5	1.0	305	62.5

Table III. Conversion of Higher Acids to Ketones over Thoria Aërogel

Run	Acid	Temp.	Rate	Yield of Ketone	
	Grams	° *C.*	*G./min.*	*Grams*	%
		A. Propionic acid to diethyl ketone			
1	37	305	3.0	16.8	99.4
2	37	300	5.8	16.0	94.5
3	37	326	5.8	16.5	97.0
4	37	345	6.5	16.5	97.0
5	37	370	9.0	17.0	100.0
6	37	374	12.3	17.0	100.0
		B. *n*-Valeric acid to di-*n*-butyl ketone			
1	51	305	2.0	34.0	96.0
2	102	325	3.0	71.2	100.0
3	102	325	5.0	68.5	96.5
4	102	325	8.2	67.5	95.0
5	102	340	5.0	70.0	98.7
6	102	340	8.0	69.0	97.2
7	102	340	12.0	67.0	94.4
8	102	360	12.0	70.5	99.3
		C. Caprylic acid to di-*n*-heptyl ketone			
1	37	300	3.0	26.0	92.8
2	36	326	3.0	27.4	100.0
3	37	330	6.0	23.8	84.0
		D. Phenyl acetic acid to dibenzyl ketone			
1	50	326	6.5	35.0	90.7
2	50	345	6.5	38.2	99.0
3	50	345	12.5	38.1	98.7

TABLE IV. CONVERSION OF PHENYL ACETIC AND PROPIONIC ACIDS TO ETHYL BENZYL KETONE OVER THORIA AËROGEL

RUN	PROPIONIC ACID	PHENYL ACETIC ACID	TEMP.	RATE	ETHYL BENZYL KETONE	DIBENZYL KETONE	ETHYL BENZYL KETONE[a]	DIBENZYL KETONE	RATIO ETHYL BENZYL TO DIBENZYL KETONE
	Grams	*Grams*	*° C.*	*Grams/min.*	*Grams*	*Grams*	%	%	
1	33.8	25	330	4	18.8	5.7	69.3	29.6	3.3:1
2	88	65	330–345	5	51	14	70.5	29.5	3.65:1
3	57.5	42.5	336–350	6.7	33.5	8.5	72.9	25.9	3.95:1
4	73.2	54	305–312	7.7	43	11	73.2	26.3	3.9:1

[a] The percentage yield was based on the phenyl acetic acid.

PROPIONIC ACID TO DIETHYL KETONE (*10, 11, 15*). Mailhe and Sabatier found that ferric oxide and manganous oxide converted propionic acid to diethyl ketone quantitatively at 430° to 500° C. Table IIIA shows how the rate may be increased to the limit of the apparatus (12.3 grams per minute) by increasing the temperature to 375° C. Higher rates could probably be used with a larger distilling flask.

n-VALERIC ACID TO DI-*n*-BUTYL KETONE (*10, 11, 13, 14, 15*). The best yield was obtained by Sabatier and Mailhe, 80 per cent over manganous oxide at 400° C.

The crude ketone from the aërogel was practically pure, 93 per cent boiling between 89° and 93° C. at 22 to 24 mm. The remainder boiled between 70° and 89° C.; the temperature rose rapidly to 89° C.

CAPRYLIC ACID TO DI-*n*-HEPTYL KETONE (*10*). In order to study the operation of the catalyst under reduced pressure and the behavior of an acid of much higher molecular weight than those used, caprylic acid was chosen. The best yield of di-*n*-heptyl ketone reported in the literature was obtained by Mailhe over ferrous oxide—77 per cent obtained, at 450° C.

The acid was distilled over the catalyst at 30 mm. pressure; it boiled at 163° C. In run 3 (Table IIIC) it was extremely difficult to maintain constant pressure. The most convenient rate was 3 grams per minute. The lowest temperature at which quantitative yields of ketone could be obtained was 326° C.

PHENYL ACETIC ACID TO DIBENZYL KETONE (*9, 11*). It was thought advisable to study mixed acids; consequently, phenyl acetic acid was studied alone and with propionic acid. The best yield of dibenzyl ketone reported in the literature was obtained over a thoria catalyst by Senderens—100 per cent at 430° to 470° C. The optimum conditions for the preparation of dibenzyl ketone are probably a temperature slightly in excess of 345° C. at a rate of 12.5 grams per minute (Table IIID).

ETHYL BENZYL KETONE FROM PHENYL ACETIC AND PROPIONIC ACIDS (*10*). The best yield reported in the literature was obtained by Mailhe (70 per cent) over ferrous oxide at 450° C.

The purity of the crude products resulting from the aërogel catalysis was excellent. The color even in the case of the materials of high molecular weight was never darker than a pale yellow. If the rate over the catalyst was too low, the product was dark because of condensation of the ketone; i. e., the odor of mesityl oxide would be detected in the acetic acid runs.

A striking property of the aërogel was its retention of activity with long usage. The same aërogel catalyst was used for the conversion of several of the acids to ketones without apparent loss of activity. It was found in preliminary runs that the acid must be vaporized over the catalyst; i. e. liquid acid must not be allowed to be vaporized in the catalyst because it causes pulverization. Hence the acids were always distilled through the catalyst chamber. When high rates were employed, the solid carbon dioxide–acetone trap was very necessary, particularly for trapping low-boiling ketones.

CONCLUSION

Thoria aërogel has proved to be an exceptional catalyst for converting aliphatic or mixed acids to ketones. The optimum conditions have in all cases been superior to those found for other thoria catalysts. The yields of ketones over the aërogel compare favorably with those obtained over any catalyst reported in the chemical literature. Unfortunately, the data in the literature were too meager to permit a comparison of temperatures and rates.

ACKNOWLEDGMENT

The authors desire to express their gratitude to the E. I. du Pont de Nemours & Company for funds for carrying on the research. They also desire to acknowledge their indebtedness to the Division of Organic Chemistry, University of Illinois, for suggestions, and to Penniman and Browne of Baltimore, Md., for the use of their office.

The analytical work was done by M. T. Goebel of the Division of Organic Chemistry. The fractionation of the products obtained from the decomposition of phenylacetic and propionic acids was carried out by H. E. Carter.

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RECEIVED November 3, 1933. Presented before the Division of Industrial and Engineering Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

CORRECTION. Through an inadvertence, in Parts VI and VII of the series on "The Cooking Process" by S. I. Aronovsky and R. A. Gortner, appearing in January (page 61) and February (page 220), 1934, the graphed data for the two papers have been interchanged in printing. Thus, in Part VI dealing with sodium sulfide the graphs refer to Part VII dealing with sodium hydroxide, and vice versa.

Physical Properties of Ternary Systems

Specific Gravities, Refractive Indices, and Changes in Volume on Solution of the System Methyl Alcohol–Isobutyl Alcohol–Water at 60° F.

DONALD M. SMITH, E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

This paper indicates an adaptable and convenient line of attack for the worker who wishes to determine precisely and in detail the properties of an undescribed ternary system composed of water and two organic liquids, or to interpolate accurately published data on such systems. It also indicates the rather simple relationships existing between the various common methods of expressing percentages. The charts obtained by this method can be used to read off precisely the properties of a given mixture or to pick out exactly the composition of a solution for which the properties are known. The specific gravities, refractive indices, and changes in volume on solution are determined for the system methyl alcohol–isobutyl alcohol–water at 60° F.; the ternary diagrams used to present these data are not in error by more than ±0.2 per cent, estimated in terms of the compositions represented.

IN THE course of work on the high-pressure synthesis of organic compounds, it is frequently necessary to make accurate estimates of such physical properties as specific gravity and refractive index for various systems, particularly solutions of two pure alcohols in water. Systematic studies of these physical properties for a number of such systems have appeared in the literature: methyl alcohol–benzene–water and ethyl alcohol–benzene–water (*1*); methyl alcohol–ethyl alcohol–water (*2*); ethyl alcohol–*n*-propyl alcohol–water, ethyl alcohol–isobutyl alcohol–water, and ethyl alcohol–isoamyl alcohol–water (*3*); methyl alcohol–isobutyl alcohol–water (*4*);[1] and ethyl alcohol–ether–water (*5*). But, in general, the data as presented require interpolations over too wide ranges for the present purposes. In this paper the method is presented whereby detailed charts of the specific gravities, refractive indices, and the function D/C (defined below) of the system methyl alcohol–isobutyl alcohol–water at 60° F. were prepared from relatively few experimental points.

In expressing compositions, volume rather than the customary weight percentages are frequently used. The relations between weight per cent, actual volume per cent, and ideal volume per cent can be derived as follows:

Let v_a, v_b, v_c; w_a, w_b, w_c; d_a, d_b, d_c, be, respectively, the volumes, weights, and densities of the three components A, B, C, making up a solution whose volume, weight, and density are, respectively, V, W, and D, all at 60° F. Then,

$$\text{Weight \% of } A = \frac{w_a \times 100}{w_a + w_b + w_c} = \frac{v_a d_a \times 100}{VD} \tag{1}$$

$$\text{Actual vol. \% of } A = \frac{v_a \times 100}{V} \tag{2}$$

$$\text{Ideal vol. \% of } A = \frac{v_a \times 100}{v_a + v_b + v_c} = \frac{w_a/d_a \times 100}{w_a/d_a + w_b/d_b + w_c/d_c} \tag{3}$$

Calcd. density (assuming no contraction),

$$C = \frac{v_a d_a + v_b d_b + v_c d_c}{v_a + v_b + v_c} = \frac{w_a + w_b + w_c}{w_a/d_a + w_b/d_b + w_c/d_c} \tag{4}$$

$$D = \frac{v_a d_a + v_b d_b + v_c d_c}{V} = \frac{w_a + w_b + w_c}{V} \tag{5}$$

$$D/C = \frac{v_a + v_b + v_c}{V} = \frac{w_a/d_a + w_b/d_b + w_c/d_c}{V} \tag{6}$$

$$(\text{Actual vol. \% of } A) = (\text{weight \% of } A)\,\frac{D}{d_a} \tag{7}$$

$$(\text{Ideal vol. \% of } A) = (\text{weight \% of } A)\,\frac{C}{d_a} = (\text{weight \% of } A)\,\frac{D}{(D/C)d_a} \tag{8}$$

$$(\text{Actual vol. \% of } A) = (\text{ideal vol. \% of } A)\,\frac{D}{C} \tag{9}$$

It is evident that, if the observed specific gravity and the ratio of observed specific gravity to calculated specific gravity (D/C) are available for a given system, any one of the percentages can be readily converted to the others.

EXPERIMENTAL PROCEDURE

Figure 1 shows the compositions for which specific gravities, refractive indices, and the ratio D/C were determined at 60° F. The compositions selected for experiment were taken to lie on lines of constant isobutyl alcohol–methyl alcohol ratio (I/M) at varying percentages of water (W). The data for the ratios 10 to 0, 7.5 to 2.5, 5 to 5, 2.5 to 7.5, and 0 to 10 were used in preparing the charts; the remaining experimental points were used in checking the curves and estimating the probable errors. The experimental points also lie on lines of constant water content. The known mixtures were made up of carefully purified components using thermostated Bureau of Standards burets with compositions expressed in ideal volume per cents which were used exclusively in the experimental work reported in this paper; the errors in composition were, in general, less than ±0.1 per cent for any component. Specific gravities were measured with sensitive

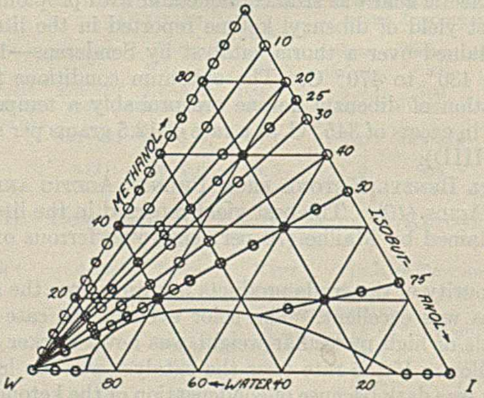

FIGURE 1. COMPOSITIONS OF THE TERNARY SYSTEM

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[1] The data of Jänecke (*4*) were used in plotting the phase-equilibrium curve at 60° F. used in this paper.

calibrated hydrometers in a thermostated bath; in each case, readings were readily reproducible to 0.0002, and the average of the several readings, on the whole, did not differ from the true value for the compositions taken by more than ±0.0002. (Δ0.1 per cent in composition corresponds to about Δ0.0002 in specific gravity.) Refractive indices were measured with a Zeiss dipping refractometer in cups contained in a thermostated bath. Readings were readily reproducible to 0.00005; the average was rounded off to the nearest 0.0001 and, in general, did not differ from the true value for the composition taken by more than ±0.0001. (Δ0.1 per cent in composition corresponds at most to Δ0.00005 in refractive index.) The ratios of observed to calculated specific gravities (×100), (*D*/*C*) (×100), were not in error, on the whole, by more than ±0.05 (which could cause errors in converted compositions of not more than ±0.05 per cent for any component). The experimental data are presented in Table I.[2]

TABLE I. EXPERIMENTAL DATA

Ratio *I*/*M*	H_2O	Methyl Alcohol	Isobutyl Alcohol	Refractive Index at 60° F.	Sp. Gr. at 60° F.	Ratio (*D*/*C*) (× 100)
	%	%	%			
1/9	100.0	0.0	0.0	1.3334	1.0000	100.00
	75.0	22.5	2.5	1.3409	0.9680	101.96
	50.0	45.0	5.0	1.3467	0.9301	103.48
	25.0	67.5	7.5	1.3464	0.8745	....
	0	90.0	10.0	1.3368	0.7970	99.96
2/8	75.0	20.0	5.0	1.3426	0.9692	102.06
	50.0	40.0	10.0	1.3497	0.9298	103.40
	25.0	60.0	15.0	1.3510	0.8745	....
	0	80.0	20.0	1.3432	0.7977	99.94
2.5/7.5	90.0	7.5	2.5	1.3370	0.9876	100.79
	80.0	15.0	5.0	1.3412	0.9761	101.70
	70.0	22.5	7.5	1.3454	0.9623	102.42
	60.0	30.0	10.0	1.3487	0.9477	103.06
	50.0	37.5	12.5	1.3511	0.9291	103.29
	40.0	45.0	15.0	1.3526	0.9087	103.34
	30.0	52.5	17.5	1.3534	0.8861	103.12
	20.0	60.0	20.0	1.3529	0.8602	102.54
	10.0	67.5	22.5	1.3509	0.8311	101.49
	0	75.0	25.0	1.3466	0.7979	99.90
3/7	75.0	17.5	7.5	1.3443	0.9696	102.08
	50.0	35.0	15.0	1.3525	0.9284	103.19
	25.0	52.5	22.5	1.3554	0.8735	
	0	70.0	30.0	1.3498	0.7981	99.86
4/6	90.0	6.0	4.0	1.3381	0.9882	100.84
	80.0	12.0	8.0	1.3434	0.9770	101.76
	70.0	18.0	12.0	1.3482	0.9622	102.35
	60.0	24.0	16.0	1.3520	....	....
	50.0	30.0	20.0	1.3552	0.9271	103.00
	40.0	36.0	24.0	1.3577	0.9066	103.02
	0	60.0	40.0	1.3565	0.7993	99.88
5/5	90.0	5.0	5.0	1.3387	0.9886	100.88
	75.0	12.5	12.5	1.3474	0.9700	....
	70.0	15.0	15.0	1.3498	0.9611	102.22
	65.0	17.5	17.5	1.3521	0.9533	....
	60.0	20.0	20.0	1.3540	0.9444	102.61
	55.0	22.5	22.5	1.3559	0.9348	....
	50.0	25.0	25.0	1.3577	0.9252	102.72
	40.0	30.0	30.0	1.3609	0.9050	102.76
	30.0	35.0	35.0	1.3634	0.8829	102.57
	20.0	40.0	40.0	1.3650	0.8587	102.12
	10.0	45.0	45.0	1.3653	0.8317	101.30
	0	50.0	50.0	1.3632	0.7998	99.85
7.5/2.5	30.0	17.5	52.5	1.3729	0.8793	101.95
	20.0	20.0	60.0	1.3768	0.8565	101.61
	10.0	22.5	67.5	1.3797	0.8317	101.03
	0	25.0	75.0	1.3801	0.8024	99.84

DISCUSSION OF RESULTS

The problem, then, was to convert these data into ternary diagrams showing lines, respectively, of constant specific gravity, refractive index and ratio *D*/*C*, so that these properties could be read off at any desired composition with a precision as nearly that of the experimental data as possible. In working up data such as that indicated by Figure 1, the final decision as to methods will obviously depend on the nature of the experimental material, but the procedure used here should be of rather general application for ternary systems containing water and two homologous aliphatic compounds.

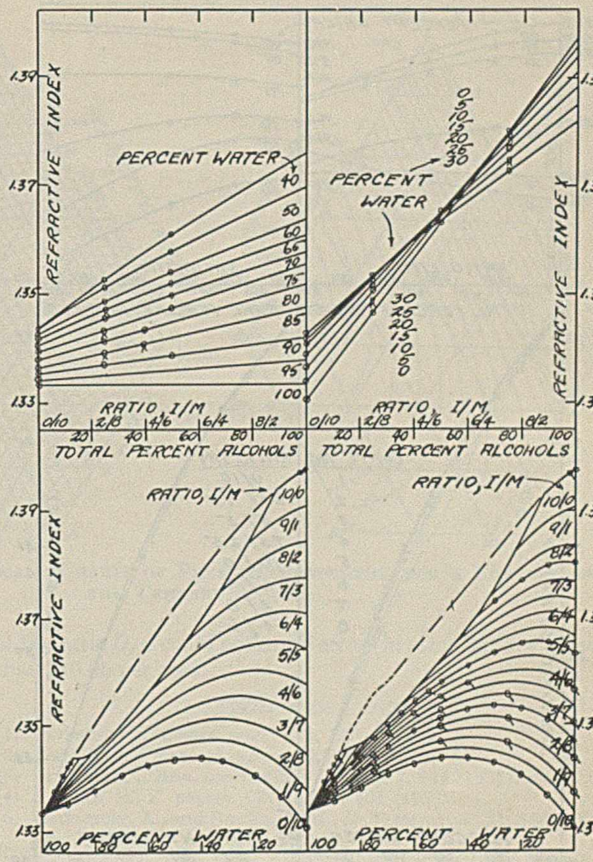

FIGURE 2. APPLICATION TO REFRACTIVE INDEX DATA

Figure 2 illustrates the method as applied to the refractive index data. When refractive index at 60° F. is plotted against percentage water for the systems methyl alcohol–water and isobutyl alcohol–water, two divergent curves are obtained, the latter largely interpolated; and, in the absence of other experimental information, lines of constant isobutyl alcohol–methyl alcohol ratio may be interpolated, but the results will be in error by amounts up to about ±0.0010. When, in addition, a few representative lines of constant isobutyl alcohol–methyl alcohol ratio (for example, 2.5 to 7.5, 5.0 to 5.0, 7.5 to 2.5) are determined by enough experimental points to draw these curves accurately, the remaining curves can be directly interpolated with a maximum error of about ±0.0003. It was found, however, that lines of constant percentage water, drawn from the experimentally determined lines of constant isobutyl alcohol–methyl alcohol ratio, were relatively simple curves which could be drawn precisely (except for long extrapolations) with very few experimental points. Any desired number of lines of constant percentage water could be drawn, and from them all the lines of constant isobutyl alcohol–methyl alcohol ratio that proved necessary. None of the lines of constant isobutyl alcohol–methyl alcohol ratio so obtained was in error, on the whole, by more than ±0.0001 as shown by the fact that nearly all the "confirma-

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[2] The data of Doroshevskii [*J. Russ. Phys. Chem. Soc.*, 41, 977 (1909)] and Holmes (in "Alcohol," by Charles Simmonds, Macmillan, 1919) were used in conjunction with some determinations of the present writers for specific gravities and refractive indices at 60° F. of methyl alcohol–water mixtures, and isobutyl alcohol–water mixtures; these data are not included in Table I.

The original experimental data quoted in Table I were obtained in May, 1930, by D. M. Smith and W. M. D. Bryant. The carefully purified materials used had physical constants as follows:

Substance	B. P. at 760 mm.	Sp. Gr. at 60° F.	Refractive Index at 60° F.
Methyl alcohol	64.5° C.	0.7963	1.3304
Isobutyl alcohol	107.4–107.6	0.8060	1.3975
Water	100.0	1.0000	1.3334

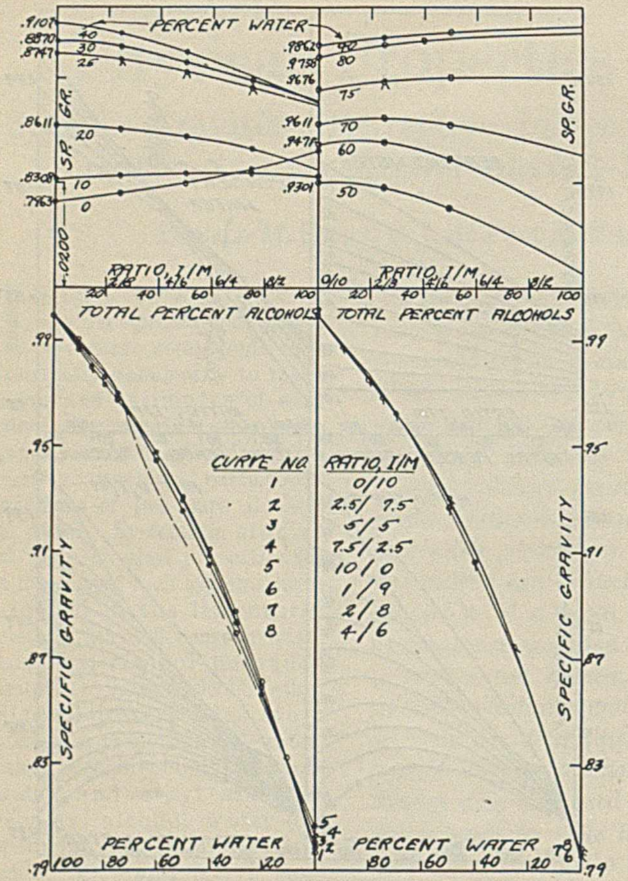

FIGURE 3. APPLICATION TO SPECIFIC GRAVITY DATA

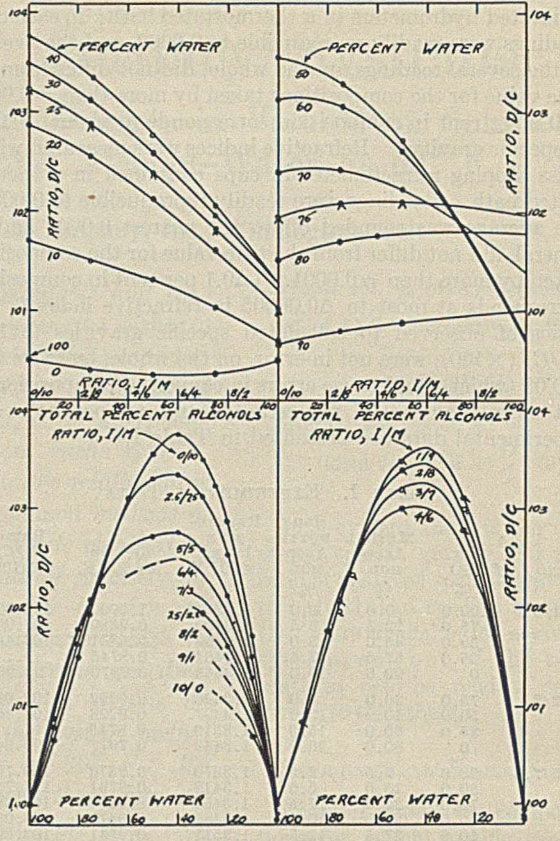

FIGURE 4. APPLICATION TO DATA FOR THE RATIO (D/C) (× 100)

tory" (as well as the "charted") experimental points[3] lay within ±0.0001 of the appropriate curves; a few points were off by ±0.0002, which was consistent with errors of ±0.0001 in both the curves and these experimental points. The ternary charts showing lines of constant refractive index were readily drawn by plotting the intersections of constant refractive index lines with this family of curves at the corresponding percentage of water. The portions of the curves for isobutyl alcohol–water, obtained by long extrapolations of the lines of constant percentage water in this and succeeding figures must not be regarded as exact; they serve, however, to emphasize the trends of the other lines.

Figure 3 illustrates the method as applied to the specific gravity data. In this case it obviously would be very difficult to draw a family of exact lines of either constant isobutyl alcohol–methyl alcohol ratio or constant percentage water without the use of the procedure described above, or a great many more experimental data. In Figure 3 lines of constant isobutyl alcohol–methyl alcohol ratio through the charted experimental points are shown at the lower left while some of the confirmatory points are shown on the appropriate curves at the lower right. The actual curves used in preparing the ternary diagrams were drawn on a large scale in greater number than those illustrated and were drawn on several sheets of paper to avoid confusion. By the same type of criteria as used for the refractive index data, the specific gravity curves, in general, were not in error by more than ±0.0002.

Figure 4 illustrates the method as applied to the data for the ratio (D/C) (× 100). Here again it would be very difficult to draw directly a family of exact lines of either constant isobutyl alcohol–methyl alcohol ratio or constant percentage water from the few experimental points available. In Figure 4 lines of constant isobutyl alcohol–methyl alcohol ratio through the charted experimental points are shown at the lower left while the confirmatory points are shown on the appropriate curves at the lower right. The lines of constant percentage water for the ratio D/C are more difficult to extrapolate than the corresponding lines for specific gravity and refractive index,

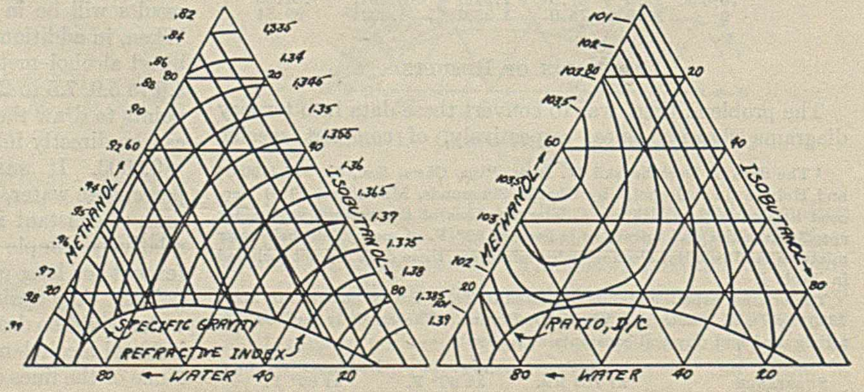

FIGURE 5. TERNARY DIAGRAMS WITH LINES OF THE CONSTANT PHYSICAL PROPERTIES

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[3] Charted direct experimental points are indicated on Figures 2 to 4 by plain circles; a few charted points obtained by interpolation from adjacent direct experimental points (not used as confirmatory points) are indicated by circles with a double tail. Confirmatory experimental points are indicated by circles with a single tail.

so that the hypothetical lines of constant isobutyl alcohol–methyl alcohol ratio in the region of partial miscibility would be best drawn through points obtained by direct calculation from the corresponding lines of observed specific gravity (Figure 3).

By the same type of criteria as used for the refractive index and specific gravity data, the curves for the ratio (D/C) (× 100), on the whole, were not in error by more than ±0.05.

Conclusion

Figure 5 shows the general appearance of the ternary diagrams with lines respectively of constant specific gravity, refractive index, and ratio (D/C) (× 100); and Figure 6 illustrates large-scale detailed charts of the same properties for a portion of the system.[4] These charts are designed to be read with an accuracy corresponding to that with which they represent the system. Prepared from large-scale drawings, similar to those illustrated in Figures 2 to 4, the resulting diagrams, in general, were not in error by amounts greater than the corresponding charts of Figures 2 to 4 when judged by the same criteria. Thus, expressed in terms of the corresponding compositions, the lines of constant specific gravity and refractive index, on the whole, were not in error, respectively, by more than ±0.1 and ±0.2 per cent; and use of the ratio D/C could not cause errors in compositions of more than ±0.05 per cent.

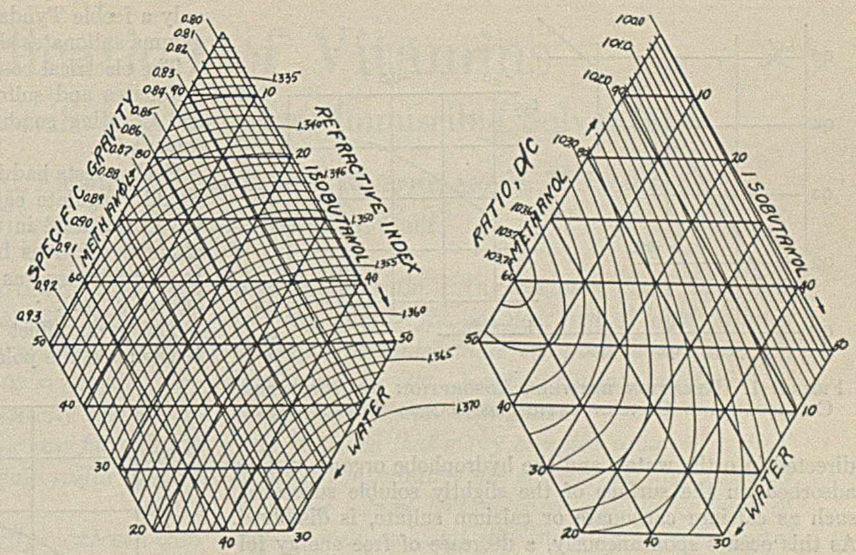

Figure 6. Large-Scale Charts of Physical Properties for a Portion of the Ternary System

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[4] In the original of Figure 6, the coördinates are plotted for each 1 per cent, and points can be located to ±0.1 per cent for each component.

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Received September 23, 1933. Presented before the Division of Physical and Inorganic Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Sulfonic Acids from Petroleum

Physico-Chemical Characteristics

E. Neyman and S. Pilat, Institute of Petroleum Technology, Lwow, Poland

The sulfonic acids obtained as by-products (*13*, *14*, *17*) in petroleum refining are attracting increased attention because of new and better methods of recovering the excess sulfuric acid with which they are mixed and still more because of their increasing use as fat-splitting reagents and for emulsifying oils with aqueous solutions.

Of these acids one group of relatively low molecular weight gives water-soluble calcium salts and another of higher molecular weight gives calcium salts insoluble in water. Solubility of the calcium salts in ether is helpful in separating the acids (*15*). The characteristics of the three main groups of sulfonic acids are shown in the following table:

Sulfonic Acid	Source	Solubility of Ca Salts	
		In water	In ether
Alpha	Recovered from acid sludge	Insoluble	Insoluble
Beta	Recovered from alkali sludge when oil has been treated with fuming acid	Insoluble	Soluble
Gamma	Recovered from acid sludge only	Soluble	Insoluble

The gamma sulfonates can be further divided by means of the water solubility of the barium (of cobalt) salts into two groups.

The alpha and gamma classes were studied in this work as they showed the property of affecting the solubility of other substances in water and also because they showed strongly those properties (*16*) upon which commercial use of the acids is based.

Surface tension determinations showed these salts to be much more effective in decreasing the tension of water than is sodium oleate. The effect of 0.1 per cent solutions was 65, 51, and 54 for the oleate, alpha salt, and gamma salt, respectively:

Surface Tension against Air by Use of Stalagmometer (*18*)[a]			
γ Salt (approx. $C_{13}H_{13}SO_3Na$)		α Salt (approx. $C_{28}H_{30}SO_3Na$)	
Mole/liter	*Dynes/cm.*	*Mole/liter*	*Dynes/cm.*
0.0312	36.3	0.0213	41.2
0.0156	39.4	0.0106	43.0
0.0078	45.4	0.0053	46.5
0.0039	54.4	0.0026	48.6
0.0019	64.7	0.0013	55.1
C.0009	71.7	0.0006	61.5
		0.0003	63.7

Interfacial Tension against Toluene by Donnan Method(*1*)[b]			
γ Na Salt soln.		α Na salt soln.	
% C	*Drops*	*% C*	*Drops*
0.85	310	0.50	218
0.425	181	0.25	181
0.212	128	0.125	143
0.106	87	0.062	114
0.053	83	0.031	95
0.026	79	0	

[a] $t = 20°$ C.
[b] 68 toluene drops in water.

Two other properties have been studied—i. e., the effect termed "hydrotropy" (*3*, *7*, *9*, *10*, *19*) by Neuberg, and the adsorption on activated carbon, silica gel, etc. It is probable that with these substances the lyophile sulfonic group is

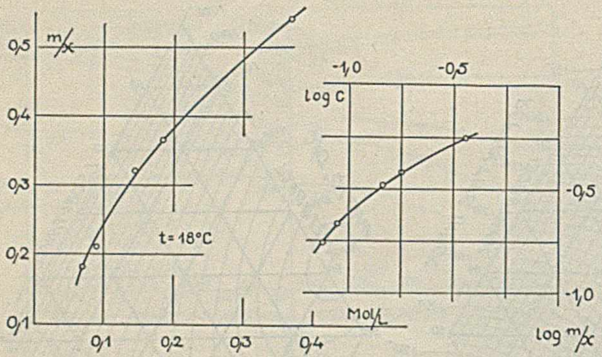

FIGURE 1. RELATION BETWEEN ADSORPTION ON ACTIVATED CHARCOAL AND CONCENTRATION OF GAMMA SODIUM SALT

directed into the water, and the hydrophobe organic residue adsorbed on the surface of the slightly soluble substance, such as calcium carbonate or calcium sulfate, is dissolved. As this occurs spontaneously, a decrease of free energy follows and consequently an increase of surface by which a higher degree of solubility is obtained. We would expect, and do so find, that the larger the molecule (*5*) the more the solubility is increased. Comparisons, however, must be made with the inorganic salt in the same condition—i. e., not with calcium carbonate in one case freshly precipitated and in the other dried at elevated temperatures:

Na Salt in Water	Soly. of $CaCO_3$	Na Salt in Solvent	Soly. of $CaSO_4$
%	%	%	%
4	0.15	1.6	0.62
6	0.45	3.3	0.98
10	0.62	7.5	1.16
16	0.69	13.3	1.77
20	0.95	14.3	2.85

These effects are not limited to inorganic salts of calcium but are shown by the water-insoluble alpha calcium sulfonates when treated with solutions of the alpha sodium salts.

The peptization of coal and oil by means of soaps (*2*) is paralleled to some extent by the effect of the solutions of the gamma sulfonates on activated carbon or silica gel. Adsorption was determined by shaking 20 cc. of the neutral sodium salt with 2 grams of the carbon for 10 minutes, filtering, and evaporating an aliquot to dryness.

In Figure 1 log m/x has been plotted against log C. The value of the coefficient n in the Freundlich equation is 0.772. Other investigations (*2*) on the adsorption of mixtures of homologous substances such as oxalic and succinic acids have given a slightly bent curve rather than a straight line. The sulfonates used here are also mixtures and give a slightly bent curve.

It follows from those experiments that the gamma sodium sulfonate is highly adsorbed—e. g., from a 10 per cent solution 0.539 gram is adsorbed by 1 gram of charcoal (that is, 54 per cent).

Dialysis using a triple collodion film (*11*) permitted the gamma sulfonate to be completely separated from the larger molecule alpha sulfonate. The gamma salt, by analysis, contains about thirty-one atoms and the alpha salt twice that number. Accordingly, the separation by dialysis agrees with the experience of Biltz (*4*) that only when the number of atoms in the molecule is less than forty-five does diffusion proceed easily.

Examination of 0.01 per cent solutions of these sulfonates under the ultramicroscope with magnifications of 600 showed only a feeble Tyndall effect and no Brownian motion. The gamma sulfonates showed least Tyndall effect.

The electrical conductivity of the solutions of the gamma sulfonates and sulfonic acid (Figure 2) was determined at 25° C. using conductivity water ($\lambda = 3.47 \times 10^{-6}$) as the solvent (*8*).

Earlier tests had indicated that sulfonates from petroleum would coagulate egg albumin. Purified sulfonates such as have been used in this work were found not to precipitate albumin solutions but actually prevented their coagulation by electrolytes, as would be expected with hydrotropic agents (*9, 12*).

The great effect of the petroleum sulfonates on surface tension and the polar character of the free acids are already industrially important, and it is hoped that industry will soon find some equal use for them on account of their pronounced hydrotropic and peptizing properties.

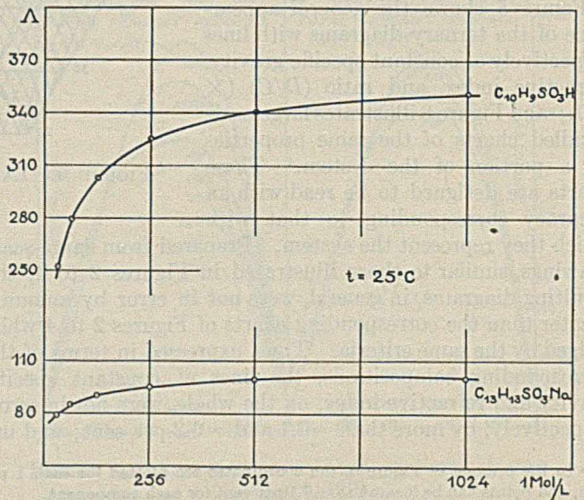

FIGURE 2. RELATION BETWEEN EQUIVALENT CONDUCTANCE AND CONCENTRATION OF GAMMA SODIUM SALT AND OF FREE GAMMA ACID (*6*)

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RECEIVED October 12, 1933.

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Purification of Vitamins

Fractional Distribution between Immiscible Solvents

R. E. Cornish, R. C. Archibald, Elizabeth A. Murphy, and H. M. Evans
University of California, Berkeley, Calif.

While systematic fractional distillation has been so perfected as to become almost the standard method for concentrating or purifying any volatile substance, it is remarkable that the analogous systematic fractional distribution has been practically ignored by industry, although the Edeleanu process for refining petroleum by countercurrent of liquid sulfur dioxide is certainly a beginning.

The present authors are primarily concerned with vitamins, but it is thought that the principles developed here of fractional distribution (i. e., engineering of liquid-liquid systems) have as broad application as the better known principles of fractional distillation (i. e., engineering of liquid-vapor systems). Fractional distribution may be, moreover, applied to almost any substances rather than being limited to volatile ones; decomposition due to heating may thus be avoided.

The mathematical theory is developed for purification of materials such as vitamins by fractional distribution between a pair of immiscible solvents. Only a few solvents seem to be suitable for fat-soluble vitamins; purification of these solvents is described. A machine is described which systematically carries out 500,000 fractionations in a 2-day run; the fractionations depend on differences in distribution ratio. Any quantity from 10 grams to 1 mg. may be fractionated; use of highly diluted solutions precludes those complications which are analogous to the constant-boiling mixtures of ordinary fractional distillation.

It is shown that many accepted values of critical solution temperatures are entirely too high, because the polar solvent had not been completely freed of water; methanol and ethylene diamine are typical examples. Except by fractional distillation, it is difficult completely to dry a polar liquid.

Numerous critical solution temperatures are given. Also given are distribution ratios of various sterols, and of the pure fat-soluble vitamins A, D, E, and F, at various temperatures. Choice of solvent or temperature shifts these ratios but only slightly affects their relative positions.

It is proved beyond doubt that vitamin A exists in at least three distinct chemical forms, although the complete therapeutic effect is obtainable from any one of the three. Again, the therapeutic effect of vitamin D seems to be produced by a single substance, or at most by a mixture of substances each having nearly the same distribution ratio as the other. With these same qualifications, vitamin E is also proved to be a single chemical substance.

A SPECIAL machine has been constructed which permits a remarkable if not complete purification of the fat-soluble vitamins A, D, and E by fractional distribution between immiscible solvents. At the same time, the machine provides an accurate method for measuring the distribution ratios of the absolutely pure vitamins, without its being necessary to isolate them as pure substances.

Methods of securing crude, concentrated vitamins for purification in the machine, and methods of testing activity with animals are considered in a current separate paper by the present authors. The present paper deals with choice of solvents and theory of operation and construction of the column, and the preparation of desirable solvents. Distribution ratios of various sterols, especially when considered at different temperatures, show that lowering of temperature of operation of the column will considerably increase the frationating effectiveness. By numerous long and arduous runs with the column, the present writers have, by method of trial and error, accurately determined the distribution ratios for each of the four fat-soluble vitamins. Other properties of these vitamins are now under investigation.

Theory of Distribution Column

One assumes that in a countercurrent column, two solvents (1 and 2) are flowing through in opposite directions and at constant rates. For mathematical discussion, one assumes that the column contains "theoretical plates" in each of which complete equilibrium is obtained between the flowing solvents. After a steady state has been reached, the mixture to be fractionated (in which a third substance, 3, is eventually desired in pure state) is suddenly injected into the middle of the column.

If the inverse ratio of the rates of flow of the two liquids (1 and 2) is exactly equal to the distribution ratio of the dissolved substance (substance 3), there will still be a transfer of that substance in both directions. This transfer is mathematically analogous to diffusion or to conduction of heat. If the dissolved substance is originally placed in the center of the column, it will in time be dissipated through the ends.

Let r_1 = rate of flow of solvent 1, cc. per minute
r_2 = rate of flow of solvent 2, cc. per minute
V = volume of one section (theoretical plate) of column, cc.
c = number of sections in column
x = serial number of a particular section (measured from one end)
u = amount of third substance in a given section, grams
t = time, minutes
u_0, x_0, etc. = values of u, x, etc., when $t = 0$
m = any real, positive integer
I = a function of m; if m is even, $I = 0$; if m is 1, 5, 9, 13, etc., $I = +1$; if m is 3, 7, 11, 15, etc., $I = -1$.
Q = amount of third substance in whole column, grams
Q_0 = same when $t = 0$; this whole is then in the center section

We now assume that each section contains equal volumes of solvents 1 and 2. This condition is somewhat approached in practice, since the attempt is made to put the solvents through the column as fast as possible. The assumption introduces greater error the more the distribution ratio of the third substance differs from unity. In actual practice, the upper sections of the column have relatively more of the lighter solvent, and vice versa for the lower sections. Hence, if the third substance is relatively insoluble in, say, the lighter solvent, the third substance will tend to come out relatively more at the top of the column than computed by the formula. For it is evident that various molecules of substance 3 are simply shuttled back and forth between various sections of the column, substance 3 molecules eventually finding their way out of the column according to the laws of probability. The mathematical expression developed below is, in fact, identical in form with that of diffusion of a substance out of a long narrow rod of gelatin where a quantity of substance is suddenly injected into the middle of the gelatin and allowed to diffuse out, a concentration zero being maintained always at both ends of the rod as might be done by a dialyzing membrane at the ends. Or the formula is identical in form with that of the temperature of a perfectly insulated rod at original uniform temperature, zero, where both ends are constantly kept at temperature zero and where at a certain instant a finite amount of heat is suddenly released at the center of the rod. In the present case it is evident that, if the third substance is relatively insoluble in the lighter solvent, accumulation of this solvent at one end of the column will make it easier for substance 3 to work its way through that end. Ignoring, however, any such segregation of the solvents, we will also let, in the single section x, the quantity of substance 3 be u. By Taylor's theorem, the quantity of substance 3 in the two adjoining sections at the same instant of time will be, respectively, to the second order, $u + (du/dx)\cdot 1 + (d^2u/dx^2)\cdot 1^2/2$, and $u - (du/dx)\cdot 1 + (d^2u/dx^2)\cdot 1^2/2$. Now, the column is being operated so that r_2/r_1 is the distribution ratio of substance 3 (i. e., ratio of solubility in solvent 1 to solubulity in solvent 2). In section x of the column, the concentration of substance 3 in solvent 1 is $2ur_2/ (r_1 + r_2)V$, and in solvent 2 is $2ur_1/ (r_1 + r_2)V$. One then easily shows:

$$\left(\frac{\partial u}{\partial t}\right)_x = \frac{2r_1r_2}{(r_1 + r_2)V}\left(\frac{\partial^2 u}{\partial x^2}\right)_t \qquad (1)$$

Let

$$a = 2r_1r_2/(r_1 + r_2)\ V \qquad (2)$$

Also at all times, $u = 0$ if $x = 0$ or if $x = c$. Under these conditions the solution of Equation 1 is given by Byerly (*8*) and is:

$$u = 2/c \sum_{m=1}^{m=\infty}\left[e^{-m^2a^2\pi^2t/c^2}\sin(m\pi x/c)\int_0^c u_0\sin(m\pi x_0/c)\ dx_0\right] \qquad (3)$$

The integral in Equation 3 is easily seen to equal IQ_0, as only values of $\sin(m\pi x_0/c)$ where $x_0 = c/2$ have any weight (as all of substance 3 is in the middle of the column at the start), thus:

$$u = 2Q_0/c \sum_{m=0}^{m=\infty}\left[Ie^{-m^2a^2\pi^2t/c^2}\sin(m\pi x/c)\right] \qquad (4)$$

Integrating Equation 4 over the length of the column gives Q at any time:

$$Q = \int_0^c u dx = 4Q_0/\pi \sum_{m=0}^{m=\infty}\left[(I/m)e^{-m^2a^2\pi^2t/c^2}\right] \qquad (5)$$

Equation 5 becomes, if one puts $y = e^{-a^2\pi^2t/c^2}$ (6)

$$Q = (4Q_0/\pi)(y - y^9/3 + y^{25}/5 - y^{49}/7 + y^{81}/9 - \ldots.) \qquad (7)$$

If either y or Q/Q_0 is of the order of 0.5 or less, all but the first term of the expansion may be ignored for approximate purposes. Thus Equation 5 gives, using common logarithms:

$$t = \frac{-2.303c^2V(r_1 + r_2)}{2\pi^2r_1r_2}\log_{10}\frac{Q}{4Q_0} \qquad (8)$$

(approximately, if $Q/Q_0 < 0.5$)

Gravimetric values of amounts left in the column in runs with pure cholesterol occur at around 55 per cent of the theoretical time. From Equation 8, this time varies as c^2V—that is, as c, the number of sections, times cV, the total capacity of the column. Hence the column may be said to have an "efficiency" of 55 per cent and to behave as if composed of 210 × 0.55 = 115 theoretically perfect sections. Experience with fat-soluble vitamins (Tables III to VI) indicates the order of 50 per cent efficiency for hexane and methanol (at − 20° C). For the other solvents, the efficiency may be somewhat less, owing to smaller density difference, or to the excessive stirrer speed required with the methyl cyanide (800 r. p. m. because of the difficulty of methyl cyanide's penetrating the nickel gauzes of the column). V was taken as 16 cc.

SOLVENTS FOR FRACTIONATION BY DISTRIBUTION

To reduce difficulties, distribution was used between two pure liquids. The polar solvent must not be too polar, since water is a poor solvent for fat-soluble vitamins. Glycerol or ethylene glycol have their high boiling points and viscosities against them. Formic acid rapidly turns ergosterol blue. Cold ethylenechlorohydrin, on standing a few days with either vitamin A concentrates or with ergosterol, develops a yellow color which cannot be extracted by shaking with 2, 2, 4-trimethylpentane; in the hot, the reaction is rather rapid. The coloring produced in sterols by concentrated sulfuric acid is well known (*1*), while sulfur dioxide may not affect vitamin D (*5*), vitamin A in cod liver oil is destroyed by a 15-minute treatment at room temperature, although the vitamin A in butter or in alfalfa is relatively stable to sulfur dioxide (*9*).

Ethylene diamine has great affinity for water; the vapor forms a dense smoke with air. The amine attacks cork and rubber, and appears to attack nickel noticeably during a month at room temperature.

Methyl cyanide appears promising from distribution ratios alone, and actual vitamin runs were made with this solvent (Table V). An unforeseen difficulty was that methyl cyanide does not wet nickel in the presence of 2, 2, 4-trimethylpentane. Even a test-tube experiment will show that drops of methyl cyanide up to 1 cc. in size will not flow through or wet nickel gauze of twenty mesh per inch (eight mesh per cm.) or finer, under action of gravity alone, assuming, of course, an atmosphere of the 2, 2, 4-trimethylpentane phase. Anhydrous methanol and anhydrous β-methoxyethanol have no difficulty in passing through the gauzes (nor do they impede the counterflow of 2, 2, 4-trimethylpentane, but, if 25 per cent water is present in them, the behavior is like that of pure methyl cyanide. Boiling nitromethane does not discolor ergosterol, but nitromethane is dangerous as an explosive. (Yet nitromethane is suggested as a lacquer solvent, *22*.)

The remaining polar solvents are methyl cyanide, methanol, and β-methoxyethanol. Having chosen any of these three, most organic liquids are completely miscible with it, except saturated hydrocarbons, carbon disulfide, and tetrachloroethylene (liquids of boiling points above 150° C. are excepted). Tetrachloroethylene gives low critical-solution temperatures; carbon disulfide is probably too reactive. Cyclohexane has its density almost the same as that of the selected polar solvents (except β-methoxyethanol). Pentane and hexane were used at first but were abandoned in favor of either *n*-heptane (so-called "abietene") from pine oil (*6*, *15*, *26*, *39*, *45*, *48*) or 2, 2, 4-trimethylpentane (*15*), which were obtainable in high purity. A method of Shepard and Henne, using chlorosulfonic acid (*41*, *42*), makes pure saturated straight-chain hydrocarbons from petroleum.

PREPARATION OF 2, 2, 4-TRIMETHYLPENTANE

Using essentially the method of Edgar (*15*) except for the use of dilute alkaline permanganate instead of concentrated sulfuric acid for washing, the present writers also distilled intermediate and final products in the 6.09-meter column previously described (*19*).

The purified 2, 2, 4-trimethylpentane had a boiling range of less than 0.1° C., and d_{20}^{20} (corrected to vacuum) 0.69335 ± 0.00011 (mean deviation of different fractions). This material was probably not quite pure, since later batches prepared as above (but also washed with concentrated sulfuric acid during manufacture) gave d_{20}^{20} 0.69314 ± 0.00001 mean deviation. Both samples gave identical operation for vitamin purification. The earlier 2, 2, 4-trimethylpentane had a boiling point of 99.3° ± 0.05° C. (corrected), a freezing point of −107.5° ± 0.5° (this checks −107.8° of Parks and Huffman, *36*), a refractive index 20°, D line 1.39162 ± 0.00012 (mean deviation from mean). Refractive index and density do not agree with Edgar (*15*) but check Edgar and Calingaert (*16*) who gave refractive index 20°, D line 1.3916, and d_4^{20} 0.6918 which gives d_{20}^{20} 0.6930.

PREPARATION OF METHYL CYANIDE

Following essentially Walden (*47*) 39.2 kg. (800 moles) of powdered sodium cyanide were placed in a 150-liter iron kettle with a steam jacket over its lower half. Forty liters of hot water were added (a greater amount might be desirable), the whole was heated to boiling, and the steam was shut off. During 2 hours 50.4 kg. (400 moles) of dimethyl sulfate were slowly added. The kettle was equipped with a reflux condenser, and a rapid stream of cold water was flowed over the outside of the kettle. Unless effective means are used for dissipating the heat of reaction, it is hardly possible to make methyl cyanide. The crude product was distilled off and successively washed with solid sodium hydroxide and P_2O_5, using a 50-liter glass bottle which rotated end over end. Following another rough distillation, the material was carefully fractioned in the 6.09-meter column. The finished product is much purer than samples from two well-known manufacturers. Methyl cyanide (boiling point about 82° C.) forms a constant-boiling mixture at 76° with 15 weight per cent water. The purified methyl cyanide gave d_4^{20} 0.78215 (corrected for buoyancy of air), compared with d_4^{20} 0.7828 (*7*).

PURIFICATION OF *n*-PENTANE AND *n*-HEXANE

Pentane and hexane were purified as described previously (*19*). The critical solution temperatures (c. s. t.) of *n*-pentane–methanol (13.2°) and of *n*-hexane–methanol (30.1°) as found with the solvents used in vitamin column runs were rechecked with Eastman Kodak Company synthetic hexane (presumably from propyl iodide) and with a sample of *n*-pentane (from petroleum, less than 0.1° boiling range) carefully purified by Bernhardt Weidenbaum who used the 6.09-meter column and by great care obtained pentane with 0.1° C. or less boiling range. The c. s. t. results were: *n*-pentane–methanol 14.75° C., and *n*-hexane–methanol 32° C.

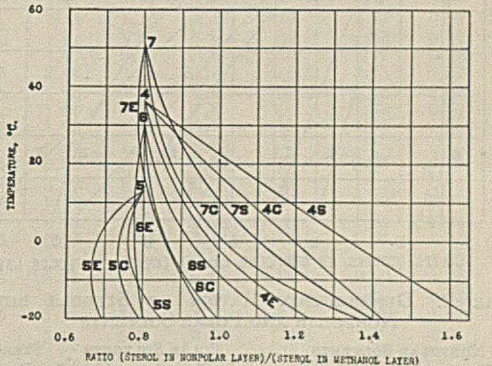

FIGURE 1. DISTRIBUTION RATIOS OF STEROLS BETWEEN NONPOLAR SOLVENTS AND METHANOL

NONPOLAR SOLVENTS
4. Carbon disulfide
5. *n*-Pentane
6. *n*-Hexane
7. *n*-Heptane

STEROLS
E. Ergosterol
C. Cholesterol
S. Sitosterol

PURIFICATION OF METHANOL

Synthetic methanol was carefully rectified in the 6.09-meter column; the boiling point was constant to 0.1° C. or less. At the end of a distillation the kettle smelled of formaldehyde and the resulting methanol was acid (about 0.4 milli-equivalents per liter) unless a little sodium hydroxide had been dissolved in the crude methanol. A value of d_4^{25} 0.78656 (corrected for air buoyancy) is found, compared with d_4^{25} 0.78658 of McKelvy and Simpson (*33*) and d_4^{25} 0.78661 of International Critical Tables (*27*). While values discussed by International Critical Tables agree with this or are higher, Rising and Hicks (*37*) give d_4^{15} 0.79578 (International Critical Tables gives d_4^{15} 0.79601). If Rising and Hicks neglected to add 0.00026 for buoyancy of air, the check would be close.

Critical solution temperatures have been given for carbon disulfide and methanol as 36.2° C. (present authors), 35.7° (*33*), 40.5° (*38*), 40.6° (*13*), 48.5° (*46*); for *n*-hexane and

TABLE I. CRITICAL SOLUTION TEMPERATURES, ° C.

				DECREASING POLARITY					
INCREASING POLARITY	$(C_2H_5)_2O$	Iso-$(C_3H_7)_2O$	C_2Cl_4	N-C_5H_{12}	N-C_6H_{14}	CS_2	Cyclo-C_6H_{12}	Iso-C_8H_{18}[a]	N-C_7H_{16}
C_5H_5N	....	....	[b], [c]	....	....	....	....	−15.0	− 22.8
SO_2	....	....	....	....	10.2 (*40*)	....	13.5(*14*)	....	18.5?[d]
CH_3OH	....	....	−10	14.75[e]	32[f]	36.2	45.?[g]	42.5	51.5
$CH_3OC_2H_4OH$	....	< −85[c]	< −25[c]	....	....	....	....	45.5	47.5
$C_6H_5NH_2$	....	....	....	72 (*11*)	59.6 (*29*)[h]	....	31 (*46*)	....	70.0 (*17*)[i]
CH_3CN	....	< −40[c]	13	....	....	....	....	81.0	84.0
$C_2H_4(NH_2)_2$	−5 to −10[k]	36.0	15.8	....	....	....	....	112.0	108.0
ClC_2H_4OH	< −100[c]	< −100[c]	30	....	....	....	....	119.5	118.0
CH_3NO_2	< −43[c]	< −35[c]	41	....	....	....	....	....	......
SnI_4	....	....	....	....	149.4 (*12*)	....	....	195.3 (*12*)	136.8(*12*)
P_4	....	....	....	....	....	− 6.5 (*25*)	....	....	300?? (*25*)

[a] 2,2,4-Trimethylpentane.
[b] Mixture turns brown on standing a few minutes.
[c] C. s. t. not reached owing to separation of solid phase.
[d] Interpolated from *n*-hexane and *n*-octane (*40*).
[e] Less pure *n*-pentane used for Tables III, IX, X, XI gave 13.2° C.
[f] Less pure *n*-hexane used for Tables IV, IX, X, XI gave 30.1° C.
[g] Eastman Kodak cyclohexane; Kahlbaum's cyclohexane gave 20° (probably contained benzene).
[h] Chavanne and Simon (*11*) give 69° C.; Ducker (*13*) gives 65.9°; Chavanne (*10*) gives 68.9°.
[i] Chavanne and Simon give 70° C. also.
[k] Two liquid phases are metastable with respect to solid phase.

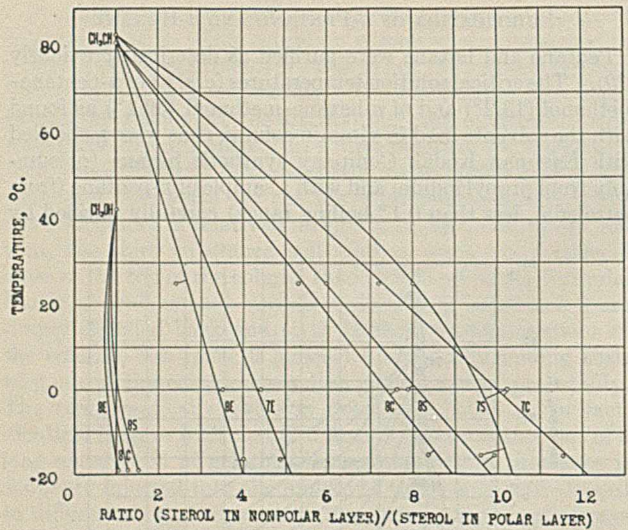

FIGURE 2. DISTRIBUTION RATIOS OF STEROLS BETWEEN NONPOLAR AND POLAR SOLVENTS

NONPOLAR SOLVENTS	POLAR SOLVENTS	STEROLS
7. *n*-Heptane	Methyl cyanide	*E.* Ergosterol
8. Isoöctane(2,2,4-trimethylpentane)	Methyl alcohol	*C.* Cholesterol
		S. Sitosterol

methanol as 32° (present authors), 42.6° (*38*), 42.2° (*46*), 42.6° (*20*), >36.55° (*37*); for cyclohexane and methanol as 45.0° (present authors), 49.1° (*34*), 59.5° (*46*).

The present authors' value for *n*-hexane and methanol has recently been essentially confirmed, both with the authors' methanol and with other methanol carefully dried by chemical means (*21*).

Thus the authors are able to make large quantities of dry methanol by distillation, while others have failed to secure even small quantities by elaborate chemical means. One per cent water in the methanol would raise the c. s. t. about 10° C. (*33*, *37*).

PURIFICATION OF ETHYLENE DIAMINE

Ethylene diamine boils at 116° and forms a maximum boiling mixture with about 20 to 25 per cent by weight of water at 118°. Equal volumes of ethylene diamine and aqueous 50 per cent sodium hydroxide were heated to 100°, giving two layers. A sample from the hot upper layer gave d_{15}^{17} 0.9424. Since the specific gravity of pure ethylene diamine is $d_4^{26.1}$ 0.8919 (*7*), more solid sodium hydroxide is needed. The above experiment, using, however, aqueous 75 per cent sodium hydroxide, gave d_4^{16} 0.908, indicating excellent dehydration. This would be expected from vapor pressures of aqueous sodium hydroxide at 120°—i. e., 50 per cent, 262 mm. and 75 per cent, 2.7 mm. (*28*).

Accordingly, our commercial ethylene diamine (from F. C. Bersworth) was purified by fractionating in the 6.09-meter column, with aqueous 75 per cent (or stronger) sodium hydroxide present in the kettle. It is obviously essential that the kettle vapor composition be richer (in amine) than the maximum boiling mixture with water.

Amine so purified gave a value of $d_4^{20.7}$ 0.896 but was completely miscible with both ethyl ether and benzene at all temperatures above freezing point of the mixtures, contrary to the literature (*30*, *31*), although the correct result has been obtained by Bersworth (*4*). Here, as also with methanol, one sees that many chemists do not know how to dehydrate a water-soluble liquid.

Distribution measurements with ethylene diamine are complicated by a (water-soluble) tarry residue formed by evaporating (anhydrous) solutions containing ethylene diamine to dryness. The solutions are almost colorless until dryness is approached, where the remaining impurity seems to darken and polymerize suddenly. The residue is said to be increased by overheating during the evaporation (*4*). The residue is enormously increased by evaporating along with isopropyl ether (unless the ether has been very freshly distilled), although isopropyl ether alone gives no dry residue. With the pure, freshly distilled amine, about 150 mg. residue are found per liter, but, if the amine stands a few days in contact with air, considerably more residue is found on evaporating.

PURIFICATION OF OTHER SOLVENTS

Carbon disulfide, ethyl ether, and isopropyl ether were purified by fractionating in the 6.09-meter column, but with ethyl ether, sticks of solid sodium hydroxide were placed on top of the beads of the column for dehydrating the ether vapor.

β-Methoxyethanol was purified as with methanol (shown above). Ethylenechlorohydrin was purified by distilling in a 75-cm. glass bead column. However, the chlorohydrin was first dehydrated from the commercial 40 per cent solution in water, using the benzene distillation process with a fractionating column as in the commercial manufacture of absolute ethanol. The first distillate contained only water and benzene, the latter being returned to the column. Considerable hydrolysis of the chlorohydrin took place.

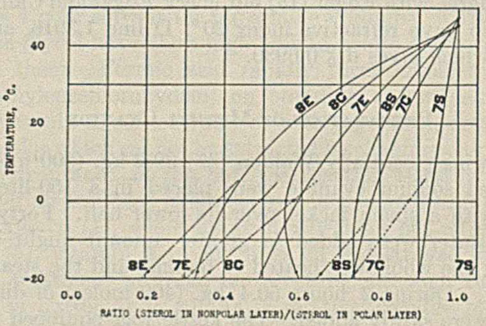

FIGURE 3. DISTRIBUTION RATIOS OF STEROLS BETWEEN NONPOLAR AND POLAR SOLVENTS

NONPOLAR SOLVENTS	POLAR SOLVENTS	STEROLS
7. *n*-Heptane	— Ethylenechlorohydrin	*E.* Ergosterol
8. 2,2,4-Trimethylpentane	--- β-Methoxyethanol	*C.* Cholesterol
		S. Sitosterol

Other solvents for which data are given below were commercial high-grade laboratory chemicals. In some cases, as that of cyclohexane, the purity is probably not sufficient for satisfactory determination of critical solution temperature.

CRITICAL SOLUTION TEMPERATURES OF SOLVENT PAIRS

In Table I the critical solution temperatures were found, except where otherwise noted, from solvents as above prepared. Determinations were made in test tubes, heated, and allowed to cool slowly in air. Where necessary, air pressure was used to prevent boiling. Thermometers were roughly calibrated. These data throw considerable light on relative values of different solvent pairs for fractional distribution—presumably the higher c. s. t., the greater the efficiency of the fractional distribution column.

DISTRIBUTION RATIOS OF STEROLS

Further light is thrown on the problem by measuring actual distribution ratios of sterols, using solvent pairs which might be expected to give fair differences in distribution ratio for different substances. The following sterols were examined: sitosterol (from nonsaponifiable matter of wheat germ oil),

Table II. Distribution Ratios of Sterols

Solvents	C. S. T.	Ergosterol				Cholesterol				Sitosterol			
		t	Nonpolar layer	Polar layer	Ratio	t	Nonpolar layer	Polar layer	Ratio	t	Nonpolar layer	Polar layer	Ratio
	° C.	° C.	Grams/liter			° C.	Grams/liter			° C.	Grams/liter		
CS_2, CH_3OH	36.2	0	9.74	7.16	1.36	0	64.0	38.9	1.64	0	69.8	31.6	2.20
CS_2, CH_3OH		−17	7.82	4.96	1.58	−17	35.4	16.2	2.18	−17	32.9	12.5	2.64
n-C_5H_{12}, CH_3OH	13.2	0	...	...	0.76	0	2.61	2.98	0.87	0	2.39	2.60	0.92
n-C_5H_{12}, CH_3OH		−18	1.39	1.80	0.77	−15	2.83	3.06	0.92	−15	2.76	2.71	1.02
n-C_6H_{14}, CH_3OH	30.1	0	...	...	0.95	0	2.16	1.93	1.12	0	6.31	5.06	1.25
n-C_6H_{14}, CH_3OH		−18	1.54	1.54	1.00	−15	3.37	2.58	1.31	−15	7.10	4.56	1.56
n-C_7H_{16}, CH_3OH	51.5	1	0.89	0.79	1.13	1	1.12	0.80	1.40	1	1.17	0.74	1.58
n-C_7H_{16}, CH_3OH		−16.5	0.96	0.74	1.29	−16.5	1.27	0.66	1.91	−16.5	1.19	0.58	2.04
Iso-C_8H_{18},[a] CH_3OH	42.5	−19	0.87	0.83	1.05	−19	1.48	1.16	1.27	−19	1.32	0.87	1.52
n-C_7H_{16}, CH_3CN	84.0	25	...	...	..	25.0	1.24	0.17	7.2	25.0	1.35	0.17	8.1
n-C_7H_{16}, CH_3CN		0	0.44	0.10	4.4	0	1.97	0.19	10.2	0	1.97	0.19	10.2
n-C_7H_{16}, CH_3CN		−16.5	0.45	0.09	4.9	−15.5	2.04	0.18	11.5	−15.5	1.61	0.17	9.6
Iso-C_8H_{18},[a] CH_3CN	81.0	25.0	0.14	0.06	2.4	25.0	1.10	0.21	5.3	25.0	0.96	0.16	6.0
Iso-C_8H_{18},[a] CH_3CN		0	0.35	0.10	3.5	0	1.96	0.26	7.6	0	1.92	0.24	7.9
Iso-C_8H_{18},[a] CH_3CN		−16.5	0.28	0.07	4.0	−15.5	1.93	0.23	8.4	−15.5	1.91	0.20	9.2
n-C_7H_{16}, C_2H_4ClOH	118.0	0	0.42	0.85	0.49	0	0.99	1.14	0.88	0	...	....	...
n-C_7H_{16}, C_2H_4ClOH		−18.5	0.27	0.85	0.32	−18.5	0.96	1.29	0.74	−19	0.97	0.94	1.03
Iso-C_8H_{18},[a] C_2H_4ClOH	119.5	0	0.30	0.79	0.39	0	0.77	1.33	0.58	0	...	....	...
Iso-C_8H_{18},[a] C_2H_4ClOH		−18.5	0.15	0.72	0.21	−18.5	0.54	1.49	0.36	−19	0.82	1.26	0.65
n-C_7H_{16}, $CH_3OC_2H_4OH$	47.5	0	0.57	0.97	0.59	0	0.84	1.07	0.78	0	1.01	1.09	0.93
n-C_7H_{16}, $CH_3OC_2H_4OH$		−18.5	0.47	0.95	0.50	−18.5	0.92	1.25	0.74	−18.5	1.04	1.16	0.90
Iso-C_8H_{18},[a] $CH_3OC_2H_4OH$	45.5	0	0.45	1.10	0.41	0	0.75	1.34	0.56	0	0.90	1.21	0.74
Iso-C_8H_{18},[a] $CH_3OC_2H_4OH$		−18.5	0.37	1.13	0.33	−18.5	0.74	1.26	0.59	−18.5	0.85	1.15	0.73
Iso-C_8H_{18},[a] $C_2H_4(NH_2)_2$	112.0	35.0	0.48	0.83	0.57	35.0	0.61	0.59	1.05	35.0	0.71	0.59	1.20
Iso-C_8H_{18},[a] $C_2H_4(NH_2)_2$		35.0	1.07	1.64	0.65	35.0	1.71	1.60	1.07	35.0	1.82	1.44	1.27
Iso-$(C_3H_7)_2O$, $C_2H_4(NH_2)_2$	36.0	8.5	2.1	2.9	0.7[b]	8.5	2.5	0.8	3.0[b]	8.5	1.7	0.5	3.5[b]
n-C_7H_{16}, $C_2H_4(OH)_2$		....	...	...	..	....	...	...	...	−18	0.70	0.056	12.5
Iso-C_8H_{18},[a] $C_2H_4(OH)_2$		−18.0	0.064	0.056	1.14	....	...	...	...	....	...	....	...

[a] Iso-C_8H_{18} is 2,2,4-trimethylpentane.
[b] These values are approximate.

commercial ergosterol (both Fleischmann's and Mead Johnson's were used), and c. p. cholesterol (Pfanstiehl). For the lower temperatures a cold room was used.

Distribution ratios were mostly single determinations at a single concentration. Twenty-five cc. of solvent were used for each determination of concentration; this was evaporated to constant weight in a tared beaker in a 110° C. oven.

Possibility of Unstirred Two-Liquid Phase Distribution Column

For countercurrent mutual washing of liquids, a tower filled with Raschig rings is in common commercial use. A test was made with a column 2 meters long and 2 cm. in diameter at −20° C. filled with glass beads 2 mm. in outside diameter and 1 to 2 mm. thick. The lower half of the column contained methanol and the upper half hexane (each liquid being first saturated with the other). The column was inverted, and at the same moment some dissolved ergosterol was injected into the middle. (Ergosterol has a distribution ratio about unity under these conditions.) After the liquids had again come to rest, the ergosterol was found (gravimetrically, using eight distributed samples) to be almost uniformly distributed along the length of the column. One may assume $2n$ theoretical sections and an initial concentration of ergosterol as $c/2$ in each of the two center sections. When material from a center section has fallen to the end of this experimental column, the ergosterol concentration should have fallen to about $c/2^n$, but the experimental value is $c/2n$. Equating $2n$ to 2^n, $n = 2$ or there are four theoretical sections.

Construction of Stirred Two-Liquid-Phase Distribution Column

Granting that stirring is desirable, and that a packed column is unsuitable, the column then requires machine construction, impossible with glass. First results were obtained with a steel ("iron") column of 105 sections; later a nickel one of 210 sections was used.

The nickel column is held inside a nickel tube 4.13 cm. in outside diameter, 8.23 meters long, and 0.148 cm. in wall thickness. Inside the tube are slipped nickel cylindrical blocks 3.82 cm. in diameter and 2.54 cm. thick (Figure 4*A*). The method of mounting and the stirring shaft (0.794 cm. diameter) are shown in Figure 4 (*B* and *C*). The shaft turns 400 revolutions per minute. The diameter of the bearing in the cylindrical blocks should be 0.03 cm. greater than the shaft diameter. Each cylindrical block has a 1.27-cm. hole to permit the passing of liquids and to provide a quiet space for settling the emulsion. Quiescence is aided by nickel gauze (Figure 4*A*) welded to the ends of the hole; the gauze is 10 mesh per cm., the wire diameter is 0.0457 cm. Without gauze, cylindrical blocks twice as thick are necessary. Numerous tests were made on the design. One test was to set up a column of three blocks (i. e., with two open sections) in a glass tube, and to fill the upper open section with aqueous 0.1 *N* acid with phenolphthalein added and the lower open section with aqueous 0.2 *N* base. The stirrer was started, and the time measured for the upper section to flash to a pink color. If more than one hole was made for solvents in the cylindrical block, the pink color flashed almost as soon as the stirrer started. With a single hole, provided its length exceeded a certain minimum

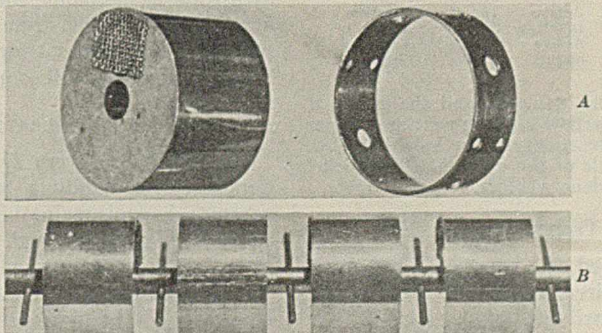

Figure 4. Details of Column Construction

A. Polished nickel blocks and rings
B. Arrangement of segments on stirring shaft with rings removed to show method of stirring
C. Section of inside of column completely assembled; all parts are polished pure nickel

TABLE III. IRON COLUMN TESTS WITH FAT-SOLUBLE VITAMINS, USING *n*-PENTANE AND METHANOL

Run	Duration	C_5H_{12} Rate	CH_3OH Rate	Ratio	C_5H_{12} Fraction	CH_3OH Fraction	Middle Fraction
	Hours	*Cc./min.*	*Cc./min.*				
A. VITAMIN A AT 0° C.							
4	12	27.3	9.5	0.348	Active	Inactive	Not tested
6	24	23.1	9.5	0.411	Active	Active	Active
8	24	22.1	9.5	0.430	Active	Active	Active
7	24	21.2	9.5	0.448	Active	Active	Active
5	12	19.2	9.5	0.495	Inactive	Slight	Active
9[a]	24	21.2	10.5	0.496	Inactive	Inactive	Active
1	12	19.2	13.5	0.703	Inactive	Active	Not tested
2	12	13.2	9.5	0.719	Inactive	Active	Not tested
3	12	21.2	19.4	0.915	Inactive	Active	Not tested
10[b]	24	19.2	9.5	0.495	Active	Inactive	Inactive
11[c]	20	19.8	7.8	0.394	Inactive	Active	Active
B. VITAMIN E AT 0° C.							
3	12	27.3	9.5	0.348	Active	Inactive	Not tested
4	12	19.2	9.5	0.495	Active	Inactive	Inactive
7	24	17.7	10.5	0.593	Active	Inactive	Inactive
5	22	19.2	13.5	0.703	Active	Inactive	Inactive
6	24	14.7	12.6	0.857	Active	Slight	Inactive
11	2 × 10[e]	15.4	13.5	0.877	Slight	Inactive	Active
2	12	21.2	19.4	0.915	Inactive	Active	Not tested
8	24	14.7	13.5	0.918	Slight	Active	Active
9[d]	24	14.7	15.1	1.027	Inactive	Active	Active
10	24	14.7	15.1	1.027	Inactive	Active	Active
1	12	13.2	16.5	1.250	Inactive	Active	Not tested

[a] With Marcus nonsaponifiable matter of cod liver oil.
[b] With unsaponified cod liver oil.
[c] Same as runs 1 to 8 except that the column was kept at −20° C.
[d] Run 9 with Marcus nonsaponifiable matter of wheat germ oil.
[e] Run 11 was actually two separate runs of 10 hours each; the middle fraction of the first run was used as the charge for the second run.

TABLE IV. NICKEL COLUMN TESTS WITH FAT-SOLUBLE VITAMINS, USING *n*-HEXANE AND METHANOL

Run	Duration	C_6H_{14} Rate	CH_3OH Rate	Ratio	C_6H_{14} Fraction	CH_3OH Fraction	Middle Fraction
	Hours	*Cc./min.*	*Cc./min.*				
A. VITAMIN A AT −20° C.							
3	34	18.3	5.0	0.273	Active	Inactive	Inactive
7	72	18.0	5.3	0.295	Active	Inactive	Slight
9	48	19.2	5.8	0.302	Active	Active	Active
6	72	19.8	6.1	0.309	Active	Active	Slight
5	72	18.4	5.8	0.316	Inactive	Active	Inactive
8	72	18.1	5.9	0.326	Slight	Active	Slight
2	30	18.5	6.2	0.335	Inactive	Active	Slight
4	67	16.9	5.7	0.338	Inactive	Active	Inactive
1	16	14.0	10.0	0.714	Inactive	Active	Inactive
B. VITAMIN D AT −20° C.							
1	21	18.0	13.7	0.763	Active	Inactive	Inactive
2	25	14.8	15.8	1.068	Active	Slight	Active
8	72	10.3	11.9	1.160	Active	Inactive	Inactive
7	72	11.2	13.7	1.223	Inactive	Active	Inactive
4	24	19.5	24.5	1.257	Inactive	Inactive	Active
6	72	10.8	13.8	1.274	Inactive	Active	Active
5	34	9.2	12.0	1.304	Inactive	Active	Active
3	24	11.2	16.3	1.455	Inactive	Active	Active
C. VITAMIN E AT −20° C.							
1	24	14.0	15.7	1.121	Active	Inactive	Inactive
2	24	11.9	15.8	1.333	Active	Slight	Active
4	72	9.8	13.7	1.398	Active	Inactive	Inactive
3	30	9.6	14.1	1.468	Inactive	Slight	Active
6	72	8.6	12.7	1.475	Active	Active	Active
5	72	9.8	14.8	1.510	Slight	Active	Slight

TABLE V. NICKEL COLUMN TESTS WITH FAT-SOLUBLE VITAMINS, USING 2,2,4-TRIMETHYLPENTANE AND METHYL CYANIDE

Run	Duration	C_8H_{18} Rate	CH_3CN Rate	Ratio	C_8H_{18} Fraction	CH_3CN Fraction	Middle Fraction
	Hours	*Cc./min.*	*Cc./min.*				
A. VITAMIN A AT 0° C.							
1	49	19.7	3.7	0.188	Active	Active	Active
2	37	18.8	4.3	0.229	Active	Active	Active
B. VITAMIN D AT 0° C.							
2	48	3.1	12.4	4.0	Active	Active	Active
1	49	3.1	16.4	5.3	Inactive	Active	Slight
C. VITAMIN E AT 0° C.							
1	22	2.3	13.1	5.7	Inactive	Inactive	Active
2	66	2.2	13.0	5.9	Inactive	Active	Active

TABLE VI. NICKEL COLUMN TESTS WITH FAT-SOLUBLE VITAMINS, USING 2,2,4-TRIMETHYLPENTANE AND METHANOL AT 0° C.

Run	Duration	C_8H_{18} Rate	CH_3OH Rate	Ratio	C_8H_{18} Fraction	CH_3OH Fraction	Middle Fraction
	Hours	*Cc./min.*	*Cc./min.*				
A. VITAMIN A AT 0° C.							
1	49	15.1	4.2	0.278	Active	Inactive	Active
3	50	12.3	3.7	0.303	Active	Active	Active
2	49	12.0	3.95	0.329	Inactive	Active	Active
B. VITAMIN D AT 0° C.							
2	51	9.8	8.8	0.902	Active	Slight	Active
1	51	6.7	7.5	1.120	Inactive	Active	Active
C. VITAMIN E AT 0° C.							
1	50	8.3	8.9	1.075	Active	Active	Slight

TABLE VII. NICKEL COLUMN RUNS WITH FAT-SOLUBLE VITAMINS, USING 2,2,4-TRIMETHYLPENTANE AND METHANOL AT −20° C.

Run	Duration	C_8H_{18} Rate	CH_3OH Rate	Ratio	C_8H_{18} Fraction	CH_3OH Fraction	Middle Fraction
	Hours	*Cc./min.*	*Cc./min.*				
A. VITAMIN A (BIOSTERIN FORM) AT −20° C.							
2	43	7.7	2.25	0.293	Inactive	Slight	Active
1	26	9.6	2.66	0.277	Inactive	Inactive	Active
3	42	8.25	2.26	0.274	Inactive	Active	Active
4	41	7.8	1.91	0.245	Slight	Slight	Active
6[a]	40	7.85	1.80	0.229	Slight	Slight	Active
5	48	7.9	1.79	0.226	Slight	Slight	Active
B. VITAMIN A (OTHER THAN BIOSTERIN FORM) AT −20° C.							
1[b]	42	3.15	6.3	2.0	Active	Inactive	Inactive
2[b]	39	1.73	9.7	5.6	Active	Inactive	Inactive
3[c]	24	2.03	12.0	5.9	Active	Inactive	Inactive
4[d]	30	1.79	9.7	5.4	Active	Inactive	Inactive

[a] With nonsaponifiable matter of halibut liver oil.
[b] With unsaponified cod liver oil.
[c] With unsaponified carrot oil.
[d] With nonsaponifiable matter of carrot oil.

value (this value depending on the diameter, and the gauze, if any), the maximum solvent counterflow in cubic centimeters per minute varied approximately as the square of the hole diameter. Figures 5 to 7 show further details of the column. The nickel side tubes are attached by "acetylene welding."

MAINTENANCE OF TEMPERATURES

A 350-liter insulated can served as a reservoir for thermostatic liquid (water or brine); circulation around the column (Figure 5) was supplied by a centrifugal pump. For −20° C., the returning liquid flowed first into a large wire basket containing rock salt (sodium chloride), then through the crushed ice. The system was insulated with commercial cork covering, and the temperature could be kept very constant.

SOURCES OF VITAMINS AND METHODS OF TESTING (WITH RATS)

Vitamin A sources are briefly discussed in the section on "Three Forms of Vitamin A;" vitamin A values of Tables III to VII refer, except as otherwise noted, to vitamin A as found in the nonsaponifiable matter of cod liver oil, while vitamin E was obtained from nonsaponifiable matter of wheat germ oil. Except where otherwise noted in the tables, saponification was by the "hot" process—refluxing with potassium hydroxide in methanol, followed by ether extraction. Vitamin D was obtained from irradiated ergosterol. Details of preparing the material for charging into the column and of the tests with rats will soon be published elsewhere.

OPERATION OF COLUMN

The solvent recovery system (Figure 6) exists actually in duplicate, for handling both solvents. The constant air pressure shown is maintained by a slow stream of compressed air bubbling out through water at a constant depth (not shown). Slight adjustments in air pressure may be made if the level in the solvent standpipe (right side of Figure 6) changes. Use of hydrogen for this would be preferable but expensive; moreover, the Woulff bottle is only a surge chamber. Both Woulff bottles are kept dry by the usual calcium chloride air tubes. Rate of flow of solvent is measured by opening the middle stopcock at the left side of Figure 6, using a calibrated graduate and stop watch.

In starting an actual run, a mixture of roughly 2 liters of each of the two solvents is sucked into the column through the lower drain (Figure 5); the stirrer is started; and steam, air pressure, and cooling water (Figure 6) are turned on. Thermostatic liquid is pumped around the column (Figure 5) and the capillaries for controlling solvent flow (Figure 6). Ordinarily the column must run for several hours to become stabilized, and, if attempts are made to run the solvents through too fast, both solvents will come out at the same end of the column (although there is an unstirred space 10 cm. long at each end). This condition requires that solvent flow be stopped at once (by releasing the constant air pressure of Figure 6), and that the column be run idle for at least 10 minutes, and even an hour or more in extreme cases. In runs with methyl cyanide this condition was so bad that this solvent had to be abandoned. Sometimes as much as 48 hours of running were necessary to stabilize operation, particularly if excessive solvent rates were being tested. Air bubbles sometimes may have caused trouble in the column, as running the stirrer very fast for a moment would occasionally free the column when it appeared partially blocked. The reflux condenser of Figure 6 serves to supply gas-free solvent, so that any air bubbles in the column tend to diminish rather than increase in size as the column is operated. When operation has become satisfactory and stable, the mixture to be fractionated is injected into the middle of the column through the center tap of Figure 5. The run is continued for the desired time; times given in Tables III to VII are the number of hours run after injecting the material to be fractionated. From time to time, material carried out of the column by one or the other solvent is collected by opening the upper of the three stopcocks at the left-hand side of Figure 6. To facilitate this, a quantity of solvent is used (being added through a cock not shown in Figure 6) to fill the evaporator and dissolve any solid material present; this solvent is then quickly drained out, and the operation of the column does not have to be stopped during the process. The same solvent may be used for a later washing out of the evaporator, or a new quantity may be used. At the end of the run, these quantities of solvent are combined, thus giving two fractions, one carried out of the column by each of the two circulating solvents. At the end of the run the entire contents of the column (Figure 5) is also collected as the middle fraction. Each of the three fractions is evaporated to dryness in vacuum and tested for biological activity (Tables III to VII). Where proper solvent rates have been used, the purified vitamin is found principally in the middle fraction, and hence heating that fraction is avoided. Solvents recovered from these final vacuum evaporations are carefully purified and rectified in the 6.09-meter column, before using again.

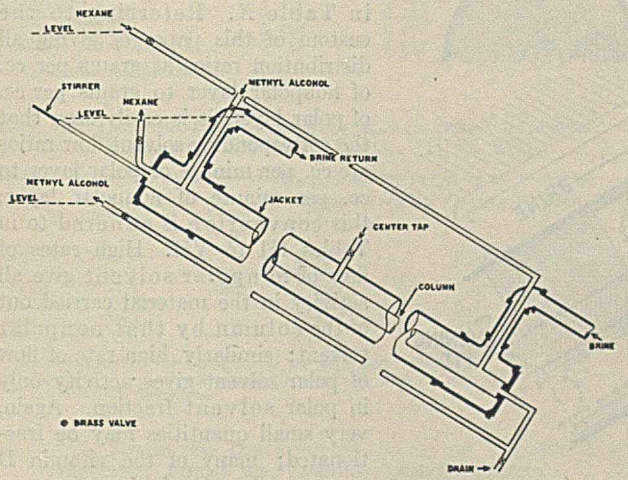

FIGURE 5. DIAGRAMMATIC DRAWING OF FRACTIONATING COLUMN MOUNTING, SHOWING LIQUID LEVELS IN THE VARIOUS TUBES

Construction of the column itself is not shown here.

An idea of the behavior of a pure substance in the column is obtainable from two runs with presumably pure cholesterol (at −20° C.), as shown in Table VIII.

TABLE VIII. WEIGHTS OF CHOLESTEROL FRACTIONS EVERY 24 HOURS

TIME	RUN 1, RATIO 1.412		RUN 2, RATIO 1.502	
Fraction:	C_6H_{14}	CH_3OH	C_6H_{14}	CH_3OH
Rate; cc./min:	10.33	14.60	8.83	13.25
Hours	*Grams*	*Grams*	*Grams*	*Grams*
0–24	0.331	0.078	0.250	0.159
24–48	0.483	0.094	0.336	0.202
48–72	...	...	0.190	0.172
72–96	...	...	0.122	0.121
96–120	...	...	0.085	0.073
Total fractions	0.986		1.710	
Left in column	1.098		0.457	
Total recovery	2.084		2.167	

Thus it appears that in run 2 all three fractions would be listed as active if there were a biological test for cholesterol analogous to tests used for the vitamins in Tables III to VII. From run 1, however, the methanol fraction would be found inactive or more possibly slight. Thus it is apparent how data of Tables III to VII may be used to estimate actual distribution ratios of the vitamins (Table X). From Table VIII it appears that two substances of distribution ratios 1.412 and 1.502, respectively, would be difficult to separate completely from each other in the column used here, but with distribution ratios differing by 20 per cent or more it is probable that very good separation would be obtainable. Naturally only one of the two substances could be recovered as the middle fraction in a single run. The capillary in Figure 6 should preferably be operated at a temperature between that of the column (Figure 5) and of the room, if one wishes to avoid separation of two liquid phases, or of gas bubbles, in the capillary, thus interfering with constant flow. Numerous other tricky precautions are necessary to secure satisfactory operation, but space limitations prevent further digressions.

Since choice of solvent may increase the possible separation, numerous solvent pairs have been investigated critically in this laboratory; data not directly applicable to fat-soluble vitamins are considered elsewhere (*2*, *24*, *43*). The column used here is analogous to Tswett's chromatoscope (*35*) in which the remarkable separations obtained are due to use of the column idea, but where a solid-absorbing substance replaces the polar solvent. The chromatoscope uses a saturated hydrocarbon (possibly containing an additional few per cent of a polar solvent) for the nonpolar solvent, just as does the distribution column described here. The present writers wish to emphasize the importance of the column principle, rather than any special devices, for performing difficult fractionations.

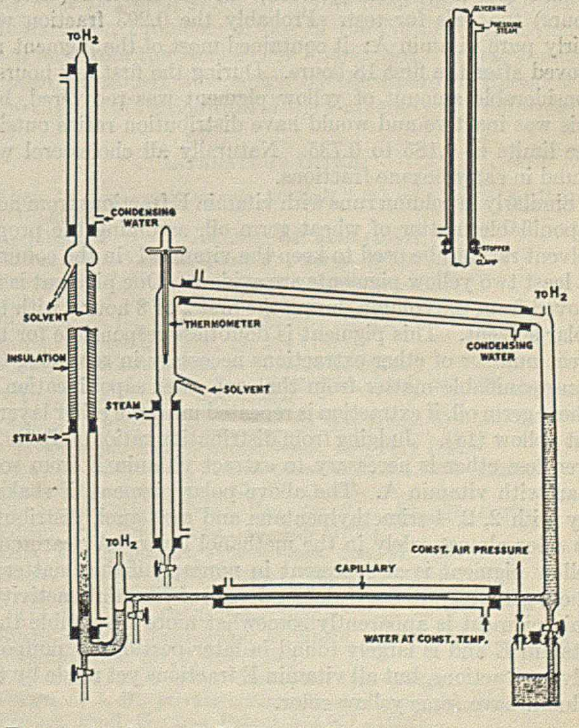

FIGURE 6. SOLVENT FEED AND RECOVERY SYSTEM SHOWING METHOD OF CONTROLLING SOLVENT FLOW

Inset in upper right-hand corner shows pressure steam evaporator for evaporating higher boiling solvents.

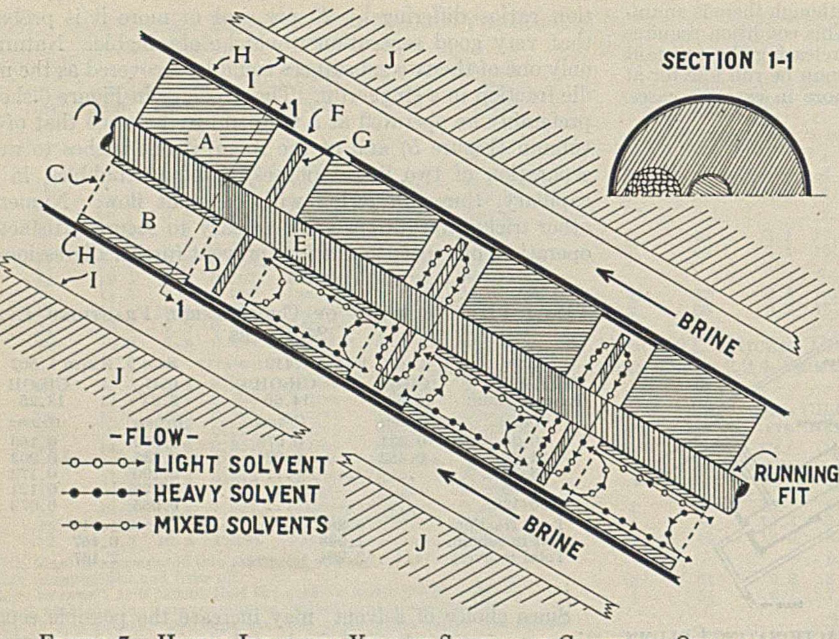

FIGURE 7. HIGHLY IDEALISTIC VIEW OF SECTION OF COLUMN IN OPERATION

A. Nickel block
B. Hole in *A* for separating solvents
C. Nickel gauze
D. Stirring chamber
E. Stirring shaft
F. Nickel ring for spacing blocks
G. Stirring rod
H. Nickel shell of column
I. Brine pipe
J. Cork insulation (actually thicker than shown)

Further illustrating the action of the fractionating column is the vitamin A experiment using a ratio 0.326—i. e., too much methanol was run through the column (Table VIA, run 8). Only the methanol fraction (and presumably only the last half of this) had any great biological activity. Colorimetric distribution ratios (−20° C.) of the fractions were: methanol (18 to 36 hours), 0.185; methanol (36 to 72 hours), 0.293; hexane (24 to 72 hours), 0.735; middle fraction (after 72 hours) too pale for test. Probably the 0.293 fraction was fairly pure vitamin A; it contained most of the pigment removed after the first 18 hours. During the first few hours a considerable amount of yellow pigment was recovered, but this was inactive and would have distribution ratios outside the limits of 0.185 to 0.735. Naturally all cholesterol was found in early hexane fractions.

Similarly in column runs with vitamin E fractions from nonsaponifiable matter of wheat germ oil, assuming the proper solvent ratio to be used to keep the vitamin E in the column, at least two yellow pigments are evident. One pigment is removed from the column during the first 2 or 3 hours, with the polar solvent. This pigment is doubtless responsible for the great number of ether extractions necessary in removing the nonsaponifiable matter from the soap after saponification of wheat germ oil, if extraction is repeated until the ether layer is not yellow (*18*). Judging from distribution ratios of Table X, even less ether is necessary to extract vitamin E from soap than with vitamin A. The above polar pigment, if shaken, say with 2, 2, 4-trimethylpentane and methanol, distributes its color almost solely in the methanol layer. A "carotene" yellow pigment is also present in nonsaponifiable matter of wheat germ oil (although almost devoid of vitamin A activity). This pigment is apparently somewhat more fat-soluble than vitamin E and is largely found in later portions of nonpolar solvent fractions, but all vitamin E fractions yet made by the column have some yellow color.

Fractionation of Vitamin Concentrates

Tables III to VII show that for a certain definite ratio of rates of flow of solvents, which ratio is also the distribution ratio of the vitamin in question, there is a tendency for the vitamin to be carried out of both ends of the column in equal amounts. These estimated ratios are given in Table X. Referring to the custom of this paper of giving all distribution ratios as grams per cc. of nonpolar layer to grams per cc. of polar layer, it is easily seen that the corresponding solvent flow ratios are cc. per minute of polar layer to cc. per minute of nonpolar layer; this convention is adhered to in Tables III to VII. High rates of flow of nonpolar solvent give all activity in the material carried out of the column by that nonpolar solvent; similarly, high rate of flow of polar solvent gives activity only in polar solvent fraction. Again, very small quantities may be fractionated; many of the vitamin D runs used as little as 10 mg. or even 1 mg. of irradiated ergosterol for the entire fractionation. In some runs, several grams have been fractionated at once, but in that case the bulk of sterols should have been first removed by crystallization; otherwise, especially at −20° C., they may precipitate in the column.

Tables II and X show that vitamin E and cholesterol have nearly the same distribution ratio. Particularly, actual column runs with pure cholesterol agree closely with vitamin E values. Vitamin D appeared in some of the runs to have slightly more tendency than ergosterol to appear in the nonpolar solvent.

Tabulation of Distribution Ratios

Runs of Tables III to VII are numbered in chronological order, run 1 being carried out in each case before any of the others in the same part of the table, etc. Slight discrepancies will be noted owing to fluctuations during operation of the column, but in general, later runs, particularly those in close proximity to the true distribution ratio, are quite accurate. Moreover the runs using pentane and hexane are, in general, less reliable than the ones using 2, 2, 4-trimethylpentane. In the nickel column (especially at −20° C.) the rates of flow are (and must be) considerably less than in the iron column. The gauzes used on the nickel blocks (as shown above) are doubtless responsible. The iron blocks were like the nickel ones, but twice as thick and hence required no gauzes. From Tables III to VII are calculated the actual distribution ratios of the vitamins, as given in Table X.

Possibility of Improved Fractionation

Increased speed of solvents, besides reducing time length of runs, should also increase the efficiency above the 55 per cent found with *n*-hexane and methanol at −20° C. Thus, other things being equal, the solvents should differ considerably in density.

Three Forms of Vitamin A

Tables III to VII show that, where 2, 2, 4-trimethylpentane at −20° C. is used, the same definite distribution ratio is obtained for vitamin A as is found in the nonsaponifiable matter of either cod liver oil or halibut liver oil; this form of the vitamin has been called "biosterin" (*44*).

TABLE IX. APPROXIMATE SPECIFIC GRAVITIES OF PHASES COEXISTING AT 0° C., d^{0}_{15}

LIQUID PAIR	NONPOLAR LAYER	POLAR LAYER	DIFFERENCE
n-C_5H_{12}, CH_3OH	0.646	0.714	0.068
n-C_6H_{14}, CH_3OH	0.691	0.756	0.065
CS_2, CH_3OH	1.249	0.932	0.317
Iso-C_8H_{18},[a] CH_3OH	0.711	0.782	0.071
Iso-C_8H_{18},[a] CH_3CN	0.694	0.777	0.083
Iso-C_8H_{18},[a] $CH_3OC_2H_4OH$	0.715	0.947	0.232

[a] 2,2,4-Trimethylpentane.

TABLE X. DISTRIBUTION RATIOS OF FAT-SOLUBLE VITAMINS, FROM RUNS WITH COLUMN (TABLES III TO VII)

Ratio of (grams per cc. nonpolar layer) to (grams per cc. of polar layer)]

SOLVENTS	TEMP. ° C.	VITAMIN A[a]	VITAMIN D	VITAMIN E	VITAMIN F[b]
n-C_5H_{12}, CH_3OH	0	0.43	..	0.89	..
n-C_5H_{12}, CH_3OH	−20	<0.38	..	..	..
n-C_6H_{14}, CH_3OH	−20	0.305	1.20	1.47	..
Iso-C_8H_{18},[c] CH_3CN	−20	0.21	4.0	5.7	..
Iso-C_8H_{18},[c] CH_3OH	0	0.305	0.98	1.08	0.49
Iso-C_8H_{18},[c] CH_3OH	−20	0.235	..	..	..

[a] Biosterin form; for other forms see text and Table VII.
[b] Vitamin F—i. e., linoleic acid, from Smith and Norton (*43*).
[c] 2,2,4-Trimethylpentane.

TABLE XI. ESTIMATED DISTRIBUTION RATIO OF VITAMIN A (BIOSTERIN FORM) AT VARIOUS TEMPERATURES

[Ratio of (grams per cc. of nonpolar layer) to (grams per cc. of polar layer)]

SOLVENTS	+20° C.	0° C.	−20° C.
n-C_5H_{12}, CH_3OH	..	0.43[a]	<0.38[a]
n-C_6H_{14}, CH_3OH	..	....	0.305[a]
Iso-C_8H_{18},[b] CH_3CN	0.24	0.21[a]	....
Iso-C_8H_{18},[b] CH_3OH	..	0.305[a]	0.235[a]
Iso-C_8H_{18},[b] $CH_3OC_2H_4OH$	..	0.09	....
n-C_7H_{16}, CH_3CN	0.35	0.32	0.30
n-C_7H_{16}, CH_3OH	..	0.34	0.29
n-C_7H_{16}, ClC_2H_4OH	0.18	....	0.19

[a] Values copied from Table X; other values are colorimetric (see text) and much less reliable.
[b] 2,2,4-Trimethylpentane.

Ratios of an entirely different order (in each case greater than 6.0), using 2, 2, 4-trimethylpentane and methanol at −20° C., are found for the vitamin A of original cod liver oil, of carrot oil, or of the nonsaponifiable matter of carrot oil (Table IIIA, run 10; more especially Table VIIB). Owing to the great dilution in the column, impurities in the vitamin concentrates cannot make any great differences in these results. Thus, in fractionating original cod liver oil, most of the glyceryl esters were found in the 2, 2, 4-trimethylpentane fraction along with the vitamin, although the methanol fraction consisted of a small amount of crystals, presumably cholesterol. Thus it has been absolutely proved that the vitamin activity of carotene or of carrot oil cannot be even partly due to contamination by biosterin. That vitamin A appears in cod liver oil in a form different from that in its nonsaponifiable matter has been suggested previously, based on evidence similar to but much less certain than the above (*3*). "Cold saponification" by the method of Marcus (*32*) is seen from Table IIIA, run 9, to be sufficient to convert vitamin A of cod liver oil into biosterin; run 9 is particularly to be compared with runs 5 and 10 of Table IIIA.

COLORIMETRIC DETERMINATIONS OF DISTRIBUTION RATIO OF VITAMIN A (BIOSTERIN FORM)

The yellow color of active vitamin A fractions from the column makes possible a colorimetric measurement of distribution ratio in numerous solvent pairs. If one layer is evaporated to dryness (in vacuum) and redissolved in the same volume of the other coexisting solvent mixture (thereby eliminating any effect of solvent on relative color intensity), the results are ordinarily changed less than the experimental error; but ethylenechlorohydrin intensifies the yellow color. Values are given in Table XI but, unlike values of Table X, are necessarily based on uncertain assumptions.

DEGREE OF CONCENTRATION OF VITAMINS BY COLUMN

No reliable estimate can be given of the purity of vitamins as obtained from the middle fraction, but in the case of vitamin A or vitamin E (as contained in the nonsaponifiable matter of cod liver oil and wheat germ oil, respectively, minus their cholesterol and sitosterol, respectively) a concentration of five to ten times is readily obtainable, as shown by tests with rats. This indicates that the writers' vitamin A is at least the equal of the "nearly pure" product recently obtained elsewhere (*23*). Although β-methoxyethanol has not yet been used with vitamin E, cures of sterility have already been obtained here with a single 1-mg. dose of middle fraction; this can perhaps be readily exceeded, as at that time considerable activity had been lost during the saponification, and other conditions were not optimal. While carefully irradiated ergosterol is said to contain about 10 per cent of vitamin D, it appeared that the runs with hexane and methanol were inadequate to give more than a two- or threefold concentration of the vitamin. Whether use of 2, 2, 4-trimethylpentane and β-methoxyethanol at −20° C. would completely purify vitamin D has not been determined, but, since the contaminating substances presumably have the same empirical formula as the vitamin, it is possible that a longer column would be needed even with more favorable solvent and temperature conditions. Existence of definite distribution ratios for each vitamin is strongly indicative that each is a single substance, respectively. Thus if the biological activity of vitamin A required simultaneous presence of two different substances, each having a somewhat different distribution ratio, it would be impossible to obtain activity in the middle fraction, no matter what solvent flow ratio was used. However, as above stated, vitamin A, at least, occurs differently in certain different raw materials, although probably in one form only in any one material investigated.

ACKNOWLEDGMENT

This work has been aided by grants from the Committee for Research on Problems of Sex of the National Research Council and from the Rockefeller Foundation. These funds have been generously augmented by the Board of Research and the College of Agriculture of the University of California.

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RECEIVED October 27, 1933.

Phosphate Fertilizers by Calcination Process

Action of Silica and Water Vapor on Phosphate Rock

D. S. REYNOLDS, K. D. JACOB, AND L. F. RADER, JR., Bureau of Chemistry and Soils, Washington, D. C.

A study has been made of the action of silica and water vapor on phosphate rock at high temperatures in relation to the volatilization of the fluorine content of the rock and the conversion of the insoluble phosphate into forms readily available as plant food. Water vapor and silica are both important reagents in effecting the decomposition of phosphate rock at high temperatures; water vapor is more important than silica, and a combination of the two is much more effective than either alone. In the presence of sufficient silica and water vapor, heating the 40-mesh rock for 30 to 60 minutes at 1400° C. results in the volatilization of 95 to 100 per cent of the fluorine and the conversion of 85 to 95 per cent of the phosphorus into the citrate-soluble condition; a sintered or semifused product is obtained.

No increase in the citrate solubility of the phosphorus is obtained until all the fluorine in excess of that combined as calcium fluorphosphate, $Ca_{10}F_2(PO_4)_6$, and all that equivalent to one atom of fluorine in the fluorphosphate itself is volatilized. From that point, the percentage citrate solubility of the phosphorus is more or less directly proportional to the percentage volatilization of the second atom of fluorine in the fluorphosphate.

IN SEVERAL publications from this bureau (*13*, *18*, *20*, *28*, *38*), it has been shown (1) that fluorine is an important constituent of all types of phosphate rock produced in the United States and most foreign countries; (2) that for a given type of domestic phosphate rock the fluorine content is usually roughly proportional to the phosphorus content; and (3) that the principal phosphatic constituent of phosphate rock is calcium fluorphosphate, identical in crystal structure with fluorapatite, $Ca_{10}F_2(PO_4)_6$. Data have also been obtained which indicate that the presence of this calcium fluorphosphate is largely responsible for the comparatively low citrate solubility (*17*, *19*) and fertilizer efficiency (*42*) of the phosphorus in raw phosphate rock, and for the sluggishness of the reaction between phosphoric acid and phosphate rock (*29*). It may be concluded, therefore, that the conversion of the phosphorus of phosphate rock into a condition that will permit its ready utilization by plants is largely dependent upon the extent to which the calcium fluorphosphate is decomposed by the processing treatment.

It is reasonable to suppose that any method which would effect complete or nearly complete removal of the fluorine from phosphate rock might also increase the availability of the phosphorus, provided that substantial quantities of calcium meta- and pyrophosphates, which have comparatively low plant-food values (*3*), are not formed in the process. Also, the treatment of phosphate rock by such methods should make it possible to effect a more complete recovery and utilization of the fluorine than is possible in the manufacture of superphosphates (*20*). Because of the deleterious effect of fluorine on the health of animals (*30*, *34*), its presence in phosphate rock has prevented the general use of this cheap source of calcium and phosphorus in mineral mixtures for livestock feeding; removal of the fluorine from phosphate rock is of interest in this connection (*6*).

TREATMENT OF PHOSPHATE ROCK BY CALCINATION PROCESSES

Various processes have been proposed for the manufacture of available phosphates by so-called calcination methods (*1*, *8*, *9*, *10*, *12*, *32*, *41*)[1] which usually involve the heating of phosphate rock with alkali salts (usually the sulfates or carbonates of sodium and potassium), with or without added silica and carbonaceous material, in a nonreducing atmosphere up to about 1500° C. With the exception of the work of Guernsey and Yee (*12*) and Kuusk (*24*), very little information is available on the factors involved in the production of available phosphates by calcination processes. Inasmuch as the products obtained by such processes have properties similar in many respects to those of basic slag, which is an important phosphate fertilizer material in Europe, it seemed desirable to make a thorough laboratory investigation of the behavior of phosphate rock towards various reagents at high temperatures, in order to determine the factors influencing the reaction and to determine, in particular, what relation exists between the amount of fluorine removed from the rock

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[1] U. S. Patents through 1922 are listed by Guernsey and Yee (*12*).

Table I. Chemical Composition of Natural Phosphates

(Results on air-dry basis except as indicated)

Type or Source of Phosphate	P_2O_5	CaO	F[a]	SiO_2[b]	Al_2O_3	Fe_2O_3[c]	CO_2	SO_3[d]	H_2O A 105° C.
	%	%	%	%	%	%	%	%	%
Florida land pebble[e]	31.62	47.69	3.87	8.98	1.00	1.63	3.66	1.37	..
Florida hard rock	35.81	50.82	3.87	4.98	0.52	0.69	2.18	0.56	0.50
Tennessee brown rock[e]	34.06	48.08	3.75	7.56	1.80	2.27	1.73	0.82	..
Tennessee blue rock	30.83	45.17	3.85	9.09	1.21	3.40	2.58	6.61[f]	0.46
Tennessee white rock	35.63	50.55	3.83	1.90	1.44	0.92	3.04	0.35	0.48
Wyoming	30.08	46.06	3.48	7.16	1.19	0.87	4.12	3.08[g]	0.35
Morocco	34.77	52.50	4.20	0.85	0.45	0.12	4.08	1.45	0.95
Fluorapatite	37.40	48.63	2.85[h]	3.07	..	..	..	..	0.08

[a] Determined by the Willard and Winter method (*51*).
[b] Total Si.
[c] Total Fe.
[d] Total S.
[e] Ignited at 400–500° C.
[f] Contained 5.19 per cent SO_3 as acid-insoluble sulfide.
[g] Contained 1.30 per cent SO_3 as acid-insoluble sulfide.
[h] Contained less than 0.2 per cent Cl.

and the availability (solubility in neutral ammonium citrate solution) of the phosphate. As a part of this investigation a study was made of the action of silica and water vapor on phosphate rock at high temperatures and the results are presented in this paper.

Previous Investigations on High-Temperature Volatilization of Fluorine from Phosphate Rock

A few data on the volatilization of fluorine from phosphate rock at elevated temperatures have been reported by Reynolds, Ross, and Jacob (*39*), Rozanov (*44*, *45*, *46*), Memminger, Waggaman, and Whitney (*31*), Britzke and Pestov (*5*) and Reynolds and Jacob (*37*). However, these data do not relate directly to the preparation of available phosphates by calcination methods.

As indicated in several United States and foreign patents (*22*, *33*, *40*, *43*), the effect of removal of the fluorine on the availability of phosphates produced by various processes of calcining phosphate rock with alkali salts has been recognized in a general way for several years. Most of these patents indicate the importance of silica, and some of them the importance of water vapor, in the reaction. Kuusk (*24*, *25*) made an extensive study of the action of silica on phosphate rock at high temperatures but failed to stress the effect of water vapor and did not control this important factor; he showed that, to a certain extent, a relation existed between the amount of fluorine removed from the rock and the solubility of the phosphorus in citric acid solution.

According to Caldwell (*6*), substantially complete removal of the fluorine is obtained by heating presintered phosphate rock at 1400° to 1450° C. in the presence of an excess of oxygen. No mention is made, however, of any effect of silica and water vapor on the reaction.

Materials Used

The phosphate rocks used in this study were representative of the majority of the domestic commercial types of this material produced at present. For comparison, a few experiments were also made with Tennessee white-rock phosphate, commercial phosphate rock from Morocco, and fluorapatite from Quebec Province, Canada. Except as stated otherwise, the Florida land-pebble and Tennessee brown-rock phosphates used in most of the experiments were ground to pass a 200-mesh sieve and were ignited at 400° to 500° C. to remove the greater portion of the water. The other phosphates were ground to pass a 100-mesh sieve and were used without preliminary ignition. Partial chemical analyses of the samples are given in Table I.

The silica used in most of the experiments was specially purified quartz flour which completely passed a 200-mesh sieve. The coarser sizes of silica used in the other experiments (Table IX) were prepared in the laboratory from pure quartz crystals.

Apparatus and Experimental Method

Figure 1 is a diagrammatic sketch of the electric furnace arrangement used in the investigation.

The platinum-wound furnace, *E*, which was similar to the one described by Madorsky (*27*), had an inner heating unit, *A*, composed of No. 26 B and S gage platinum wire wound over a distance of 29.0 cm. on a spiral-grooved alundum tube; the outer heating unit, *B*, consisted of No. 18 B and S gage nichrome wire (No. 4) wound on an alundum tube. The space between the inner and outer heating units was packed with 120-mesh RR alundum "specially prepared for carbon determinations." The temperature of the outer unit was maintained at approximately 1000° C., and that of the nichrome-wound furnace, *C*, used for preheating the air and water vapor, at approximately 900° C.

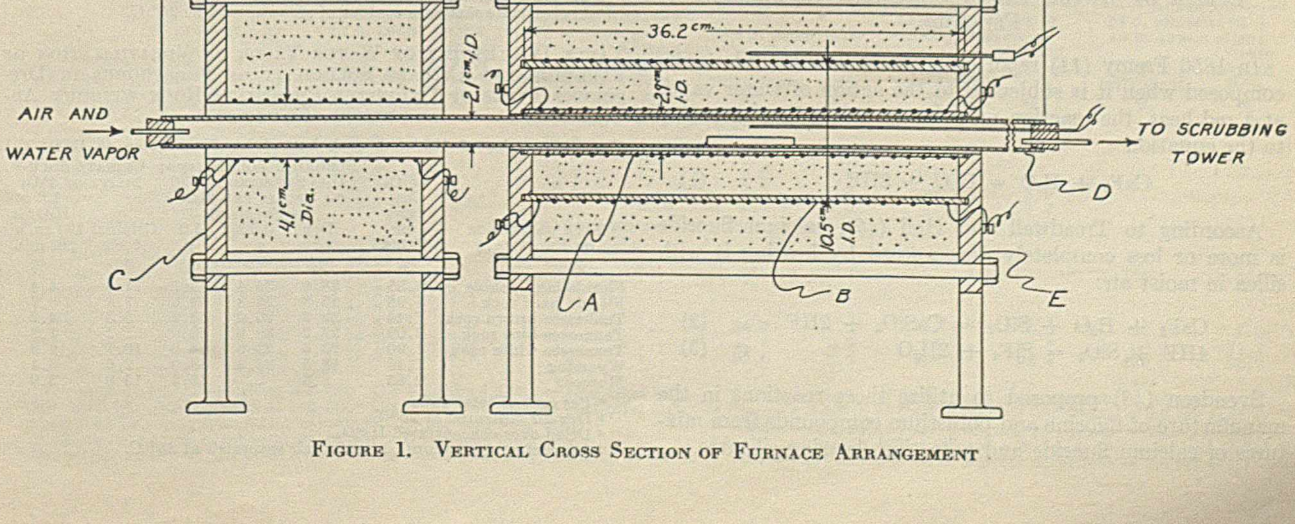

Figure 1. Vertical Cross Section of Furnace Arrangement

The reaction tube, *D*, of McDanel refractory porcelain, carried the platinum–platinum rhodium thermocouple and the furnace charge. In some of the experiments (Table III) known amounts of water were supplied to the furnace by saturating dry air at fixed temperatures. In the other experiments the water was boiled at such a rate that approximately 1.0 gram per minute was carried into the furnace; as indicated in Table III, this was far in excess of the amount actually required for the reaction. In all experiments the flow of air through the furnace was maintained at 120 cc. per minute (dry air measured at 25° C.). Varying the dry-air supply between the limits zero and 240 cc. per minute had no significant effect on the reaction.

The platinum–platinum rhodium thermocouple used for measuring the temperature of the charge was calibrated against a standard couple of the Bureau of Standards; it was protected against the furnace atmosphere by a gas-tight McDanel refractory porcelain tube. The axial temperature gradient from the hottest portion of the furnace outward was approximately 4° C. per cm. over a distance of 3.8 cm. The charge was heated in a platinum boat 7.6 cm. long, 1.3 cm. wide, and 0.9 cm. deep, placed so that the center of the boat coincided with the hottest portion of the furnace. Temperatures were measured at a point approximately 1.3 cm. from the hottest portion of the furnace towards the gas exit end. Tests indicated that the maximum and minimum temperatures of the charge were usually within 10° C. of the average temperatures measured in this way. During a run the temperature was usually maintained within ±5° C. of the desired average temperature.

In making the experiments the furnace was brought to a temperature about 10° C. higher than that at which it was desired to heat the charge; at the same time the desired flow of gas was passed through the furnace. The boat was then introduced, and, after heating for the desired length of time (reckoned from about the third minute after the introduction of the boat), it was withdrawn, cooled, and weighed, and the residue if fused or greatly sintered was ground to pass a 200-mesh sieve, or, if only slightly sintered, to pass a 100-mesh sieve.

The fluorine content of the original phosphates, and also that of the residues containing less than 0.5 per cent fluorine, was determined by the Willard and Winter method (*51*); the fusion–acid extraction method (*36*) was used on residues containing more than 0.5 per cent fluorine. Later, excellent results for fluorine in all the furnace residues were obtained by slightly modifying (*35*) the original procedure of Willard and Winter. The majority of the experiments were run in duplicate, the results agreeing within less than 5 per cent of the total fluorine volatilized.

All samples for the citrate-insoluble phosphorus determinations were ground to pass a 200-mesh sieve, and the analyses were made by the recently adopted modification (*26*) of the official neutral ammonium citrate method. Comparative determinations showed the same percentages of citrate-insoluble phosphorus in 200-mesh and 100-mesh samples.

All silica determinations were made by the Hoffman and Lundell (*14*, *16*) modification of the Berzelius method.

EFFECT OF WATER VAPOR AND SILICA ON CALCIUM FLUORIDE

In 1856 Fremy (*11*) reported that calcium fluoride is decomposed when it is subjected to the action of water vapor at a red heat, the reaction presumably proceeding according to the equation

$$CaF_2 + H_2O = CaO + 2HF \qquad (1)$$

According to Treadwell and Hall (*49*), calcium fluoride is more or less completely decomposed by heating it with silica in moist air:

$$CaF_2 + H_2O + SiO_2 = CaSiO_3 + 2HF \qquad (2)$$

$$4HF + SiO_2 = SiF_4 + 2H_2O \qquad (3)$$

Svendsen (*48*) proposed to utilize these reactions in the manufacture of fluorine and potassium compounds from mixtures of calcium fluoride and potassium-bearing silicates.

In order to obtain data on the extent to which fluorine is volatilized from calcium fluoride at various temperatures, experiments were carried out with a silica-free synthetic calcium fluoride and with fluorspar (Bureau of Standards sample No. 79). The results (Table II) show that water vapor and silica are both important reagents in effecting the decomposition of calcium fluoride at high temperatures, that water vapor is more important than silica, and that a combination of the two is much more effective than either alone.

TABLE II. EFFECT OF WATER VAPOR AND SILICA ON VOLATILIZATION OF FLUORINE FROM CALCIUM FLUORIDE

(Samples heated for 30 minutes)

TEMP.	FLUORINE VOLATILIZED: SYNTHETIC CALCIUM FLUORIDE[a] HEATED IN WATER VAPOR[b]	2.38 G. FLUORSPAR[c] + 2.62 G. SILICA HEATED IN: Water vapor[b]	Dry air[d]
° *C.*	%	%	%
800	..	11.3	..
900	..	31.5	..
1000	8.9	38.2	3.0
1100	16.7	54.5	3.1
1200	31.5	84.5	12.2
1300	92.1	90.5	52.9
1400	..	84.8	..

[a] Containing 99.8 per cent CaF_2.

[b] Water supplied at the rate of 1.0 gram in 120 cc. air per minute (dry air measured at 25° C.).

[c] Bureau of Standards standard sample No. 79, containing 94.9 per cent CaF_2 and 1.89 per cent SiO_2. 1:1 mole ratio of CaO to SiO_2.

[d] 120 cc. per minute; dried over H_2SO_4 and measured at 25° C.

EFFECT OF WATER VAPOR AND SILICA ON PHOSPHATE ROCK

As shown in Tables III and IV, the volatilization of fluorine from phosphate rock increased with the moisture content of the furnace atmosphere. The results obtained on straight Florida pebble phosphate (Table III) indicate that the optimum effect of water vapor is obtained when the water is supplied at the rate of at least 0.067 gram per minute per 5 grams of phosphate rock; larger quantities of water caused but little improvement in the volatilization of fluorine. Several experiments with various types of phosphate rock showed that preignition of the phosphate at 400° to 500° C. to remove moisture reduces the amount of fluorine volatilized when the rock is heated at 1300° C. for 30 minutes in a dry atmosphere.

TABLE III. EFFECT OF WATER VAPOR ON VOLATILIZATION OF FLUORINE FROM FLORIDA LAND-PEBBLE PHOSPHATE

[5 grams of ignited (400–500° C.) 200-mesh phosphate heated for 30 minutes at 1200° C.]

APPROX. QUANTITY OF H_2O SUPPLIED TO FURNACE ATMOSPHERE[a]	F VOLATILIZED	APPROX. QUANTITY OF H_2O SUPPLIED TO FURNACE ATMOSPHERE[a]	F VOLATILIZED
Gram/min.	%	*Gram/min.*	%
[b]	12.4	0.030	38.0
0.0006	18.5	0.067	50.8
0.003[c]	29.7	1.0	51.7
0.011	33.2		

[a] In 120 cc. air per minute (dry air measured at 25° C.).

[b] Air dried over concentrated sulfuric acid.

[c] Approximate moisture content of air saturated at 25° C.

TABLE IV. EFFECT OF WATER VAPOR ON VOLATILIZATION OF FLUORINE AND CITRATE SOLUBILITY OF PHOSPHORUS IN DIFFERENT TYPES OF UNIGNITED PHOSPHATE ROCK WITHOUT ADDITION OF SILICA

(5-gram samples of 100-mesh rock heated for 30 minutes at 1300° C.)

TYPE OR SOURCE OF PHOSPHATE	SiO_2 CONTENT OF ROCK	FLUORINE VOLATILIZED; H_2O SUPPLIED IN 120 CC. OF AIR PER MIN.[b] AS FOLLOWS: Dry air[c]	0.003 g.[d]	1.0 g.	CITRATE SOLUBILITY OF P_2O_5[a]: Original rock	1.0 g. H_2O in 120 cc. air per min.
	%	%	%	%	%	%
Florida land pebble	8.89	28.6	34.4	64.7	11.0	4.4
Florida hard rock	4.98	25.3	28.8	53.6	7.8	3.7
Tennessee brown rock	7.44	23.3	30.0	58.9	5.5	4.2
Tennessee blue rock	9.09	37.2	39.0	58.9	7.2	2.8
Tennessee white rock	1.90	23.5	25.0	54.0	10.7	9.3
Wyoming	7.16	18.5	26.3	58.0	2.6	5.1
Morocco	0.85	8.3	..	46.5	13.0	3.9

[a] Per cent of total P_2O_5.

[b] Dry air measured at 25° C.

[c] Dried over concentrated H_2SO_4.

[d] Approximate moisture content of air saturated at 25° C.

Although the results (Table IV) obtained on different types of rock containing different percentages of silica show no general relation between the silica contents and the percentages of fluorine volatilized, the low results on the Morocco phosphate are probably due, at least in part, to its very low silica content. In general, the citrate solubility of the phosphorus in the products obtained under the conditions of these experiments was lower than that of the phosphorus in the original phosphates.

TABLE V. EFFECT OF VARIOUS AMOUNTS OF ADDED SILICA ON VOLATILIZATION OF FLUORINE AND CITRATE SOLUBILITY OF PHOSPHORUS IN FLORIDA LAND-PEBBLE PHOSPHATE IN PRESENCE OF WATER VAPOR

[Mixtures of 200-mesh materials heated for 30 minutes at 1300° C. in water vapor supplied at the rate of 1.0 gram of water in 120 cc. of air per minute (dry air measured at 25° C.)]

COMPOSITION OF MIXTURE: Phosphate rock[a]	Added SiO_2	Total SiO_2	F VOLATILIZED	CITRATE SOLUBILITY OF P_2O_5
Grams	*Grams*	*Grams*	%	%
5.00	0	0.45	58.6	4.3[b]
5.00	0	0.45	19.1[c]	..
4.75	0.25	0.68	57.9	10.4
4.50	0.50	0.90	50.7	9.0
4.25	0.75	1.13	55.5	6.4
4.00	1.00	1.36	64.8	17.3
3.50	1.50	1.81	79.7	33.9
3.50	1.50	1.81	25.3[c]	..
3.00	2.00	2.27	84.1	55.1
2.50	2.50	2.72	82.7	45.9

[a] Ignited at 400° to 500° C.
[b] Citrate solubility of P_2O_5 in original phosphate (ignited at 400° to 500° C.) = 8.2 per cent.
[c] Charge heated in a dry atmosphere.

The data given in Table V indicate that increasing the total silica content of the charge within the approximate limits 9.0 to 22.6 per cent (0.45 to 1.13 grams) has no pronounced effect either on the volatilization of fluorine or on the citrate solubility of the phosphorus, when Florida pebble phosphate is heated for 30 minutes at 1300° C. in the presence of an ample supply of water vapor. Increases in the volatilization of fluorine and the citrate solubility of the phosphorus were obtained, however, when the total silica was increased within the approximate limits 22.6 to 45.4 per cent (1.13 to 2.27 grams); larger quantities of silica apparently have a depressing effect. In the absence of water vapor, increasing the silica content of the charge within the limits 9.0 to 36.2 per cent (0.45 to 1.81 grams) did not have an important effect on the reaction.

The frequently noted deficiency of fluorine in fluorapatite (7) (see also the analysis given in Table I) may have been caused in part by the action of silica and water vapor on the fluorapatite at high temperatures.

EFFECT OF TEMPERATURE

Table VI and Figure 2 show the effect of temperature on the volatilization of fluorine and the citrate solubility of various phosphates heated alone and with added silica for 30 minutes in the presence and absence of water vapor. With all charges heated (1000° to 1400° C.) in a dry atmosphere, less than 32 per cent of the fluorine was volatilized and the citrate solubility of the phosphorus in the products was less than that of the phosphorus in the original phosphates.

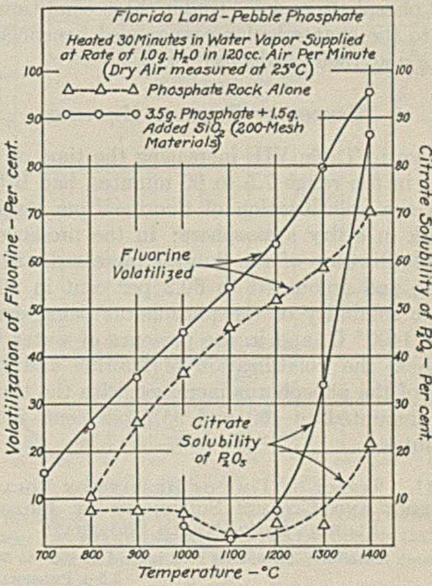

FIGURE 2. EFFECT OF TEMPERATURE ON VOLATILIZATION OF FLUORINE AND CITRATE SOLUBILITY OF PHOSPHORUS IN FLORIDA PEBBLE PHOSPHATE

In the presence of water vapor, but without added silica, the volatilization of fluorine from Florida pebble phosphate increased with the temperature within the range 800° to 1400° C. but amounted to less than 70 per cent at 1400° C. Heating the rock at 800° to 1300° C. decreased the citrate solubility of the phosphorus, and even at 1400° C. the solubility did not exceed 23 per cent. The results of a few experiments (see also Table IX) indicate that neither the volatilization of the fluorine nor the citrate solubility of the

TABLE VI. EFFECT OF TEMPERATURE ON VOLATILIZATION OF FLUORINE AND CITRATE SOLUBILITY OF PHOSPHORUS IN VARIOUS PHOSPHATES

(200-mesh silica used in all experiments)

TEMP.	FLORIDA LAND-PEBBLE PHOSPHATE[a]				TENNESSEE BROWN-ROCK PHOSPHATE[b]		MOROCCO PHOSPHATE[c]				APATITE[d]	
	5.0 G. PHOSPHATE		3.5 G. PHOSPHATE + 1.5 G. ADDED SILICA		5.0 G. PHOSPHATE		5.0 G. PHOSPHATE		3.5 G. PHOSPHATE + 1.5 G. ADDED SILICA		3.5 G. PHOSPHATE + 1.5 G. ADDED SILICA	
	F volatilized	Citrate soly. of P_2O_5	F volatilized	Citrate soly. of P_2O_5	F volatilized	Citrate soly. of P_2O_5	F volatilized	Citrate soly. of P_2O_5	F volatilized	Citrate soly. of P_2O_5	F volatilized	Citrate soly. of P_2O_5
° C.	%	%	%	%	%	%	%	%	%	%	%	%
HEATED FOR 30 MINUTES IN DRY AIR[e]												
1000	9.6	..	18.8	..	11.6	...	..	...	...	..	...	..
1100	12.9	..	16.9	..	17.3	...	..	...	...	..	...	..
1200	12.4	..	25.1	..	17.2	...	5.0	3.2[h]	24.1	4.4	...	..
1300	19.1	..	25.3	..	20.4	...	8.3	4.3	29.1	2.9	...	..
1400	26.9	4.6[f]	26.8	3.8	20.9	3.6[g]	7.4	4.2	31.3	1.7	...	..
HEATED FOR 30 MINUTES IN WATER VAPOR[i]												
700	..	..	15.2	..	..	...	..	...	...	..	...	..
800	10.4	7.3	25.3	..	..	...	..	...	...	..	...	..
900	25.9	7.4	35.5	..	..	...	..	...	...	..	...	..
1000	36.2	6.9	44.9	4.2	..	...	..	...	...	..	...	..
1100	45.9	2.4	54.6	1.7	..	...	..	...	...	..	...	..
1200	51.7	4.7	63.4	7.4	..	...	35.3	4.4	62.1	5.3	36.1	4.7[j]
1300	58.6	4.3	79.7	33.9	..	...	46.5	3.9	75.7	17.5	69.3	11.2
1400	69.6	22.4	95.5	86.4	..	...	52.0	6.4	100.0	94.4	100.0	95.2
1450	62.5	23.1	..	..	..	...	..	...	...	..	...	..

[a] 200-mesh phosphate ignited at 400–500° C.; contained 8.98 per cent total SiO_2.
[b] 200-mesh phosphate ignited at 400–500° C.; contained 7.56 per cent total SiO_2.
[c] Unignited 100-mesh phosphate; contained 0.85 per cent total SiO_2.
[d] Unignited 100-mesh phosphate; contained 3.07 per cent total SiO_2.
[e] 120 cc. per minute of air, dried over concentrated H_2SO_4, and measured at 25° C.
[f] Citrate solubility of P_2O_5 in original phosphate = 8.2 per cent.
[g] Citrate solubility of P_2O_5 in original phosphate = 5.5 per cent.
[h] Citrate solubility of P_2O_5 in original phosphate = 13.0 per cent.
[i] 1.0 gram water in 120 cc. air per minute (dry air measured at 25° C.)
[j] Citrate solubility of P_2O_5 in original phosphate = 2.5 per cent.

phosphorus is improved by heating the rock at higher temperatures (1450° C.).

Heating mixtures of mineral calcium phosphates (3.5 grams) and added silica (1.5 grams) at 1300° C. for 30 minutes in an atmosphere of water vapor resulted in the volatilization of 69.3 to 79.7 per cent of the fluorine and the conversion of only 11.2 to 33.9 per cent of the phosphorus into the citrate-soluble condition; at 1400° C., 95.5 to 100 per cent of the fluorine was volatilized and the conversion into citrate-soluble phosphorus amounted to 86.4 to 95.2 per cent. At 1400° C. as good results were obtained with fluorapatite as with the phosphate rocks. Under these conditions addition of silica to the charge had a pronounced beneficial effect on the reaction at 1300° and 1400° C.

EFFECT OF TIME OF HEATING

As shown in Table VII, increasing the time of heating at 1200° C., in the range 7.5 to 60 minutes, had little, if any, effect on the volatilization of fluorine from straight phosphate rock in a dry atmosphere; in the presence of water vapor, volatilization of the fluorine increased with the time of heating and amounted to 60.2 per cent in 60 minutes, the citrate solubility of the phosphorus being only 6.4 per cent. At 1400° C. and in the presence of water vapor and added silica, the volatilization of fluorine and the citrate solubility of the phosphorus increased with the time of heating and amounted to 100 and 95.7 per cent, respectively, in 60 minutes.

TABLE VII. EFFECT OF TIME OF HEATING ON VOLATILIZATION OF FLUORINE AND CITRATE SOLUBILITY OF PHOSPHORUS IN FLORIDA LAND-PEBBLE PHOSPHATE

(200-mesh materials; phosphate rock ignited at 400° to 500° C.)

	5.0 G. PHOSPHATE[a] HEATED AT 1200° C. IN:			3.5 G. PHOSPHATE + 1.5 G. ADDED SiO_2, HEATED AT 1400° C. IN WATER VAPOR[b]	
	DRY AIR[c]	WATER VAPOR[b]			
TIME OF HEATING	F volatilized	F volatilized	Citrate soly. of P_2O_5	F volatilized	Citrate soly. of P_2O_5
Minutes	%	%	%	%	%
7.5	12.8	42.4	...	78.7	44.2
15.0	12.2	46.5	...	87.2	68.4
30.0	12.4	51.7	4.7[d]	95.5	86.4
60.0	16.3	60.2	6.4	100.0	95.7

[a] Containing 8.98 per cent total SiO_2.

[b] 1.0 gram H_2O in 120 cc. air per minute (dry air measured at 25° C.).

[c] 120 cc. per minute of air dried over concentrated H_2SO_4 and measured at 25° C.

[d] Citrate solubility of P_2O_5 in original phosphate = 8.2 per cent.

TABLE VIII. PHOSPHORUS AND FLUORINE CONTENTS OF DIFFERENT PARTICLE SIZES OF GROUND FLORIDA LAND-PEBBLE PHOSPHATE

(All samples ignited at 400° to 500° C.)

PARTICLE SIZE		P_2O_5	FLUORINE
Mesh	*Mm.*	%	%
10–20	1.651–0.833	32.90	3.85
20–40	0.833–0.381	32.96	3.90
40–80	0.381–0.175	31.08	3.76
80–200	0.175–0.074	31.34	3.76
<200[a]	<0.074	31.62	3.87

[a] Entire sample ground to 200 mesh; other fractions separated from material ground to pass a 10-mesh sieve.

EFFECT OF PARTICLE SIZE

Kuusk (*24*) reported that the completeness of the reaction between Estonian phosphorite and sand at high temperatures to form citric acid–soluble phosphates is dependent, to a certain extent, upon particle size of the phosphorite and sand. Therefore, several experiments were carried out to determine whether particle size is an important factor in the volatilization of fluorine and the formation of citrate-soluble phosphates in Florida land-pebble rock. The dimensions of the square openings of the sieves used in preparing the samples were 1.651, 0.833, 0.381, 0.175, and 0.074 mm. for the 10-, 20-, 40-, 80-, and 200-mesh sieves, respectively. Since the various sizes of particles in a ground phosphate rock usually do not have the same chemical composition (*15*), the different fractions were analyzed for fluorine and phosphorus, and these figures (Table VIII) were used as a basis for calculating the percentage changes in the fluorine and phosphorus during the experiments.

In general, the data (Table IX) indicate that when phosphate rock is heated at 1400° C. in the presence of water vapor, either with or without added silica, the best results are obtained with 40- to 80-mesh materials. On the other hand, if the phosphate rock is ground to 200 mesh and additional silica is used, the data indicate that the best results are obtained when the silica is also ground to 200 mesh. The results as a whole indicate that there is no significant advantage in grinding the materials finer than about 40 mesh. Although addition of silica to the charge significantly increased the reaction when the other factors were kept constant, complete removal of the fluorine was nevertheless obtained by heating 40- to 80-mesh phosphate alone for 1.0 hour at 1400° C. This phosphate contained approximately 9 per cent silica.

TABLE IX. EFFECT OF PARTICLE SIZE ON VOLATILIZATION OF FLUORINE AND CITRATE SOLUBILITY OF FLORIDA LAND-PEBBLE PHOSPHATE

[Heated 30 minutes in water vapor supplied at rate of 1.0 gram H_2O in 120 cc. air per minute (dry air measured at 25° C.)]

COMPN. OF CHARGE	PARTICLE SIZE Phosphate rock[a]	Silica	TEMP.	F VOLATILIZED	CITRATE SOLY. OF P_2O_5
	Mesh	*Mesh*	*° C.*	%	%
5.0 g. phosphate rock containing 8.98% (0.45 g.) SiO_2	40–80	....	1400	84.8	53.0
	40–80[b]	....	1400	100.0	94.1
	40–80	....	1450	74.6	48.5
	<200	....	1400	69.6	22.4
	<200	....	1450	62.5	23.1
3.5 g. phosphate rock + 1.5 g. added SiO_2	<200	10–20	1400	83.6	60.8
	<200	20–40	1400	87.1	67.8
	<200	40–80	1400	84.7	61.9
	<200	80–200	1400	82.6	61.2
	<200	<200	1400	95.5	86.4
	<200[b]	<200	1400	100.0	95.7
	10–20	10–20	1400	81.6	47.0
	20–40	20–40	1400	93.1	75.1
	40–80	40–80	1400	100.0	95.1
	80–200	80–200	1400	94.6	84.0

[a] All phosphates ignited at 400° to 500° C. before use. [b] Heated for 60 minutes.

TABLE X. COMPOSITION OF CALCINED PHOSPHATES OBTAINED FROM FLORIDA LAND PEBBLE

[Charges heated at 1400° C. in water vapor supplied at the rate of 1.0 gram water in 120 cc. air per minute (dry air measured at 25° C.)]

COMPN. OF FURNACE CHARGE	TIME OF HEATING	COMPOSITION OF PRODUCT Total P_2O_5	Citrate-sol. P_2O_5	F	CITRATE SOLY. OF P_2O_5	F VOLATILIZED
	Min.	%	%	%	%	%
5.0 g. phosphate rock (40–80 mesh)	60	34.01	32.02	0.00	94.1	100
3.5 g. phosphate rock + 1.5 g. SiO_2 (200-mesh materials)	30	23.48	20.32	0.13	86.4	95.5
	60	23.54	22.52	0.00	95.7	100
3.5 g. phosphate rock + 1.5 g. SiO_2 (20- to 40-mesh materials)	30	24.59	18.46	0.20	75.1	93.1
3.5 g. phosphate rock + 1.5 g. SiO_2 (40- to 80-mesh materials)	30	23.03	21.92	0.00	95.1	100
3.5 g. phosphate rock + 1.5 g. SiO_2 (80- to 200-mesh materials)	30	23.26	19.54	0.15	84.0	94.6

Contrary to the results obtained at lower temperatures (Table VI), increasing the temperature from 1400° to 1450° C. caused a decrease in the amount of fluorine volatilized. It is believed that this behavior is due to the increase in the degree of sintering, or semi-fusion, of the charge at the higher temperature, the total surface of charge available for contact and reaction with the water vapor being reduced thereby. Similar results were obtained in several other experiments carried out at temperatures between 1400° and 1450° C. It seems, therefore, that 1400° C. is the optimum temperature for the reaction under the conditions of the experiments reported in this paper. Guernsey and Yee (*12*) state that the optimum temperature for the preparation of calcined phosphates from mixtures of phosphate rock, carbonaceous material, and alkali salts is that temperature at which the charge just begins to sinter.

Table X gives the composition of several of the products obtained by heating Florida pebble phosphate at 1400° C. in the presence of water vapor, with and without addition of silica. None of the products contained significant amounts of water-soluble phosphate.

Relation between Ammonium Citrate- and Citric Acid-Soluble Phosphorus in Calcined Phosphates

In this country the neutral ammonium citrate method is used for the laboratory determination of the fertilizer value of the phosphorus in all phosphatic materials except basic slag which is evaluated by the 2 per cent citric acid method (*2*). It has been shown (*19*) that, under the conditions imposed by the official method of analysis, the calcium phosphates are, as a rule, more soluble in 2 per cent citric acid than in neutral ammonium citrate solution. Also, the results of pot and Neubauer tests (*21*, *42*) indicate that under certain conditions the fertilizer efficiencies of the water-insoluble calcium phosphates, such as tricalcium phosphate and steamed bone meal, correspond more closely with their solubilities in 2 per cent citric acid than in neutral ammonium citrate solution.

As shown in Table XI, the phosphorus in the original unheated mixture and in the calcined products was more soluble in citric acid than in citrate solution. The difference in the solvent power of the two reagents decreased, however, with increase in the citrate solubility of the phosphorus and amounted to only 6 per cent of the total phosphorus in the mixture heated at 1400° C. It will be noted that heating at about 1100° to 1200° C. caused a marked decrease in both the citrate and the citric acid solubility of the phosphorus.

Table XI. Solubility of Calcined Phosphates in Neutral Ammonium Citrate and 2 Per Cent Citric Acid Solutions

[Mixtures of 200-mesh Florida pebble phosphate (3.5 grams) and silica (1.5 grams) heated for 30 minutes in water vapor supplied at the rate of 1.0 gram of water per minute]

Temp. of Calcination	F Volatilized	Citrate Soly. of P_2O_5	Citric Acid Soly. of P_2O_5
° *C.*	%	%	%
Unheated mixture	..	14.5	31.4
1100	54.6	1.7	14.0
1200	63.4	7.4	21.0
1300	79.7	33.9	41.6
1400	95.5	86.4	92.4

Relation between Volatilization of Fluorine and Citrate Solubility of Phosphorus in Calcined Phosphates

At first glance the data given in the foregoing tables indicate no definite relation between the amount of fluorine volatilized and the citrate solubility of the phosphorus in the product. A more careful study of the figures shows, however, that a significant increase in the solubility of the phosphorus does not usually occur until more than about 60 per cent of the total fluorine is volatilized. Furthermore, the graphs in Figure 3 indicate, in general, that with a given phosphate the volatilization of a definite percentage of the total fluorine results in the conversion of a more or less definite percentage of the total phosphorus into the citrate-soluble state, regardless of the experimental conditions.

It has been shown that calcium fluorphosphate, $Ca_{10}F_2(PO_4)_6$, is the principal phosphatic constituent of all the commercial domestic varieties of phosphate rock (*13*), and that in proportion to their phosphorus content these varieties all contain more fluorine than is theoretically required for the formation of $Ca_{10}F_2(PO_4)_6$ (*18*, *20*, *28*, *38*), the excess of fluorine usually ranging from about 20 to 35 per cent. It is difficult to identify positively the form in which this excess fluorine occurs, but the available evidence indicates that it is probably present chiefly as calcium fluoride. The approximate amounts of fluorine present as calcium fluoride and as calcium fluorphosphate, $Ca_{10}F_2(PO_4)_6$, may be calculated if it is assumed (1) that all the phosphorus is present in the form of $Ca_{10}F_2(PO_4)_6$, or as $Ca_{10}(X, F)(PO_4)_6$ in which partial replacement of the fluorine by the hydroxyl group or other negative radical has occurred, and (2) that the fluorine not combined with the calcium phosphate is present as calcium fluoride. The fluorine present as calcium fluoride may be designated as F_A, one of the fluorine atoms in calcium fluorphosphate as F_B, and the other fluorine atom in the fluorphosphate as F'_B.

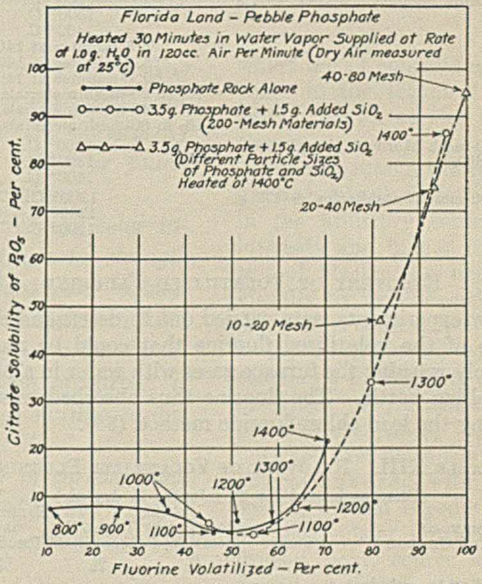

Figure 3. Relation between Volatilization of Fluorine and Citrate Solubility of Calcined Phosphate Rock

As shown in Table XII, no increase in the citrate solubility of the phosphorus of Florida pebble and Morocco phosphates and fluorapatite occurred until quantities of fluorine corresponding to all of F_A and F_B were volatilized from the furnace charges. From that point, however, the citrate solubility of the phosphorus increased with increase in fluorine volatilization, not in direct proportion to the percentage of total fluorine volatilized but approximately in proportion to the percentage of F'_B volatilized. In other words, no increase in the citrate solubility of the phosphorus was obtained until all of the fluorine in excess of that combined as calcium fluorphosphate and half of the fluorine in the fluorphosphate itself was volatilized.

A detailed discussion of the mechanism of the reaction and the nature of the citrate-soluble phosphate must be postponed until further data are available. On the basis of the present information it seems, however, that the first stages of the reaction involve the conversion of the $Ca_{10}F_2(PO_4)_6$ into $Ca_{10}(X, F)(PO_4)_6$, X probably being either the silicate or the hydroxyl radical, probably the latter (*47*, *50*). In the second stage of the reaction further volatilization of fluorine occurs, and citrate-soluble phosphate is formed. The exact nature of this citrate-soluble phosphate remains to be determined, but there is the possibility of the presence of silicophosphate (*23*), anhydrous tricalcium phosphate (*4*), and tetracalcium phosphate (*23*).

TABLE XII. RELATION BETWEEN VOLATILIZATION OF FLUORINE AND CITRATE SOLUBILITY OF PHOSPHORUS IN CALCINED PHOSPHATES

(All experiments made in presence of water vapor supplied at the rate of 1.0 gram H_2O per minute; 200-mesh materials heated for 30 minutes except as noted otherwise)

COMPN. OF FURNACE CHARGE	EXPERIMENTAL CONDITIONS	TABLE REFERENCE	PORTION OF TOTAL F IN ORIGINAL PHOSPHATE PRESENT AS: F_A	$F + F_B$	PORTION OF TOTAL F VOLATILIZED	PORTION OF F'_B VOLATILIZED	CITRATE SOLY. OF P_2O_5
			%	%	%	%	%
5.0 g. Florida pebble phosphate	1300° C.	VI	27.2	63.6	58.6	0	4.3
	1400° C.	VI	..	..	69.6	16.5	22.4
3.5 g. Florida pebble phosphate + 1.5 g. SiO_2	1200° C.	VI	..	..	63.4	0	7.4
	1300° C.	VI	..	..	79.7	44.2	33.9
	1400° C.	VI	..	..	95.5	87.6	86.4
	7.5 minutes at 1400° C.	VII	..	..	78.7	41.5	44.2
	15.0 minutes at 1400° C.	VII	..	..	87.2	64.8	68.4
	60.0 minutes at 1400° C.	VII	..	..	100.0	100.0	96.7
	10- to 20-mesh materials, 1400° C.	VIII	23.9	61.9	81.6	51.7	47.0
	20- to 40-mesh materials, 1400° C.	VIII	24.7	62.3	93.1	81.8	75.1
	40- to 80-mesh materials, 1400° C.	VIII	26.4	63.2	100.0	100.0	95.1
3.5 g. 100-mesh Morocco phosphate + 1.5 g. SiO_2	1200° C.	VI	26.3	63.2	62.1	0	5.3
	1300° C.	VI	..	..	75.7	33.9	17.5
	1400° C.	VI	..	..	100.0	100.0	94.4
3.5 g. 100-mesh fluorapatite + 1.5 g. SiO_2	1200° C.	VI	0	41.5	36.1	0	4.7
	1300° C.	VI	..	..	69.3	47.5	11.2
	1400° C.	VI	..	..	100.0	100.0	95.2

RECOVERY OF VOLATILIZED FLUORINE

A few experiments were carried out to determine the percentage of the volatilized fluorine that could be recovered by simply washing the furnace gases with water in a Milligan gas-washing bottle. The fluorine thus absorbed was determined by the lead chlorofluoride method (*36*).

TABLE XIII. RECOVERY OF VOLATILIZED FLUORINE

(Charges heated for 30 minutes in dry air)

COMPN. OF FURNACE CHARGE	TEMP.	PORTION OF TOTAL F Volatilized	Recovered[a]	EFFICIENCY OF F RECOVERY
	° *C.*	%	%	%
5.0 g. Florida pebble phosphate	1300	19.1	12.9	67.5
3.5 g. Florida pebble phosphate + 1.5 g. SiO_2	1100	16.9	10.3	60.9
	1300	25.3	17.6	69.6
5.0 g. Tennessee brown-rock phosphate	1100	17.3	12.5	72.3
	1300	20.4	15.6	76.5
2.38 g. fluorspar + 2.62 g. SiO_2	1200	12.2	11.0	90.2
	1300	53.0	46.1	87.0

[a] By absorption of volatilized fluorine in water.

The results (Table XIII) indicate that about 60 to 75 per cent of the fluorine volatilized from phosphate rock and from mixtures of phosphate rock and silica can be recovered as an aqueous solution probably consisting principally of hydrofluosilicic acid. About 90 per cent of the fluorine volatilized from mixtures of fluorspar and silica was recovered in the same manner. At present no explanation can be offered for the more efficient recovery of the fluorine volatilized from fluorspar as compared with that from phosphate rock.

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RECEIVED October 19, 1933. Presented before the Division of Fertilizer Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Some Properties of Carbon Black

IV. Color[1]

W. B. Wiegand and J. W. Snyder, Binney & Smith Company, New York, N. Y.

The technic of color testing, and color testing by photometric instruments are described; the accuracy of the Nigrometer is statistically analyzed. Instrumental color testing is found less sensitive than visual examination.

In a series of carbons of increasing color intensity there is a maximum in tinctorial strength at a point well below the highest color values. This is not to be explained by variations in fixed carbon contents. The increase in color intensity with increasing concentration of carbon is illustrated by Nigrometer readings on lithographic varnish grinds.

The evidence connecting color of carbon black with particle size is reviewed, and further experimental data are furnished on oil absorption and rubber properties.

The conditions essential to the production of high-color blacks are briefly mentioned. High-color blacks are sensitive to vibration, compression, and manipulation of almost any kind.

Color is enhanced by incorporation in a liquid vehicle. Color relationships may be altered and even reversed through change in vehicle.

The hitherto unavoidable increase in oil absorption with each step up in color intensity has been overcome by new process blacks. These are available in various qualities suitable to the particular vehicle and procedure involved.

The reënforcement of rubber by carbon black is rapidly finding its analog in the paint industry.

THE intensity and strength of the black color displayed by carbon black were primarily responsible for its original introduction and rapid development in the printing ink industry, to the displacement of the older type of carbon pigment known as lampblack and formed by the collection of free soot from the flame of burning hydrocarbon oils.

For thousands of years lampblack had been produced in China, Egypt, and elsewhere (*9*). It is remarkable that, by the simple expedient of interposing a stone or metallic plate within the luminous flame of a hydrocarbon, there should result so striking an improvement in color and tinctorial strength, and also remarkable that, in view of the known occurrence of natural gas flames in the ancient world, the superiority of an impingement deposit should not have been stumbled upon.

The next upward surge in carbon black production and application took place during the second decade of the present century when the unique rubber toughening or reënforcing properties of this pigment enabled it to contribute to, and therefore share in, the mushroom growth of the automobile industry; thus, at the present time about three-quarters of all the carbon black produced is used not because of its color but literally in spite of it!

During recent years the color of carbon black has been made the subject of intensive research with the result that new and superior varieties have been evolved, and new methods of manufacture and of dispersion technic have extended their usefulness in diverse fields, including the newer paint materials; it may now fairly be said that the third stage in the evolution of carbon black is again centered on its property of color.

In the present communication no attempt will be made to discuss the theoretical side of "blackness." The definition of blackness as absence of light must be regarded as of little practical importance in the technical study of high-color carbon blacks. As will later be pointed out, no optical device has as yet been made available of sufficient refinement to evaluate the delicate distinctions in blackness which are of controlling importance in the technical uses of carbon black at the present time.

For this reason the color of a carbon black is here defined in the arbitrary sense of the intensity and tone of the sensation of blackness as determined visually by experienced observers. Thus defined it is possible to lay down certain conditions calculated to influence apparent blackness or, as will be designated in this paper, "color."

In the first place the color of objects covered with a black enamel or film is ordinarily determined under illumination from a point source as represented by the sun, or some sort of artificial light. Next, such objects are customarily examined from a direction other than that of the reflected beam of light from such objects. Thirdly, the sensation of blackness registered by the eye is governed solely by the light projected in that direction and not by the total light energy returned.

From these considerations it can be deduced that in any given case the maximum intensity of black effect, or in other words, minimum incidence of light upon the retina, will be aided by the following conditions:

1. Gloss. Other things being equal, since the object is examined from an angle approaching 90° to the direction of the reflected beam, the higher the gloss the less will be the component of light reaching the eye. An undisturbed meniscus of dispersion vehicle provides maximum gloss. Where, for other reasons, a surface requires sanding or rubbing, gloss is destroyed. Hence the polishing and waxing operation are used to restore gloss.

2. Point Source of Light. In order to minimize light received by the eye, a parallel beam of incident light is best calculated to bring out maximum blackness. This is best supplied by unobstructed sunlight or by an arc.

3. Scattered Light. Incident light will be scattered, reach the retina, and therefore diminish apparent color by irregularities of surface due to scratch marks or by sandiness of film or by adventitious dust. These effects are customarily minimized by careful wiping of a panel with lint-free cloth just prior to examination or, more effectively, by covering the film with kerosene or other nonreactive liquid.

4. Secondary Reflection. The incident beam must not be permitted to excite secondary reflections. For this reason examination of films or panels, whether incident light is derived from the sun or from an arc or other artificial lamp, should be carried out in such a way as to insure that the reflected beam impinges upon a nonreflective surface, as, for example, a black

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[1] Part I, Ind. Eng. Chem., 23, 646–9 (1931); Part II, *Can. Chem. Met.*, 15, 265–6, 269 (1931); Part III, *Rubber Age* (N. Y.), 29, 311–16 (1931).

velvet of long nap. This velvet screen should be large enough and be placed close enough to the sample to cut off as much as possible of other stray light. This is particularly important when examining panels under direct sunlight.

The observance of these precautions minimizes all light from sources other than the film itself. In other words, color differences between two blacks are under such circumstances least obscured. It is only under these conditions that the finest variations in black color can be fully demonstrated.

Measurement of Color

Although a crude idea of color may be obtained by flattening two adjacent samples of dry carbon black under a spatula or other flat surface, preferred practice at the present time is to mix the blacks with a liquid dispersion medium generally mineral, linseed, or other oil. The mixtures are then customarily smeared side by side upon a glass microscopic slide, taking care to form a clean line of demarcation. The slide is then reversed and examined under a powerful light, the relative blackness of the samples being thus distinguished visually.

Of perhaps more importance is the determination of color in grinding varnishes, as typical of the paint requirements, lacquer mixtures, synthetic resin blends, etc. In such cases an actual grind is best carried out with the blacks in the respective medium, which in turn is sprayed, brushed, or flowed upon a metal panel which, after drying, is then compared with a control. In such cases the film is not observed through glass but directly under the source of light.

In addition to the net effect of blackness as registered by the eye of the observer, note is also taken of so-called color tone which may be of a brownish, reddish, bluish, or purplish tint. When pure carbon black, free from any added or toning substance, has been properly dispersed, it will be found that the undertone, whether observed through glass or directly, has a brownish hue. It is generally considered that this brownish undertone is the true color of very thin films of carbon black. The same hue can be observed in the case of dilute colloidal suspensions of carbon black. It is ordinarily obscured by the high light-absorptive power of the pigment so that only a few layers on the surface of a test panel permit the passage of light in sufficient degree to develop the brownish undertone mentioned above.

Instrumental Measurement of Color

Hock (*6*) was able by means of a polarization photometer to demonstrate a parallelism between blackness and specific surface, the latter being measured by means of heat of wetting. However, since in Hock's experiments the black was mixed with 100 parts of lithopone, his data must be regarded rather as a composite of blackness and tinctorial strength than as a measure of color *per se*. (The lack of strict parallelism between color intensity and tinctorial strength will be referred to later.)

Gholson (*3*) carried out a series of experiments with the General Electric Company type W-3 photoelectric color comparator, compared samples of color blacks in the dry state, mixed with various oil media, reduced with zinc oxide, etc., and concluded that the photoelectric comparator was not sensitive enough to distinguish between blacks of less than two or three shades difference in color. In other words, visual inspection was found much more sensitive than the instrument.

Hardy (*5*) has described a photometer for measuring the reflecting power of carbon black by comparing prepared surfaces of carbon black with a surface of standard blackness, the illumination of which can be regulated at will. This instrument (the Nigrometer, represented as more sensitive than the human eye, *7*) was employed in this laboratory in a series of determinations.

In the case of visual determinations of color an arbitrary scale of differences is employed. Based on a standard series of samples differing from each other in color by small increments, an arbitrary unit of one shade is defined as the minimum color difference that can be clearly differentiated by visual examination under an arc lamp or other intense form of illumination. Multiples of such differences are estimated and arbitrarily recorded as +1, +2, +3, +4, or −1, −2, −3, −4 "shades." Larger differences than ±4 are indicated as >+4 or >−4 "shades."

Instrumental Readings

The proximity of the variable light source which will illuminate the test surface to the same intensity as that of the sample being examined is taken as the unit of measurement. The higher the reading, therefore, the grayer the sample of black.

With a low-color black, instrumental readings are in the neighborhood of 80. With superintensity-color blacks readings are in the vicinity of 60. However, for the present work the actual readings have been subtracted from 100 in order that a higher numerical value will indicate a greater degree of blackness. The Nigrometer readings quoted will therefore be on this arbitrary scale.

In Table I is shown a series of comparisons between blacks which, by standard visual classification, show color differences, on the arbitrary scale already mentioned, of at least ±3 shades. The carbon blacks were mixed in the proportion of 0.2 gram (0.007 ounce) in 2 cc. (0.068 fluid ounce) of pale grinding linseed oil and mulled with a 15-pound weighted, 3-inch glass muller for one hundred strokes. Comparisons were then made by both the visual and instrumental methods already described. The Nigrometer index is an average of six readings with the calculated probable error.

Table I. Visual *vs.* Nigrometer Color Readings

Color Blacks	Difference by Eye	Nigrometer	Difference	Ratio of Difference to Probable Error of Difference
Highest intensity High intensity	+4	40.2 ± 0.1 38.7 ± 0.2	1.5 ± 0.2	7.5
High intensity High intensity	+3	38.7 ± 0.2 38.3 ± 0.1	0.4 ± 0.2	2.0
High intensity Medium intensity	> +4	38.3 ± 0.1 31.4 ± 0.1	6.9 ± 0.1	69.0
Medium intensity Medium intensity	+3	31.4 ± 0.1 30.0 ± 0.2	1.4 ± 0.2	7.0
Medium intensity Low intensity	> +4	30.0 ± 0.2 19.6 ± 0.2	10.4 ± 0.3	35.0
Low intensity Low intensity	+4	19.6 ± 0.2 18.2 ± 0.1	1.3 ± 0.2	6.5

Table II shows the relations between a series of blacks, all in the low-intensity color black field. In this narrower color range the lower ratio of the difference between two readings and the probable error of that difference points to less reliability in the instrumental readings. In the case of samples P-3 *vs.* S-1 the probable error exceeds the difference. The difference between S-1 and S-2 would seem significant according to the Nigrometer, yet to the eye there was no difference. P-1 and S-4 gave identical instrumental values but were three shades apart to the eye.

From Table I it can be concluded that the Nigrometer will indicate larger color differences. On the other hand, from Table II it is evident that, having due regard to the arbitrary character of the visual color scale, the difference between the Nigrometer readings for successive pairs of blacks which are known to differ on visual examination does not bear a sufficiently high ratio to the mean probable error of that difference to warrant the conclusion that the instrument is even approximately as sensitive as the human eye.

TABLE II. VISUAL *vs.* NIGROMETER COLOR READINGS FOR LOW-INTENSITY COLOR BLACKS

BLACKS	DIFFERENCE BY EYE	NIGROMETER	DIFFERENCE	RATIO OF DIFFERENCE TO PROBABLE ERROR OF DIFFERENCE
P-5 P-3	{+4}	23.2 ± 0.2 21.4 ± 0.2	{1.8 ± 0.3	6.0
P-3 S-1	{+1}	21.4 ± 0.2 21.5 ± 0.1	{0.1 ± 0.2	0.5
S-1 S-2	=	21.5 ± 0.1 20.3 ± 0.2	{1.2 ± 0.2	6.0
S-2 P-2	=	20.3 ± 0.2 20.1 ± 0.1	{0.1 ± 0.2	0.5
P-2 P-1	{+2}	20.1 ± 0.1 19.5 ± 0.3	{0.7 ± 0.3	$2^1/_3$
P-1 S-4	{+3}	19.5 ± 0.3 19.5 ± 0.2	{0 ± 0.4	0
S-4 P	{+3}	19.5 ± 0.2 17.4 ± 0.2	{2.1 ± 0.3	7.0

THE PERSONAL EQUATION IN NIGROMETER MANIPULATION

In the following table are shown results with four different observers each making ten readings on a highest intensity color black:

OBSERVER	NIGROMETER READING	PROBABLE ERROR
A	39.4	± 0.3
B	39.1	± 0.3
C	39.8	± 0.4
D	39.0	± 0.1

The probable error for each observer is shown. The result indicates that the personal equation has a significant influence on mean readings. Differences between the means for different observers are greater than the probable errors for each individual.

Taking into conjunction the inherent error of this instrument plus the personal equation factor, and considering recorded experiences with other types, it would seem that further refinement in optical photometry is essential before the visual estimation of color differences in carbon black is likely to be replaced by instrumental measurements.

COLOR AND TINCTORIAL STRENGTH

It is important to keep in mind a clear distinction between the color of carbon black and its tinctorial strength. By the latter is meant the blackness of a smear prepared by mixing, for example, 1 per cent of the black sample with 99 per cent of zinc oxide. A typical procedure is to weigh out 2 grams (0.07 ounce) of zinc oxide and 0.02 gram (0.0007 ounce) of carbon black. This mixture is stirred and mulled into, for example, 2.7 cc. (0.091 fluid ounce) of mineral oil. A similar procedure is carried out with a control. Both smears are placed parallel on a glass slide, and color or tone differences determined under strong illumination. The tinctorial strength or tinting strength of carbon black is thus deemed to be the measure of its ability to impart color (blackness) to a fixed amount of standard white pigment. A quantitative test of tinctorial strength is obtained by finding out the weight of zinc oxide necessary to reduce the color to that of the standard sample. Tinctorial strengths are thus readily referred, in terms of percentages, to a standard sample.

If a series of carbon blacks is now arranged in order of ascending color or increasing blackness, it will be found that the maximum value for tinctorial strength does not coincide with the point of maximum color or blackness. Figure 1 shows the general relationship for a typical series of blacks

In view of the generally accepted parallelism between fineness of subdivision and color, and also between fineness and tinctorial strength, the occurrence of a strength maximum at a point well below the color maximum is a rather unexpected result, and one for which at the moment no explanation is offered.[2] Kearsley (*8*) attributes these strength differences to the thickness of adsorbed gases on the carbon black surface. In view of these variations in volatile content, and therefore in fixed carbon, of various high-color blacks, it might be thought that, if compensations were made in the tinctorial strength determinations for variability in volatile matter, the above mentioned maximum in the tinctorial strength curve might be displaced and a closer parallelism between strength and color obtained.

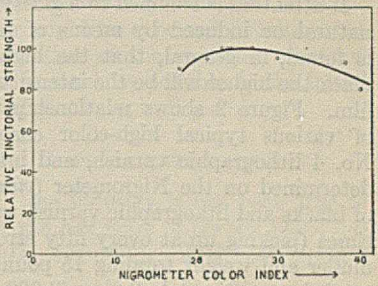

FIGURE 1. STRENGTH *vs.* COLOR

An experiment was therefore carried out to investigate this feature:

	VOLATILE MATTER	FIXED CARBON
	%	%
Highest intensity color black	12.8	87.2
High-intensity color black	8.0	92.0

The standard strength test (*vide supra*) was modified as follows: The test was based on fixed carbon content. It was therefore necessary to use 0.0212 gram (0.00074 ounce) of the highest intensity color black to equal the quantity of fixed carbon in the high-intensity color black. Such a mix was prepared. It naturally showed up darker than one with only 0.02 gram (0.0007 ounce), but at the same time it remained definitely grayer than the 0.02-gram mix with the high-intensity color black. This leads to the conclusion that fixed carbon content is not the controlling factor in the strength of a carbon black.

EFFECT OF CONCENTRATION ON COLOR

Although it might be considered self-evident that in any liquid dispersion medium the intensity of the black color would tend to increase in proportion as the percentage of black is raised, this is by no means so simple a matter. If by blackness is meant the absence of reflected light of any kind, it is found, as one might expect, that by reducing the dispersion medium to the minimum required to keep the pigment fixed, blackness reaches its maximum. Thus, for example, in the preparation of blackened surfaces for radiation studies, it has been found that best results are obtained when a sufficient quantity of volatile thinner, together with a minimum quantity of binding material, or vehicle, is used to disperse the carbon black. The same is of course true in connection with the preparation of black surfaces for cameras, etc.

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[2] The authors' tentative hypothesis, for which, however, they have no experimental proof, is that, as particle size decreases, there is a tendency towards agglomeration in small aggregates—a condition which, although clearly interfering with tinctorial strength (i. e., the ability to blacken the surrounding white medium) would not detract from its light absorption when examined by itself.

When, however, by the color is meant the impression of blackness recorded in the human eye, an almost opposite situation occurs. Thus, if an unpolished paint surface is under examination, it is found that a glossy surface, other things being equal, gives a blacker appearance than a dull surface.[3] Reduction in black content by increasing gloss may therefore increase the blackness as viewed visually.

If attention is confined to a glossy surface, whether this be natural or induced by means of rubbing and polishing, it is found, in general, that the higher the concentration of black the higher will be the intensity of color of the resultant film. Figure 2 shows relationships between concentrations of various typical high-color carbon blacks, mixed with No. 4 lithographic varnish, and intensity of black color as determined on the Nigrometer (*vide supra*). The mixtures of blacks and lithographic varnish were mulled two hundred times (picking up at every fifty strokes) with a 3-inch glass muller and weight totaling 15 pounds. The volume of mix totaled approximately 2.6 cc. (0.088 fluid ounce) in each case. The differences in color as shown by this instrumental reading are of course major differences.

The improvement in color by means of higher concentrations of black, although more or less self-evident on theoretical grounds, is often lost sight of in practice. Also there has been the manipulative difficulty in obtaining higher concentration grinds of high-color blacks in most dispersion media. Only within recent years have newer types of high-intensity color blacks been developed which have largely eliminated these difficulties in securing the desired concentration. This aspect of the color problem will be referred to under "Color *vs.* Dispersibility."

COLOR AND PARTICLE SIZE

Since the particle diameter of all blacks in the color range is well below the resolving power of the best microscopes, even when using ultra-violet light, it is impossible to secure reliable data on particle size by direct microscopic examination. The evidence for the belief that increasing color intensity goes parallel with decreasing particle size is therefore more or less indirect and circumstantial. Nevertheless, when the evidence is brought together, it is quite convincing. This evidence will now be briefly reviewed.

OIL ABSORPTION

Figure 3 and Table III show the capacity of various color blacks, with rubber black as a reference, for absorbing pale grinding linseed oil to a condition of fixed viscosity.

TABLE III. ABSORPTION OF OIL BY CARBON BLACKS

BLACKS	COLOR BY NIGROMETER	OIL ABSORPTION
		Gal./100 lb.
High color	38.3	275
Medium color	29.8	196
Low color	26.9	158
Low rubber	23.8	127
Rubber color	18.3	100

HEAT OF WETTING

Hock (*6*) has investigated blackness in relation to heat of wetting for a series of blacks. He found that, as specific surface increases, the blackness of one per cent mixtures of carbon black with lithopone increases. This may be taken in general as indicating the broad relationship between color and fineness of subdivision, with the single reservation that, since the tests were done in very dilute condition, tinctorial strength rather than color was the property measured by Hock. The experimental technic employed by Hock deserves attention because of its elegance, and it is to be hoped that this worker will extend his experiments to include a series of true high-color blacks.

EVIDENCE OF RUBBER MIXINGS

In 1928 Goodwin and Park (*4*) carried out some experiments with a color black (Super Spectra) which at that time was the most intense black available. Based on behavior in uncured mixings and also after vulcanization in various types of formulas, these authors concluded that the effect of this black on rubber indicated finer particle size than that of a standard rubber black (micronex). However, they found that the modulus showed an anomalous effect. In the meantime, there has been developed a color black of much higher intensity than Super Spectra (Royal Spectra). Table IV includes data from this laboratory comparing properties in rubber of this highest intensity color black in comparison with a high-intensity color black and a standard rubber black (Micronex).

TABLE IV. PARTICLE SIZE AS INDICATED BY RUBBER PROPERTIES

FORMULA

Smoked sheets	100	Litharge	6	Sulfur	4
Carbon black	45	Zinc oxide	5	Stearic acid	10

CURE AT 288° F.	MODULUS AT % ELONGATION: L-200	L-300	L-400	L-500	L-600	L-700	TENSILE STRENGTH/ % ELONG. AT BREAK	TENSILE PRODUCT	ENERGY
Min.	*Pounds per square inch*						*Lb./sq. in.*		*Ft.-lb./ cu. in.*
	RUBBER BLACK FOR REFERENCE								
10	250	575	1050	1650	2500	3400	3800/750	285	805
20	425	850	1500	2250	3300	4200	4300/705	303	904
30	550	1200	2000	2900	3900	....	4500/660	297	950
40	700	1400	2200	3150	4200	....	4300/620	266	896
60	825	1500	2300	3400	....	....	4200/570	241	783
	HIGH-INTENSITY COLOR BLACK								
10	200	400	725	1250	1950	2700	3300/760	251	648
20	375	725	1300	2100	3100	4100	4500/740	333	963
30	575	1150	1800	2700	3700	....	4600/680	312	973
40	650	1100	1900	2900	3950	....	4400/650	287	911
60	650	1250	2000	3000	3950	....	4100/610	250	801
	HIGHEST INTENSITY COLOR BLACK								
10	425	925	1550	2400	3300	....	4100/680	279	844
20	925	1700	2600	3750	....	....	4700/600	282	982
30	1050	1900	2850	4000	....	....	4600/560	257	909
40	1100	1900	2950	4050	....	....	4300/510	219	745
60	1200	2050	3100	....	....	....	4100/480	197	690

In connection with this same series, the following table indicates the time required for incorporating the respective blacks, together with the maximum developed values of Table IV:

BLACK	TIME OF MIXING	TENSILE STRENGTH	TENSILE PRODUCT	ENERGY
	Min.	*Lb./sq. in.*		*Ft.-lb./cu. in.*
Rubber	4.5	4500	303	950
High-intensity color	8.5	4600	333	973
Highest intensity color	11	4700	282	982

The formula of Table IV minimizes the disturbing effect on rate of cure induced by the high adsorptive power of color blacks. By examination of the advance in reënforcement and accepting the now generally held view that pigment reënforcement of rubber runs parallel with fineness of subdivision (at least for the same substance), one is impressed by the evidence of rubber compounding in favor of the view that the intensification of color in carbon black depends in large part upon increased fineness of subdivision. (The data in Table IV are also of interest as indicating the striking increase in modulus with concomitant decrease in breaking elongation, displayed by the carbon showing highest color development).

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[3] The explanation of this may be as follows: A glossy panel is usually examined from a direction at approximately right angles to the reflected ray of light. In the case of a matte-finish panel there is diffused reflection from the uneven surface. Thus in the latter case more light reaches the eye than in the former.

EVIDENCE BASED ON PORE RADII, ETC.

In the course of their important work on microscopic estimation of particle size by the count method, Gehman and Morris (*2*) have tentatively accepted the evidence adduced by Bartell and Smith (*1*) on the particle size as calculated from adhesion tension determinations of high-intensity color blacks. The actual estimated particle diameter of 0.025 micron is to be compared with the value determined by Gehman and Morris for standard rubber carbon black of 0.061 micron. Unfortunately the above mentioned value for high-intensity color black was so low as to prevent direct confirmation by ultramicroscopic count procedure.

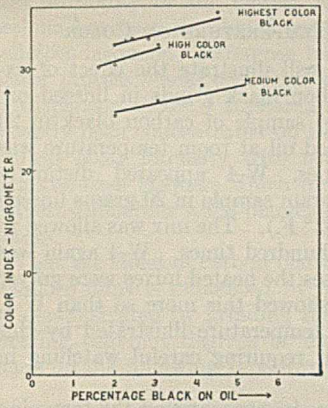

FIGURE 2. CONCENTRATION OF BLACK *vs.* COLOR IN LITHOGRAPHIC VARNISH

In weighing the evidence in favor of the view that color and particle size are closely related, due caution must be observed in case pigments of different types are involved. For example, the index of refraction of a pigment in relation to that of its dispersion medium may, and probably does, exert an effect more important in a given case than that of particle size, *per se*. Considerations of this kind are, for example, of undoubted significance in connection with the color of ivory blacks when compared with carbon blacks, as a class. The present writers expressly disclaim any intention of extending the generalization for carbon black to any other black pigment.

PRODUCTION OF HIGH-COLOR BLACK

From what has been said it would be expected that in order to produce high-intensity color black, arrangement of flames, depositing surface, etc., should be designed to minimize particle size. Such is in fact the case. High-intensity color blacks require for their manufacture a higher ratio of secondary air to hydrocarbon gas, more burning tips, closer channel settings. Resulting from these conditions it is found that the recovery of carbon black per thousand cubic feet of natural gas is drastically reduced and this reduction may, in the case of highest intensity color blacks, reach the value of only one-twentieth of the output of standard rubber black from the same natural gas.

Evidence is lacking as to the exact mechanism by which a higher color particle is released from the flame as compared to a lower color product. However, if the carbon black particle is looked upon as growing rapidly from the moment of release, it is only natural to expect that with smaller flames bathed in a more concentrated atmosphere of secondary air and placed in closer proximity to the depositing surface, the extent of accretion between release and deposition will stand to be less.

In addition to these general principles the production of high-intensity color blacks entails a refinement of technic and of adjustment far beyond that sufficient for blacks which rank lower in the color hierarchy.

EFFECT OF MANIPULATION ON COLOR

High-color blacks are sensitive to a surprising degree to vibration, compression, and manipulation of almost any kind. For this reason, compaction of high-color blacks by means of agitation in the collecting bin, or by means of compression at a later stage, must be almost entirely eliminated. Special care in packing is necessary lest vibration in transit exert a similar deteriorating effect on color. Wetting down of high-intensity color blacks followed by drying out, with a view to eliminating entrained air, has been found injurious to color. As to the mechanism of such phenomena it may be considered that the retention of a considerable envelope or cushion of entrained air might be expected to inhibit the natural adhesion or flocculation of the particles, thus extending to the final grind as much as possible of the initial fineness of particle of the black.

COLOR *vs.* DISPERSIBILITY

From the beginnings of the industry it has been true in more than one sense that the *bete noire* of carbon black has been its blackness (Table III, Figure 3). With each increase in color came increased oil absorption, increased difficulty in grinding, and, subsequent to grinding, marked tendencies towards reagglomeration, seeding, flocculation, etc. Because of this difficulty it has until recently been impossible to take full advantage of the improved color developments in carbon black manufacture. A brief account will now be given of the influence of vehicles on dispersion and on color development, and of certain recent improvements in the structure of high-intensity color blacks.

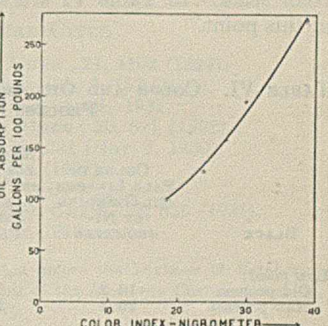

FIGURE 3. COLOR OF CARBON BLACK *vs.* OIL ABSORPTION

EFFECT OF VEHICLE ON COLOR OF NEW PROCESS BLACKS

When dry black is incorporated in, for example, pale grinding linseed oil, there is a marked improvement in color. In the following table are shown Nigrometer readings for a series of blacks, first, in powdered form and, second, when mixed in the proportion of 10 per cent by weight with the oil.

	Nigrometer Color Index			Nigrometer Color Index	
Black	Dry	Wet	Black	Dry	Wet
A	5.0	18.3	D	20.1	38.3
B	14.0	29.8	E	20.1	38.7
C	15.3	31.4	F	22.9	40.2

Although instrumental readings are here shown because of the difficulty in assigning numerical values to visual estimates, it must again be emphasized that differences as determined by the eye would be much greater than those indicated by the Nigrometer.

TABLE V. EFFECT OF VEHICLE ON COLOR

Color of Black	Vehicle	Color *vs.* Standard	Vehicle	Color *vs.* Standard
Low intensity	Mineral oil	+1	Lithographic varnish	−4
Low intensity	Mineral oil	=	Casein size	+4
Low intensity	Mineral oil	−4	Lithographic varnish	+4
Low intensity	Mineral oil	+1	Lithographic varnish	−2
High intensity	Linseed oil	−3	Nitrocellulose lacquer	+3
Higher intensity	Mineral oil	=	Nitrocellulose lacquer	+2
Higher intensity	Mineral oil	=	Nitrocellulose lacquer	+4

Again in the case of oil mixes it has long been known that where, for example, two blacks will show a certain color relationship when compared in mineral oil, this relationship may be altered and sometimes even reversed in the case of linseed oil. Data to illustrate this are shown in Table V.

Here the question of the surface tension relationship between the black and its dispersion medium was considered as likely to be the controlling factor, with the result that intensive study has of late been directed towards the development of new surface conditions in the highest intensity blacks. These were designed to provide lower interfacial tension between the black and the dispersion vehicles in common use. This has resulted in a clear differentiation among modern high-intensity color blacks. Thus, for example, for use in conjunction with linseed oil vehicles, with moderate to high acid value, new process blacks have now been made available which, while registering a marked increase in intensity of black color, show at the same time oil absorption values and ease of dispersibility which would normally be characteristic of blacks much lower in the color scale. In Table VI are shown data in substantiation of this point.

TABLE VI. COLOR AND OIL ABSORPTION FOR NEW AND OLD PROCESS BLACKS

BLACK	COLOR IN PALE LINSEED OIL GRINDING BY NIGROMETER	NEW PROCESS BLACKS AS PERCENTAGE OF OLD PROCESS BLACKS	OIL ABSORPTION OF NO. 4 LITHOGRAPHIC VARNISH PER 100 LB. BLACK	NEW PROCESS BLACKS AS PERCENTAGE OF OLD PROCESS BLACKS
		%	*Gal.*	%
Low color:				
Old process	18.3		259	
New process	20.4	111	81	31
Medium color:				
Old process	29.8		552	
New process	31.4	105	318	58
High color:				
Old process	38.3		577	
New process	38.7	101	397	69
Highest color:				
New process	40.2	105	317	55

The above will illustrate the special adaptation of high-intensity color blacks to one type of dispersion medium. In the case of a different medium—for example, nitrocellulose lacquer—color black development has moved along different and, in fact, almost opposite lines. For such a vehicle a type of high-color black has recently been evolved, the surface characteristics of which, although entirely distinct from those referred to above, also induce lower interfacial tension and lower absorption of vehicle, thus permitting higher concentration grinds with improved color and gloss.

It is proposed to discuss the surface chemistry of these new types of blacks in a separate communication. A bare reference to them is made at this time in order to bring out the principle that present-day color blacks have reached such a stage of particle fineness and color development as to necessitate special adaptation of black to vehicle.

EFFECT OF MEANS OF DISPERSION ON COLOR

As a general rule, when testing the color of carbon black, much care must be exercised in dispersion, in order that the developed color may equal, or nearly equal, the inherent color. Other things being equal, intensity of milling or grinding must go hand in hand with the color intensity inherent in the black. An illustration is found when friction under a glass muller is substituted for simple spatula mixing. The various devices employed in the paint and ink industries, including ball and pebble mills, flat stone mills, multiroller mills, may all be described as devices for promoting the more intimate association of black and vehicle.

EFFECT OF EXCESS MILLING ON COLOR

A phenomenon which will come as no surprise to the colloid chemist is experienced in case milling is carried to excess. For a given set of conditions, ingredients, etc., it is found that up to a certain point, extension of milling time improves color and dispersion but that beyond this point the color falls off. This is probably related to the phenomena of manipulation which have been discussed above.

EFFECT OF MILLING TEMPERATURE ON COLOR

The following experiment will illustrate the effect of excessive temperatures on carbon black grinds in linseed oil. An 0.08-gram (0.0028-ounce) sample of carbon black in 20 grams (0.706 ounce) of linseed oil at room temperature was mulled three hundred times. W-4 appeared distinctly darker than W-1. An 0.08-gram sample in 20 grams linseed oil was heated at 200° C. (392° F.). The mix was allowed to cool and then mulled three hundred times. W-4 again was much darker, but in both cases the heated mixes were grayer than the cold mixes. W-4 showed this more so than W-1. The bad effect of excessive temperature illustrated by this simple experiment is a point requiring careful watching in large-scale works operations.

It may not be out of place, in summarizing the foregoing general comments on dispersion as related to color in carbon black, to emphasize that optimum color results in any given case necessitate a suitable combination of black, vehicle, and milling procedure. It has been the writers' experience that, if two of these variables are fixed, the third is also determined within certain limits. Thus, in the case of a supercolor black used in conjunction with a certain vehicle, one type of dispersion technic will be found superior to all others. While this generalization may be considered self-evident and trite, it appears often to have been lost sight of in the paint, lacquer, and ink industries. The writers have, for example, encountered instances where difficulties were experienced because a black of too high a color intensity was used under conditions of vehicle and grinding procedure which could not be expected to develop the full color intensity inherent in the black.

EFFECT OF SWEATING ON COLOR

When carbon black is used in a China wood oil varnish, there is a definite sweating or aging effect which influences color, tone, and covering power as the black stands in contact with the oil, either before grinding, after grinding as it stands in the paste form, or even after cutting back. An example of the practical application of this principle is as follows: One standard factory procedure was to mix the black and oil in a "pony" mixer and then to feed this mix slowly into a stone mill. Tests showed that a paint made from the grind of the first few hours had a brown-gray cast as compared to later grinds. When the whole pony mix was allowed to stand overnight before grinding, the first grinds were then satisfactory. In other words, as the carbon black stood in contact with the oil, it became slowly wetted. This made subsequent grinding easier and a better color resulted.

COLOR, DISPERSION, AND DURABILITY

The high capacity for the absorption of light rays together with extreme fineness of subdivision which, in combination, are responsible for the intensity of color of modern "color" blacks have also been found to effect a striking improvement in the durability of protective films thus pigmented. It is probable the reënforcement of rubber by carbon black of so-called "rubber" grade or quality, which has brought about such a striking improvement in the durability and resistance to wear of automobile tires, is paralleled by an analogous effect on paint, ink, and lacquer films. This shows itself as relative freedom from chalking when exposed to the elements, longer retention of gloss and color, and greater hardness and permanence.

The attainment of these advantages presupposes, of course, adequate dispersion. In order to make available the color and durability of the newest high-intensity blacks, a new technic has been developed, especially in the field of nitrocellulose lacquers. Reference has already been made to the newer process blacks and their adaptability to special types of dispersion media. Research activities in this field have recently been concentrated on the problem of combining the highest color intensity with complete dispersion in nitrocellulose-base lacquers which until recently had offered the gravest difficulties when pigmented with superintensity-color blacks.

That the effect of carbon black on the weathering of nitrocellulose films is influenced by the degree of dispersion can be demonstrated by grinding the same formula by methods yielding different degrees of dispersion. Such a test was made on the following type formula:

1/2 second nitrocellulose	100
Ester gum	40
Dibutylphthalate	40
Carbon black	20
Solvent	500

Panels were sprayed, dried, polished, and exposed for 40 hours to an ultra-violet arc. A separate microscopic examination of thin films was made to determine relative dispersion. The film in which the black was best dispersed lost little or none of its gloss. The poorest dispersion yielded quite badly to chalking. Intermediate dispersions resulted in intermediate degrees of chalking.

FUTURE TRENDS

Carbon black owed its initial adoption to its beauty and intensity of black color and to its tinctorial strength. During the past two decades the growth of the industry has been due to the discovery of reënforcement in rubber where color played no role except that of an impediment. From present appearances it now seems that further development in the general use of carbon black will result from recent improvements in its color, in its dispersibility, and from the discovery that, through newer technic in dispersion, the principle of reënforcement which has revolutionized the art and science of rubber compounding bids fair to do a like service in the field of protective films, plastics, etc.

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Received October 4, 1933. Presented before the Division of Paint and Varnish Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Alchemia

by

HANS SEBALD BEHAM

Hans Sebald Beham was born in Nuernberg, Bavaria, in 1500 and spent the greater part of his life there. He was probably a pupil of Dürer. From 1525 he led a roving life, and in 1531 was in Frankfurt-am-Main, where he died in 1550.

Beham, whose name sometimes appears as Peham, made a large number of woodcuts and engravings, many of which were used for illustrating books. A number of his paintings are in some of the leading European galleries.

Our reproduction this month—No. 40 in the series—is from an engraving properly entitled *Alchemia*, but sometimes designated as *Astrologia*. This is one of the very few illustrations showing a female alchemist. We extend our thanks to Prof. A. P. Sy, who loaned his original engraving for making our reproduction.

A complete list of the first thirty-six reproductions in the series, together with the details for obtaining photographic copies of the originals, will be found with No. 37 in our issue of January, 1934, page 112. No. 38 was reproduced in our February, 1934, issue, page 207, and No. 39 in the March, 1934, issue, page 331. The photographs of these paintings are supplied in black and white only.

Steam-Film Heat Transfer Coefficients for Vertical Tubes

G. M. Hebbard[1] and W. L. Badger, University of Michigan, Ann Arbor, Mich.

Measurements are made of film coefficients of heat transfer for practically air-free steam condensing on the outside of a 1-inch o. d. vertical tube, 12 feet long, operated as a forced-circulation evaporator. Tube-wall temperatures are measured by a method previously described. The coefficients obtained range from about 900 to 1900 P. c. u./(hour)(square foot)(° C.). While these values appear somewhat low on account of the relatively great length of the tube employed, they actually average 33 per cent higher than called for by the theoretical Nusselt equation. No explanation is found for this deviation, since it is felt that there is no turbulence in the condensate layer, and the constancy of the tube temperature indicates the absence of dropwise condensation.

The larger part of the available data on heat transfer through films of condensed steam has been observed using horizontal tubes (*7*). Only a few workers have investigated the films on vertical tubes. Some empirical relations have been established, but generally the effort has been made to compare the data with some one of the theoretical equations that have been derived by W. Nusselt. Monrad and Badger (*8*) have reviewed the work on both types of tubes. For vertical tubes they found observed values of the steam-film coefficients, ranging from 2000 to 3000 B. t. u., that were from one-half to twice as large as corresponding values calculated by the theoretical equations.

In a recent article (*4*), Jakob discusses his work and that of his collaborators, Erk and Eck, in comparison with the Nusselt theory for vertical tubes. He finds that, for his experiments with steam passed slowly inside of a vertical heat transfer coefficient tube, the data are in close agreement with the theory (*6*). (The tube was 40 mm. in diameter and 1.20 meters long.) The results of other investigations, in which variables have been considered that are not included in the present work, also show that a theoretical correlation of the data is possible.

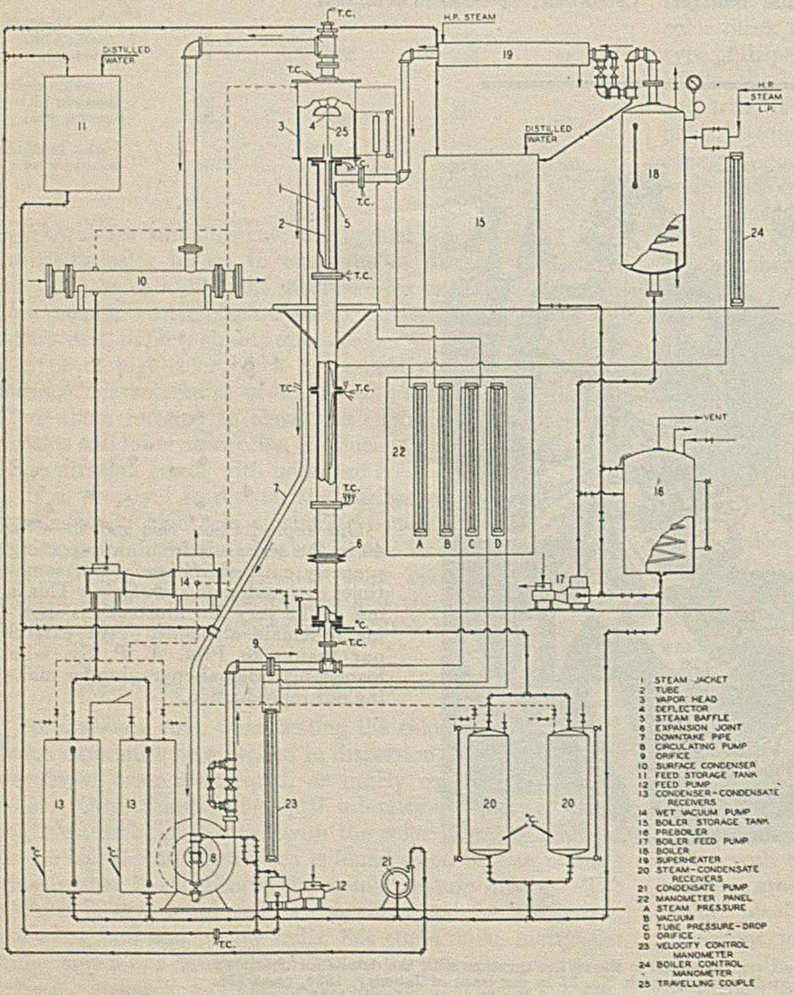

Figure 1. Diagram of Apparatus

The shortest length of tube that would be employed in a forced-circulation evaporator is about 6 feet, and the usual length is from 8 to 10 feet. No published data can be found that concern vertical tubes of a length greater than 4 feet. Philipp (*9*) worked in this laboratory with tube lengths of 4, 6, and 8 feet. In only one set of his runs was it possible to obtain consistent results. The individual coefficients obtained by him for steam were much higher than corresponding values which were calculated using the Nusselt theory.

The mathematical relationship derived by Nusselt for the case of vapor condensing on a smooth vertical surface, assuming that the vapor is pure and saturated and relatively stationary with respect to the condensate is:

$$h_s = 0.943 \left(\frac{k^3 \rho^2 g \lambda}{L \mu (\Delta t_s)} \right)^{0.25} \qquad (1)$$

where g = gravitational constant, (ft.)/(hr.)(hr.) = 4.18×10^8

h_s = steam film, P. c. u./(hr.)(sq. ft.)(° C.)

L = length of tube, ft.

k = thermal conductivity of condensate, P. c. u./(hr.)(sq. ft.)(° C./ft.)

ρ = density of condensate, lb./cu. ft.

λ = latent heat of condensation, P. c. u./lb.

μ = viscosity of condensate, (lb.)/(ft.)(hr.) = $2.42z$

z = viscosity, centipoises

Δt_s = temp. drop across condensate film, ° C.

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[1] Present address, Dow Chemical Company, Midland, Mich.

[The derivation of Nusselt's equation is given in English by Monrad and Badger (*8*) and Colburn and Hougen (*2*).]

The possibility exists that serious errors have been made in past determinations of tube-wall temperatures. This factor alone is sufficient to account for the unreliable character of many data. An accurate method for the measurement of tube-wall temperatures has been devised by Hebbard and Badger (*3*).

The present investigation was conducted for the purpose of obtaining information bearing on the characteristics and heat transfer coefficients of steam condensate films occurring on the tubes of vertical forced-circulation evaporators. The results, of course, have a fundamental application to the theory of heat transfer.

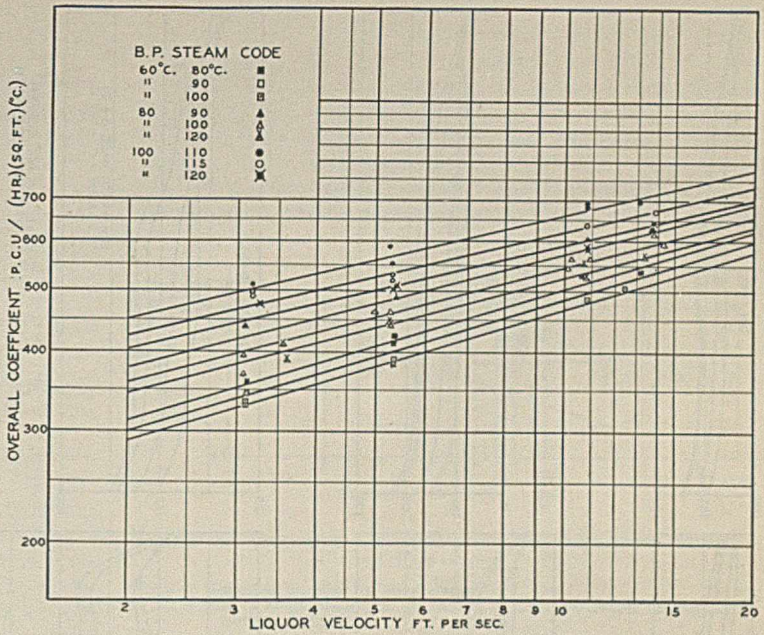

FIGURE 2. OVER-ALL COEFFICIENTS *vs.* VELOCITIES OF CIRCULATION

THE EXPERIMENTAL EVAPORATOR

The fundamental theory of Nusselt assumes conditions that may be employed as criteria in the design and operation of the experimental evaporator. These are: The steam used must be saturated and pure, and must move past the evaporator tubes at a low velocity; the outer tube surfaces must be smooth and clean, and the normal flow of the steam condensate down the tubes must not be disturbed. The physical properties of the condensate are to be taken at the arithmetic film temperature.

When this work was initiated, no equipment was available that fully met the requirements. A new apparatus was designed and assembled as shown in Figure 1:

The steam jacket, 1, constructed of four flanged sections of 6-inch i. d. standard pipe, each 3 feet long, surrounded the 1-inch eleven-gage copper experimental tube, 2, which had a length of 12 feet exposed between the tube sheets. Distilled water for the boiler, 18, was first passed through the preboiler, 16, where it was boiled continuously to remove as much of the dissolved gases as possible before it was pumped to the boiler. The boiler was heated by steam from the university main. The steam to the jacket was passed first through a separator and then a superheater, 19, to remove all entrained moisture. The dry steam contained from 2° to 4° C. superheat. Condensate from the evaporator was used as feed liquor which was stored in tank 11. When the evaporator was operating under a vacuum, feed entered the system directly at the inlet to the circulating pump, 8. At boiling points above atmospheric pressure, the feed was first piped to the feed pump, 12. The liquor level in the vapor head, 3, was maintained at a depth of approximately 4.5 inches by manual control of the amount of feed added. The rate of circulation was measured by a sharp-edged thin-plate orifice, 9, and controlled at pump 8. Steam condensate and condenser condensate were collected and measured in the respective tanks, 20 and 13. All parts of the evaporator were thoroughly lagged.

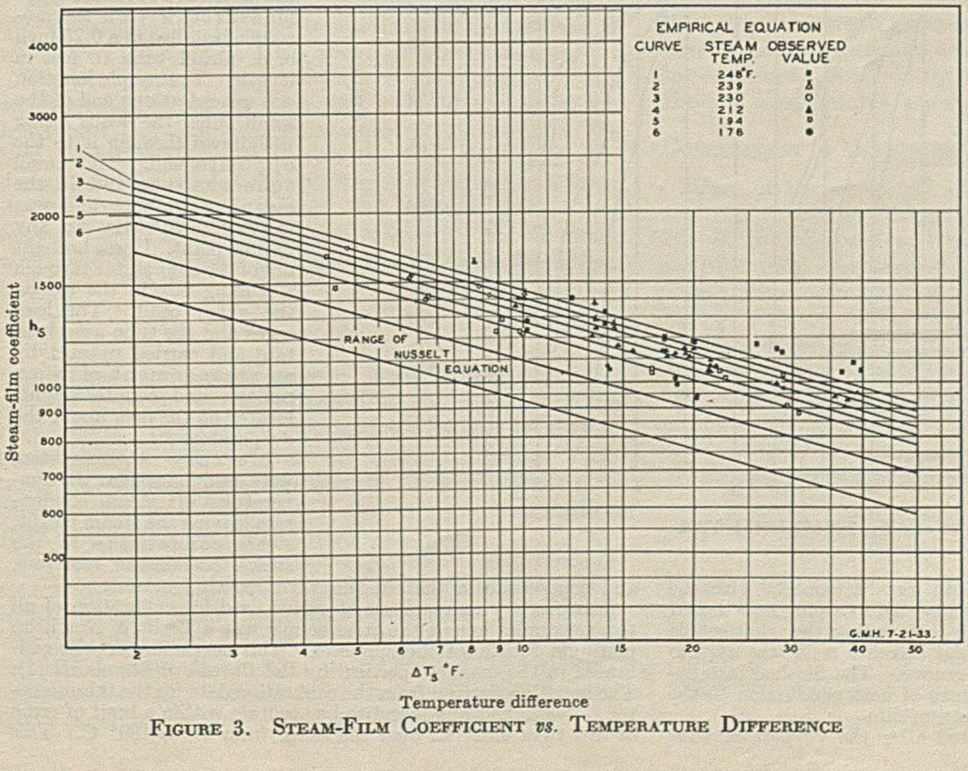

FIGURE 3. STEAM-FILM COEFFICIENT *vs.* TEMPERATURE DIFFERENCE

MEASURING AND CONTROL DEVICES

Thermocouples were used to measure the temperatures of: superheated steam, steam in the jacket, feed, circulating liquid at inlet to the tube, vapor in heat (or circulating liquid at outlet to tube), liquid temperatures in tube (traveling couple), and the tube wall. The exact points of the apparatus at which they were installed are shown in Figure 1. The thermocouples were read with a Type K-2 Leeds & Northrup potentiometer.

Briefly, the ten tube-wall thermocouples were installed in the following manner: Each couple was inserted in the tube wall in a hole drilled through a chord of the wall. The leads were withdrawn under the surface to an annular groove at opposite ends of the hole, carried in the groove to a point 180° from the junction and brought out from the wall together. The ther-

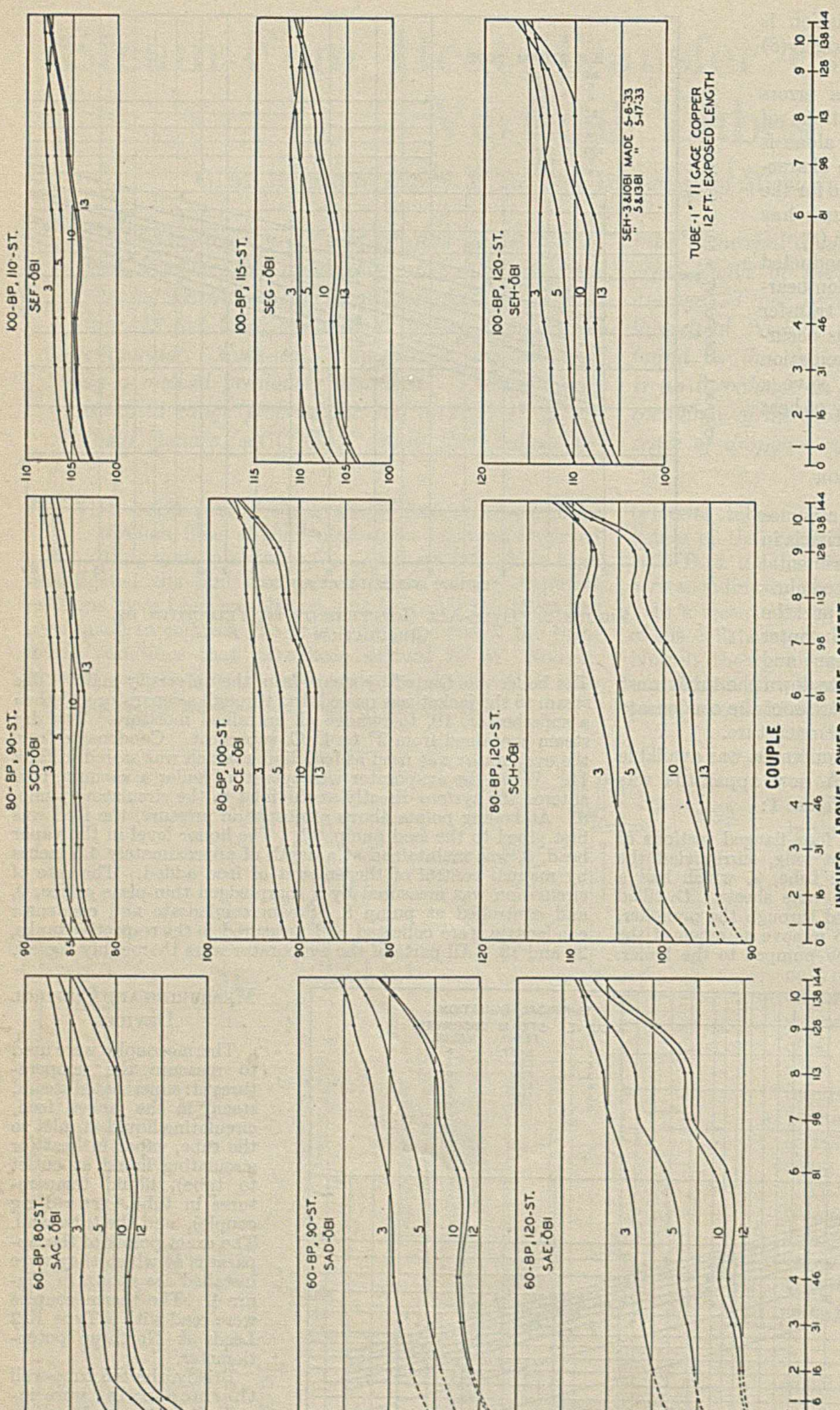

FIGURE 4. RESULTS ACHIEVED IN MEASUREMENT OF WALL TEMPERATURES

mocouple junction was brought into metallic contact with the wall by means of solder which was inserted in a plug hole drilled in the wall at right angles to and intersecting the chord hole at the middle of the latter. Special Bakelite resin was used to insulate the leads and fill in each groove. The finished installations were free from the usual causes of heat conduction to the junction and did not disturb the steam film.

The tube couples were calibrated after the evaporator tube was placed in the steam jacket. The apparatus was slightly modified for this procedure by the installation of the following units: a mixing section consisting of a 6 × 6 inch flanged nipple on the top tube sheet in place of the vapor head; a double-pipe heat exchanger in the inlet line between the circulating pump and the tube inlet; and an inlet mixing section of 6-inch pipe immediately before the tube inlet. The piping was so arranged that steam could be sent in parallel down the inside of the tube and jacket to the steam condensate tanks, and water could be circulated up the jacket and tube, the temperature of the latter being regulated by the heat exchanger. Water was used for the calibration in the range from 40° to 95° C. and steam from 100° to 130° C. When water was used, the temperature gradient up the jacket was determined by means of thermocouples installed between each pair of flanges. This gradient was small (0.1° to 0.2° C.) because of the rapid rate of circulation; and since each tube couple was calibrated against the nearest reference couple, the limit of error in calibration was small (±0.02° C.) After 150 hours of operation of the evaporator, the tube couples were recalibrated with steam at atmospheric pressure. The calibration values for all tube couples checked the original values at this point within a limit of error 0.1° C.

Liquor temperatures inside the evaporator tube were measured with a thermocouple installed in a 0.25-inch o. d. nickel tube 16 feet in length. The couple junction was placed at one end of the small tube, the leads being withdrawn through it to the opposite end. This small tube was inserted in the evaporator tube and was moved manually to any desired point. It was brought out of the evaporator through a stuffing box in the tee on the vapor head. The lead wires and the tube were held taut and carried upward by an arrangement of wires, pulleys, and counterweights located on the floor above the evaporator.

Mercury thermometers were used to measure the temperatures of: steam condensate leaving the steam jacket, steam condensate in the steam condensate receivers, and condensate in the condenser-condensate receivers.

The primary temperature standard used for calibration of all thermocouples except the tube couple was a Leeds & Northrup platinum resistance thermometer. This thermometer was calibrated in the manner specified by the Bureau of Standards (*1*). The equation derived from the calibration data for the thermometer was checked and found to be accurate within a limit of error of less than 0.01° C. over the range from 0° to 180° C. This thermometer was used to measure the temperature of a constant-temperature bath in which the thermocouples were calibrated at intervals of 10° C. over the range from 30° to 150° C. The limit of error of the calibration was ±0.01° C.

Open mercury manometers were installed to read the pressures in the boiler, steam jacket, and vapor head. A mercury manometer was used to measure the pressure drop through the evaporator.

EXPERIMENTAL PROCEDURE

In this work the evaporator was operated at three different boiling points: 60°, 80°, and 100° C. Three over-all temperature drops were employed with each boiling point, and four velocities of circulation, approximately 3, 5, 10, and 13 feet per second, were used with each combination of steam temperature and boiling point. A run consisted of a continuous experiment 40 minutes in duration, generally, and the data were so taken that each 20 minutes could be calculated separately.

During the run, a one-inch depth of steam condensate was kept on the lower tube sheet instead of allowing the condensate to drain freely to the tanks. This was necessary because of the relatively large surface area of the tanks, a fact that would have involved a correction factor of questionable accuracy for condensation of steam in the tanks. Noncondensable gases were removed from the jacket through a vent located about 10 inches above the lower tube sheet, by continuous venting of a small quantity of steam.

All tube thermocouples were read three times during each run. The liquor temperatures were taken at the corresponding points with the traveling couple. The wall temperature at any couple position did not vary in any case more than ±0.1° C. during a run. With small over-all temperature drops (10° C.) the tube couples checked consistently within 0.02° to 0.04° C. The average temperature drops across the steam film were calculated by arithmetic and graphic averaging of the observed temperatures. The graphic average temperature differences were corrected for the small temperature gradients that existed between the actual outer surface of the tube and the average depth of immersion of the couples in the walls (0.074 inch). The corrected results were employed in the calculation of the film coefficients.

The values of the steam-film coefficients (h_s) and apparent over-all coefficients (U) have been calculated on the basis of an exposed outer tube-surface area of 3.105 square feet.

The heat input was based directly on the amount of steam condensate collected per hour and included the superheat, latent heat, and sensible heat extracted from this steam. The heat output was calculated from the total amount of condenser condensate plus the sensible heat required to bring the feed to the boiling point. The amount of feed was assumed equal to the condensate collected. No allowance was made for entrainment, and radiation losses were neglected.

RESULTS

The factor limiting the accuracy of this work has been the possible error in the measurement of the volumes of the condensates. Large tanks were installed initially to provide capacity for a wide range of operating conditions. With small over-all temperature differences the quantities of condensates collected were often so slight that an error in reading of 10 to 15 per cent could have occurred.

A study of the heat balances indicated the occurrence of considerable entrainment in the vapor from the head. This factor expressed as the percentage excess of the heat output over the heat input did not show large errors, but it was considered unwise to use the data concerning the condenser condensate for any purpose other than just a semi-quantitative check of the steam condensate data. Two facts undoubtedly contribute to the cause of this entrainment: First, the deflector used was necessarily of a makeshift design. As it probably did not produce a uniform "curtain" of liquid in the head, the vapor, rising from the tube at a high velocity, did not always pass through the curtain where the major portion of the entrained moisture was removed. Further, the vapor head was not specifically designed for the evaporator. It was neither of sufficient height to provide a satisfactory space above the deflector to allow for the natural separation of the entrained moisture by a decrease in vapor velocity, nor was it constructed in such a fashion that the level of liquid in it could be kept uniform without an excessive amount of control. In the case of the latter point, the effect was a change in the size of the curtain with each change in level and an increase or decrease in the vaporization with each variation in the rate of feed.

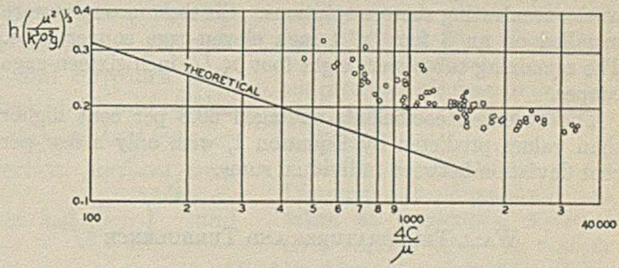

FIGURE 5. OBSERVED COEFFICIENTS COMPARED WITH NUSSELT EQUATION

$4C/\mu$ = Reynolds number for condensate
C = rate of condensate flow, lb./hr./ft. of tube perimeter (measured at bottom of tube)

Apparent over-all coefficients of heat transfer, in general, do not have any specific bearing upon the values of the individual film coefficients that are obtained for the same experiments. For this reason, no detailed consideration of the former has been made. The fact that the over-all coefficients may be correlated with themselves, however, is shown in Figure 2. Using logarithmic coördinates, the calculated over-all coefficients have been plotted against the corresponding velocities of circulation. Three groups of curves are evident, one group for each boiling point with a separate curve for each temperature drop used. The values of steam-film coefficients, obtained by using the graphically averaged tube-wall temperatures, are shown in Figure 3.

CORRELATION OF COEFFICIENTS WITH NUSSELT EQUATION

Values of the steam-film coefficients were calculated for each run from the Nusselt Equation 1. The difference between the observed and calculated coefficients for each case was then expressed as percentage of the theoretical value. These percentages were found to vary within narrow limits. When an average percentage had been obtained, the individual divergencies from this mean were observed to be within the limit of experimental error.

Equation 1 shows that a relation involving the same variables, but with a different constant, can be used to express the experimental results.

Expressed as percentage, the mean value of

$$\frac{h_s\text{ (obsvd.)} - h_s\text{ (Nusselt)}}{h_s\text{ (Nusselt)}} = 33.5\%\text{ for all runs}$$

The empirical equation is:

$$h_s = 1.27\left(\frac{k^3\rho^2 g\lambda}{L\mu\,\Delta t_s}\right)^{0.25} \qquad (2)$$

When the coefficients were recalculated by this equation, in no case was the deviation of the calculated from the observed values over ±12 per cent for any one run; and the average deviation for all runs was +2 per cent.

A correlation of the results of the present investigation with the theoretical equation is evidently possible. The question arises as to whether or not such a correlation is specific to the present apparatus.

A current project in this laboratory has made use of the same method of wall temperature measurement employed here in an investigation of the steam- and liquor-film coefficients for an eight-tube forced-circulation evaporator that was concentrating sucrose solutions. Six thermocouples were installed on an 8 foot × 1 inch eleven-gage copper tube. The remaining tubes were eight foot × $^7/_8$ inch sixteen-gage copper.

The observed coefficients averaged 60.8 per cent higher than values predicted by Equation 1, with only a few per cent deviation between individual sums.

WALL TEMPERATURES AND TURBULENCE

As previously stated, it was felt that information concerning the wall temperatures of the tube would explain much concerning the steam film. To this end, in Figure 4 the observed wall temperatures for the last half of each run were plotted against respective positions on the tube. A curve was drawn through the plotted data of each run. These curves were grouped according to the temperature drops used. A definite and orderly form was immediately noticeable in each group of curves. The wall temperature decreased with distance from the upper tube sheet. As the liquor velocity was increased, the temperatures were lowered in proportion at all points except for an irregularity displayed in several cases at the upper part of the wall, when a 3-foot velocity was used. The latter divergences from the general form of the curves are reproducible in each case, but, as a discussion of them must consider a study of conditions inside of the tube, they are left for another paper.

Jakob and Erk (*5*) working with a vertical tube, 0.466 meter (1.529 feet) in length, found that at high temperature differences the tube temperature first decreased, then increased at some point down the tube, and finally decreased slightly. A similar observation was made with the tube of the 8-foot evaporator previously mentioned, except that the last temperature decrease was usually quite large and brought the wall temperature at the bottom to a point several degrees below that of the top.

Evidently the occurrence of uniform and cyclic variations in wall temperature was not previously noted by other investigators, either because of the length of tube used or because of the inadequacy of the method of wall temperature measurement.

As pointed out by Monrad and Badger (*8*) from their results on diphenyl, turbulence in the condensate film would lead to increasing coefficients with increasing temperature differences (or other factors tending to increase the rate of condensate flow). To determine whether this effect is of importance in this present work on steam the results have been plotted in Figure 5 (supplied by T. H. Chilton and A. P. Colburn), using the dimensionless groups called for by the Nusselt theory, as related to the Reynolds number of the condensate film. It is observed that the points, in general, lie in a band parallel to the line representing the Nusselt equation, but somewhat higher. Since turbulence is not likely below values of $4C/\mu$ of 2500, this factor cannot explain the higher values obtained. Moreover, the present results might be expected to be low on account of a thin layer of iron oxide found upon examining the tube after the experimental runs. The conditions under which turbulence may be expected to begin cannot be stated from the results of this present work. A more thorough examination of conditions with tubes of different lengths and temperature differences is necessary.

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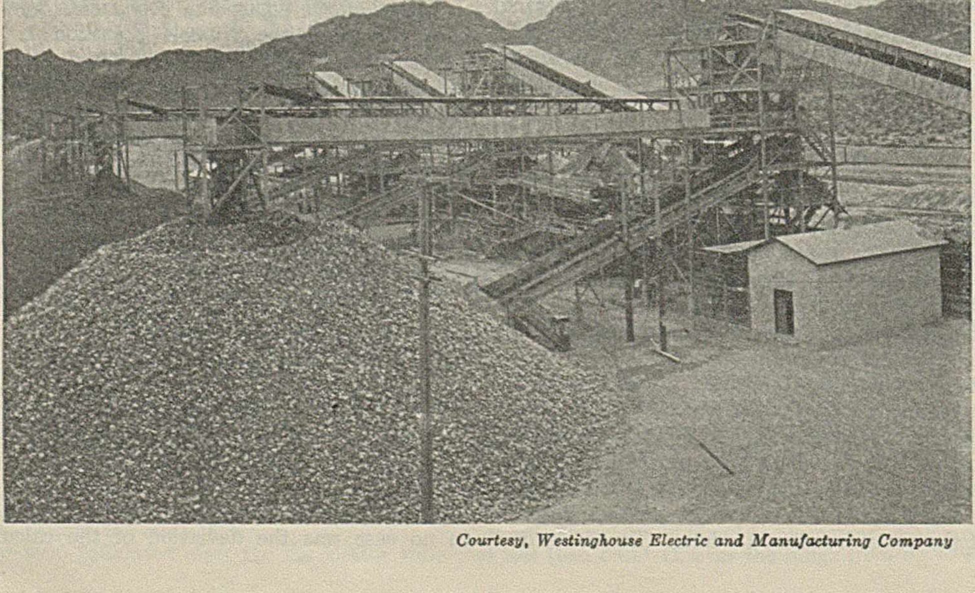
RECEIVED January 10, 1934. Presented before the session on Principles of Chemical Engineering at the meeting of the American Institute of Chemical Engineers, Roanoke, Va., December 12 to 14, 1933; abridged.



Courtesy, Westinghouse Electric and Manufacturing Company

Heat Transfer by Condensing Vapor on Vertical Tubes

C. G. Kirkbride, Standard Oil Company (Indiana), Whiting, Ind.

Data are presented on liquid films flowing down vertical walls. Film thicknesses for isothermal flow are measured and correlated with the dimensionless groups $2m^3\rho^2g/C^2$ and $4C/\mu$.

Data available in the literature on heat transfer by condensing vapor on vertical surfaces were correlated by the coördinates $h_m\left(\frac{\mu^2}{k^3\rho^2g}\right)^{1/3}$ *and* $\left(\frac{W}{\mu D}\right)_b$ *which are suggested by the Nusselt equation for viscous flow of condensate films. While the data of certain investigators appear to check the Nusselt theoretical equation for values of $4C\mu$ less than 2500, above this value the data in the literature on condensation indicate that it is probably no longer valid but instead gives results that are too low.*

VERTICAL-tube condensers are not as common in industrial practice as horizontal-tube condensers. This is due to three important reasons: Tube bundles cannot be "pulled" for cleaning as easily as horizontal tubes, less is known about predicting heat transfer coefficients for vertical tubes, and it is believed by many that lower coefficients of heat transfer are obtained with vertical tubes than with horizontal tubes. Where cleaning problems do not limit the design, it seems that the vertical-tube condenser deserves more serious consideration, and consequently an accurate method of predicting heat transfer coefficients for vertical tubes becomes of considerable importance. A method which is valid for all rates of condensation has not yet been presented in the literature, but several excellent papers dealing with this subject have been published.

Nusselt (*10*) developed the theoretical equation:

$$h_m = 0.943\left(\frac{k^3\rho^2\lambda g}{\mu L(t_c - t_w)}\right)^{1/4} \qquad (1)$$

for computing the average heat transfer coefficient, h_m, over the tube length, L, where the condensate flows down the tube in viscous motion. The thermal conductivity, k, the density, ρ, and the viscosity, μ, of the condensate are taken at the arithmetic average of the tube-wall temperature, t_w, and of the condensate film surface temperature, t_c. The heat absorbed above t_c, per unit mass of condensate, is equal to the latent heat of condensation plus the sensible heat of the vapor[1] and is represented by λ. The acceleration due to gravity, g, is 4.18×10^8 feet per hour per hour (980 cm. per second per second) at sea level.

Jakob and Erk (*6*) presented experimental results on condensing steam on a short vertical tube (46.6 cm. or 18.35 inches). They observed that Nusselt's theory gave only fair agreement. Their results, which were lower than predicted by Equation 1, varied 100 per cent at times from theoretical results. Unfortunately they did not present their data in detailed form, so that a further analysis is difficult.

Badger, Monrad, and Diamond (*1*) presented data taken on condensing diphenyl on a vertical tube. In a paper by Monrad and Badger (*9*) an attempt was made to correlate the data with Nusselt's equation (*1*). They pointed out that the data were at times 400 per cent higher than predicted by Nusselt's theory. The reason for this was given as turbulence in the condensate film which Nusselt had assumed did not exist. They observed a general trend of increasing heat transfer coefficients with increasing temperature differences but were apparently unable satisfactorily to correlate the data so that they could be applied generally.

Callendar and Nicolson (*2*) presented data taken on condensing steam inside of a short vertical tube (2 feet or 61 cm.). Their investigation was made in order to determine the amount of condensation in the cylinders of steam engines, but the data are applicable to the present subject.

Jordan (*7*) has presented data on a vertical tube one meter (3.3 feet) in length. Monrad and Badger showed that these data checked Nusselt's equation only qualitatively.

The major portion of data on condensing vapors on vertical tubes in the literature are higher than predicted by Nusselt's theory. Two different explanations have been proposed for these results. The first and probably the correct one is turbulence in the condensate film. The second is that drops form on the tube surface and, upon becoming large enough, drain from the tube in streams. Schmidt, Schurig, and Sellschopp (*11*) presented pictures to substantiate this explanation. They pointed out that it was necessary, however, to have a highly polished surface or a film would form. They condensed steam on a highly polished copper surface but noticed that, as the surface became slightly oxidized, film condensation occurred.

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[1] Nusselt considered the special case of condensing saturated vapor, but, if superheated vapor is condensed, the superheat must be added.

Table I. Properties of Oils, Diphenyl, and Water

Liquid	Viscosity 100° F.	Viscosity 80° F.	Viscosity 70° F.	Density 60° F.	Thermal Conductivity 100° F.	Thermal Conductivity 70° F.
	Centipoises	Centipoises	Centipoises	Lb./cu. ft.		
Oil 1	11.3	17.6	23.5	54.9	$k = \frac{0.0677}{\text{sp. gr. } 60°/60°}$	$[1 - 0.0003(t - 32)]$
Oil 2	23.6	49.0	75.0	55.8	$k = \frac{0.0677}{\text{sp. gr. } 60°/60°}$	$[1 - 0.0003(t - 32)]$
Oil 3	1.15	1.95	2.80	51.2	$k = \frac{0.0677}{\text{sp. gr. } 60°/60°}$	$[1 - 0.0003(t - 32)]$
Oil 4	0.49	0.56	0.62	46.2	$k = \frac{0.0677}{\text{sp. gr. } 60°/60°}$	$[1 - 0.0003(t - 32)]$
Water	0.68	0.86	0.98	62.3	0.36	0.34
	600° F.	400° F.	200° F.	400° F.		
Diphenyl	0.24	0.39	1.15	55.2	$= 0.0035\, C_p \left(\frac{\rho}{M}\right)^{1/3}$	

Wulfinghoff (*12*) claims "drop-forming" condensation does not exist in industry because too low a condensate rate and too smooth a surface are required. This is in accordance with observations made by the author on water, gasoline, and α-bromonaphthalene. Very smooth glass tubes were used but drop-forming condensation occurred only with steam and at very feeble condensate rates. Since, in industrial practice, low condensate rates are not common, the possibility of drop-forming condensation is not favorable (see also citation *4*). It was observed that at the top of the tubes clear films existed and a few inches from the top the formation of ripples or waves began. Upon approaching the bottom, the waves became closer together until near the bottom the films were in a violent disturbance which had the appearance of turbulence.

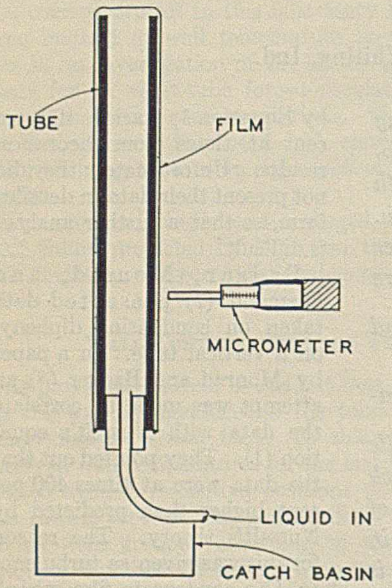

FIGURE 1. APPARATUS FOR MEASURING FILM THICKNESS

Since the literature contains so little information on condensation on vertical tubes and on liquid films flowing down vertical surfaces, it was decided to investigate this subject and attempt to develop a reliable method for predicting heat transfer coefficients for vapors condensing on vertical tubes. Data were taken on film thicknesses for isothermal flow, and were correlated by means of a dimensionless equation.

FILM THICKNESS

The thickness of a liquid layer on a vertical surface under conditions of viscous motion is given by the theoretical equation:

$$m = \left(\frac{3C\mu}{\rho^2 g}\right)^{1/3} \qquad (2)$$

If the amount of liquid flowing should become great enough, it might be expected that the layer would become turbulent, and the criterion for this change should be the Reynolds number which, for flow of liquid layers, can be expressed:

$$Re = \frac{4m\rho V}{\mu} = \frac{4C}{\mu}$$

Equation 2 can be rewritten in terms of C/μ to assist in contrasting the regions of viscous and turbulent motion as:

$$m\left(\frac{\rho^2 g}{\mu^2}\right)^{1/3} = \left(\frac{3}{4}\right)^{1/3}\left(\frac{4C}{\mu}\right)^{1/3} = 0.908\left(\frac{4C}{\mu}\right)^{1/3} \qquad (2a)$$

To compare the results with flow in pipes, it is desirable to derive from this equation a friction factor in the Fanning equation:

$$\Delta h = \frac{fLV^2}{2gm} \qquad (3)$$

Noting that for a vertical film, $\Delta h = L$, and $V = C/m\rho$,

$$f = \frac{2gm^3\rho^2}{C^2} \qquad (3a)$$

and this quantity is a function of Reynolds number, $4C/\mu$. For viscous flow this function is obtained by rearranging Equation 2 as follows:

$$f = \frac{2gm^3\rho^2}{C^2} = 24\left(\frac{4C}{\mu}\right)^{-1} \qquad (4)$$

To obtain data to compare with this equation, the phenomenon of condensate flowing down a vertical tube was reproduced artificially with a simple apparatus shown diagrammatically in Figure 1. The liquid under study was passed up through the vertical tube and down the outer wall. It was caught in a catch basin over a given period of time and weighed to 0.01 pound. The thickness of the liquid film on the outside of the tube was measured with a micrometer. The thickness was taken as that at which permanent contact was made between the liquid and micrometer. The film thickness measured was therefore the maximum and not the average. Where there is no disturbance on the film surface, the maximum thickness will be equal to the average, but such is not always the case. Four hydrocarbon oils and water were studied under isothermal conditions. Their properties are given in Table I.

When taking the data, it was made certain that the film thickness was constant all around the tube, and then all observations were made from one location of the micrometer. Observations were made at various points for each liquid varying from 1 to 2.5 feet (30 to 76 cm.) from the top of the tube, but the thickness was not found to be a function of the height.

The observed data are plotted in Figure 2 as f vs. $Re/4$ and are compared to Equation 4.[2] It is seen that the agreement with the theoretical equation is good up to a value of $Re = 8$. At this point, apparently, the ripples cause a difference in maximum and average film thicknesses, so that generally higher results were obtained above this value. Were it not for the data of Hopf (*5*) and those of Cooper, Drew, and McAdams (*3*), the theoretical equation might, on the basis of the present data, be questionable above a value of $Re = 8$. It is not possible, moreover, to determine the critical value of $4C/\mu$ from the data.

More exact data are necessary, and there are at least two methods which might be used with considerably more success than that employed by the author. The first uses a photoelectric cell. A light is directed on a group of lenses which centralize the light rays into a fine beam. The beam is directed through the condenser tube and condensate film, and finally on the photoelectric cell. The current produced in the photoelectric cell circuit is measured, and by use of a calibration curve the film thickness is obtained. The liquid must have considerable color for this method to be employed with success. The second method makes use of an interferometer, one beam of light passing through the air and the other through the tube and liquid film. The band widths are measured, and after calibration of the apparatus the actual thickness can be determined.

CORRELATION OF HEAT TRANSFER DATA

The Nusselt equation for condensation on vertical surfaces was derived by expressing the heat transfer coefficient at any point as equal to the thermal conductivity of the condensate divided by the condensate layer thickness at that point. The point condition equation was then integrated over the length of the condenser, assuming a constant temperature difference. The condensate layer was assumed to be in

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[2] Tables giving the detailed data will appear in *Trans. Am. Inst. Chem. Engrs.*

viscous motion with a thickness given by Equation 2. If the layer should be in turbulent flow, its thickness would be greater than calculated by Equation 2, but its resistance to the flow of heat would doubtless be less. It is therefore desirable to express the Nusselt equation in terms of the Reynolds number for the condensate layer, so that the region of viscous motion, where condensation data may be expected to check the theoretical equation, will be clearly defined, and beyond that point an empirical correlation of data may be obtained.

In the derivation of the Nusselt equation, the mean heat transfer coefficient over the length of condenser was defined by the equation for the total heat transferred, q, per unit of periphery:

$$q = h_m \Delta t L = \lambda C$$

Substituting for $\lambda/\Delta t L$ its equivalent, h_m/C, in Equation 1 and rearranging, the following expression is obtained:

$$h_m \left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 0.925 \left(\frac{C}{\mu}\right)^{-1/3} \qquad (5)$$

This equation is also obtainable by dimensional analysis.

Although reliable data for condensation in the viscous range are lacking, it is felt that this equation may be used with a fair degree of confidence for values of $4C/\mu$ less than 2000, since data for layer thickness show good agreement with the theoretical equation for viscous flow. Furthermore, the fair check of condensation data on horizontal tubes (*8*) with the theoretical equation for viscous flow of the condensate is additional support for this region.

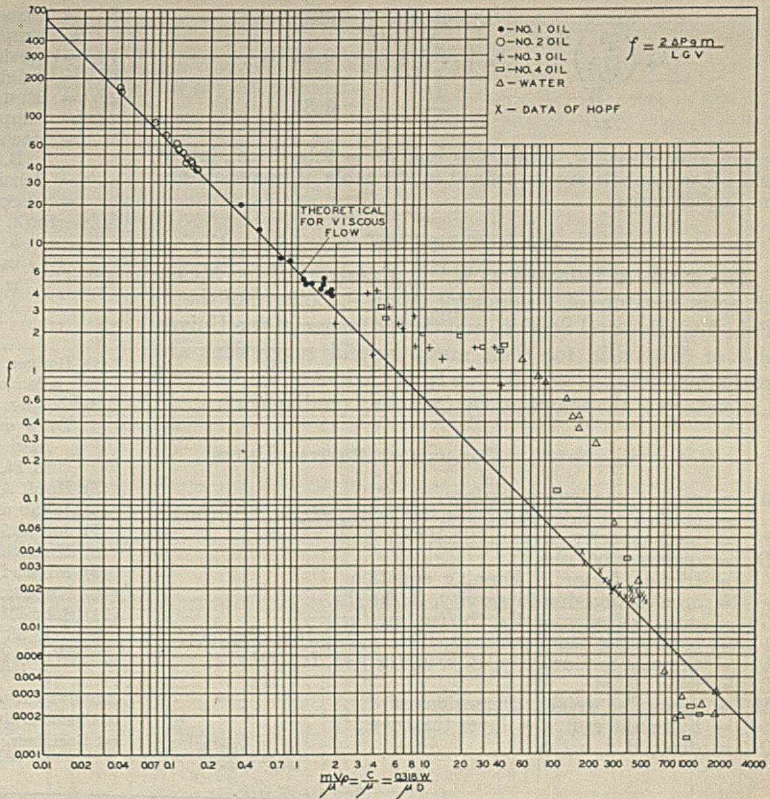

Figure 2. Variation of Friction Factor with Reynolds Number

For values of $4C/\mu$ above 2000, the type of flow of condensate is not certain. Most industrial practice occurs above this value, and according to data in the literature it is doubtful that Nusselt's equation applies.

The coördinates suggested by Equation 5 were used to correlate the data available in the literature in the turbulent region. The data of Badger, Monrad, and Diamond, of Callendar and Nicolson, and of Jordan were successfully correlated (Figure 3). One test was also available on a vertical-tube condenser being used to condense a light hydrocarbon in commercial service. No tube temperatures were taken, so the condensate film coefficient was computed from the over-all coefficient and a predicted coefficient on the water side. The coefficient on the water side was calculated from a curve which is a combination of the Morris-Whitman and Lawrence-Sherwood curves as presented by Kirkbride (*8*).

Over the range of the data the curve in Figure 3 has a slope of roughly 0.4 and can be expressed by dimensionless equations 6 and 6a:

$$h_m \left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 0.0076 \left(\frac{4C}{\mu}\right)_b^{0.4} \qquad (6)$$

$$h_m \left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 0.0084 \left(\frac{W}{\mu D}\right)_b^{0.4} \qquad (6a)$$

Such a curve indicates that the most economical type of condenser would be one which has rather long tubes. Considerably more data are needed, however, to determine the exact position of the curve in the turbulent region.

Figure 3 is plotted in terms of dimensionless groups, which must be expressed in consistent units. If the designer wishes to use certain engineering units, the following multiplying factors may be used:

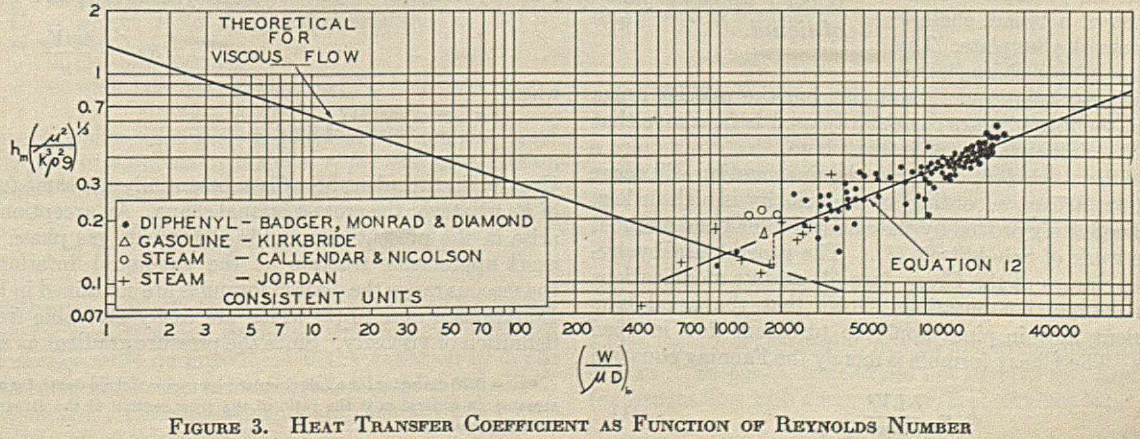

Figure 3. Heat Transfer Coefficient as Function of Reynolds Number

Using:	to obtain:	multiply by:
$h_m\left(\frac{z^2}{k^3\rho^2}\right)^{1/3}$	$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}$	0.00241
$\frac{W}{zD'}$	$\frac{4C}{\mu}$	6.31

where z = viscosity, centipoises and D' = tube diam., inches, and other symbols are as defined in the table of nomenclature, in English units.

ACKNOWLEDGMENT

The author is indebted to W. H. McAdams of the Massachusetts Institute of Technology, Allan P. Colburn of the du Pont Experimental Station, and O. A. Hougen of the University of Wisconsin for their many helpful suggestions and criticisms. Thanks are also due R. L. Geddes of the Research Laboratory of the Standard Oil Company (Indiana).

NOMENCLATURE (IN CONSISTENT BRITISH UNITS)

A = area of condensing surface, sq. ft.
C = condensate rate/unit perimeter = $W/\pi D$, lb./(ft.)(hr.)
c = heat capacity, B. t. u./(lb.)(°F.)
D = diameter of tube, ft.
f = friction factor in Fanning equation
g = acceleration due to gravity, ft./hr./hr.
G = mass velocity = $V\rho$, lb./(sq. ft.)(hr.)
h = condensing film coefficient, B. t. u./(sq. ft.)(°F.)(hr.)
k = thermal conductivity, B. t. u./(hr.)(sq. ft.)(°F./ft.)
L = tube length, ft.
M = molecular weight, dimensionless
m = hydraulic radius = layer thickness, ft.
Q = duty, B. t. u./hr.
S = cross-sectional area of flow, sq. ft.
t = temp., ° F.
V = mean linear velocity, ft./hr.
W = weight rate of condensation (per tube), lb./(hr.)(tube)
Δh = head loss, ft.
Δt = temp. difference through film, ° F.
λ = latent heat of condensation plus sensible heat of vapor, B. t. u./lb.
ρ = density, lb./cu. ft.
μ = viscosity, lb./(hr.)(ft.)
Subscript c = condensate
b = bottom of tube
m = average
w = wall

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RECEIVED November 27, 1933. Presented before the session on Principles of Chemical Engineering at the meeting of the American Institute of Chemical Engineers, Roanoke, Va., December 12 to 14, 1933; abridged.

Isothermal Flow of Liquid Layers

C. M. COOPER, T. B. DREW, AND W. H. MCADAMS, Massachusetts Institute of Technology, Cambridge, Mass.

From the data of six observers dealing with liquids flowing down the wetted smooth walls of vertical towers or over flat plates, it is concluded that the theoretical equations for steady isothermal stream-line flow apply for values of the Reynolds number, Re (=4mVρ/μ), below 2100. For Re greater than 2100, scattered data indicate that the Fanning equation, together with the friction factor curve for smooth circular pipes, may be used as an approximation. Data are not available for determining possible effects of gas velocity upon the flow of a contiguous thin layer of liquid.

THE use of vertical condensers and of wetted-wall towers in connection with such processes as absorption, rectification, and humidification lends importance to the relationships which describe the motion of thin layers of liquid flowing under the action of gravity over wetted surfaces. The radii of curvature of these surfaces are usually so great relative to the thickness of the fluid layer that the problem is essentially that of a broad, shallow, open stream on a flat plate. This case of flow in open channels may be found in any treatise on hydraulics, but the velocity range for which the formulas are customarily used is far above that met in the circumstances of interest here.

That either turbulent or viscous-laminar motion will occur in a shallow stream, according as the velocity is high or low, has been definitely proved by the classical color-band method, as in the work of Schoklitsch (*8*). The general use by hydraulic engineers of the Chezy formula and its modifications in open-channel computations shows that the usual laws of turbulent flow in pipes apply to turbulent flow in open channels. The Chezy formula is merely the Fanning equation

$$h = \frac{fLV^2}{2gm} \qquad (1)$$

solved for the mean linear velocity, V. Here

h = drop in head over length L
f = friction factor
m = hydraulic depth[1]
g = acceleration due to gravity

It is necessary to determine experimentally either f or the corresponding Chezy coefficient $\sqrt{2g/f}$. For each cross-sectional shape and kind of wetted surface, f is a function of the Reynolds number:

$$Re = \frac{4mV\rho}{\mu}$$

where

μ = viscosity
ρ = density of fluid

Usually, in turbulent flow f is substantially the same function of Re whatever the cross-sectional shape. An exception might arise in the present case if the contiguous gas phase should exert appreciable traction at the gas-liquid interface. In the viscous range the desired formulas are contained in Lamb's Equations 4 and 10 (*7*) which are easily derivable from the definition of viscosity. Since the pressure gradient as used by

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[1] m = 0.25 diameter for a full circular pipe; m = actual depth for a shallow stream; in general m is the ratio of the cross section of the stream to the wetted perimeter.

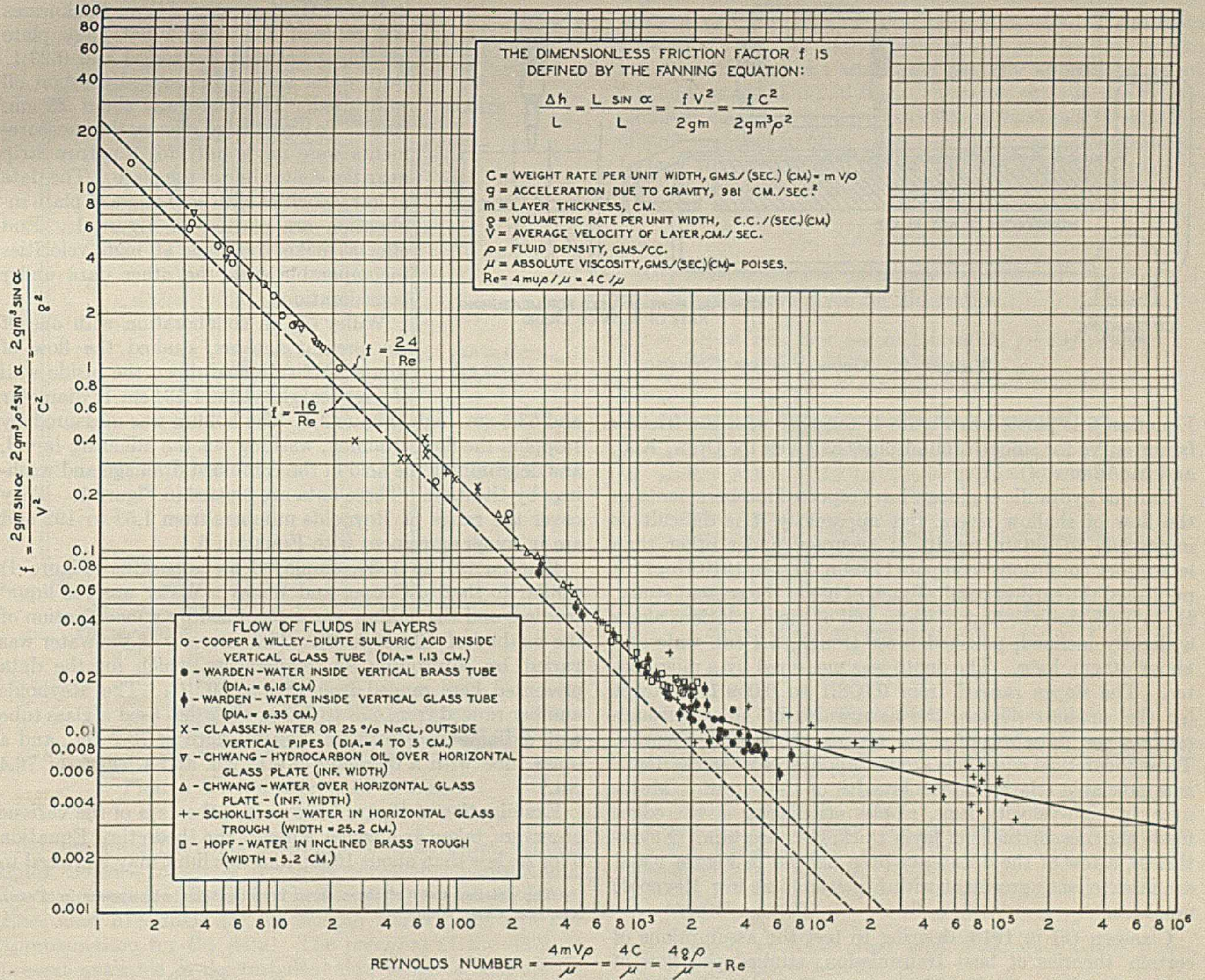

FIGURE 1. FANNING FRICTION-FACTOR *f* FOR LIQUID LAYERS *vs.* REYNOLDS NUMBER

Theoretically, for stream-line flow, $f = 24/Re$ on flat plates, and $f = 16/Re$ for circular pipes; the solid curve at the right is for smooth circular pipes.

Lamb in these equations is to be understood as the sum of the static pressure gradient and the effective gravitational force per unit volume (*7a*), a simple change in variable makes his Equation 4 become:

$$q = \frac{C}{\rho} = \frac{m^3 \rho g \sin \alpha}{3\mu} \tag{2}$$

where

q = volumetric discharge per unit breadth
C = weight rate of flow per unit breadth
m = depth of stream
μ = absolute viscosity
α = angle between the plate and the horizontal

Equation 2 applies when there is no traction at the gas-liquid interface; if a uniform tractive force, τ, per unit area acts on the exposed surface, the appropriate theoretical formula is:

$$q = \frac{C}{\rho} = \frac{m^3 \rho g \sin \alpha}{3\mu} - \frac{\tau g m^2}{2\mu} \tag{3}$$

τ is positive when it acts to oppose gravity. Both for turbulent and for viscous flow a suitable correction for change in kinetic energy must be introduced if the variation in depth is appreciable, and in short channels allowance for end effects may be needed. These refinements are generally not necessary in the case of thin films.

The theoretical velocity distribution corresponding to Equation 3 is:

$$u = \frac{\rho g \sin \alpha}{\mu}\left(my - \frac{y^2}{2}\right) - \frac{\tau y g}{\mu} \tag{4}$$

where

u = local linear velocity at height y above the bottom of the channel

The result corresponding to Equation 2 is obtained by setting $\tau = 0$ in Equation 4.

COMPARISON OF THEORY WITH DATA

For the study of the experimental data it is convenient to present the results in the form of a plot of f vs. Re, so that a comparison with the known curves for pipes may be readily made. By the substitution $mV = q$, which is the volumetric rate of flow per unit breadth, the formula used in computing f from q and the measured depth, m, is easily obtained from Equation 1:

$$f = \frac{2gm^3 \sin \alpha}{q^2} \tag{5}$$

where $\sin \alpha$ has replaced h/L. By the same substitution, Re is seen to be $4q\rho/\mu$, which does not involve m. Equation 2, for viscous flow with a free surface, is equivalent to:

$$f = 24/Re \tag{6}$$

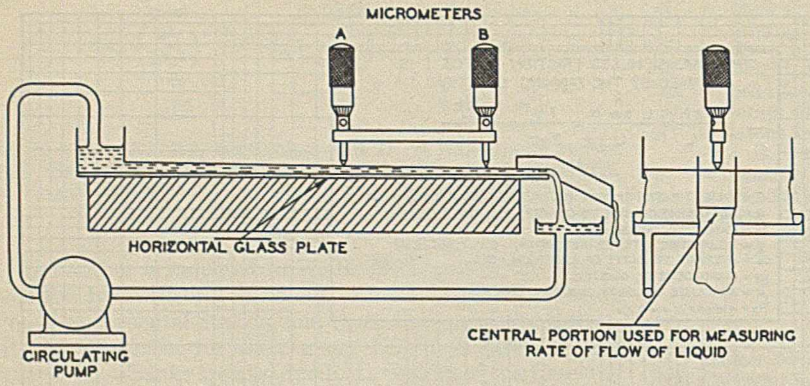

Figure 2. Apparatus of Chwang

Equation 6 is plotted in Figure 1, together with the friction factor curve for smooth round pipes as given by Drew, Koo, and McAdams (*4*).

Various hydraulic engineers have reported measurements on the flow of shallow rivers, but apparently it is difficult or impossible to obtain results of accuracy under other than laboratory conditions (compare Gibson, *5*). In 1910 Hopf (*6*) published the earliest results found of use in the present study. He investigated the flow of water and of sugar solutions along a slightly inclined, polished brass trough, 5.2 cm. wide and about 40 cm. long. The depth was measured by a micrometer. The slopes ranged from 0.008:1 to 0.059:1. Except for the smallest depths, the narrowness of Hopf's trough renders the data unsuited for testing the present theories. These theoretical equations are not applicable when the depth is appreciable relative to the breadth of the stream. Moreover, in high-velocity runs, ripples originating at the edges made the measurement of layer thickness uncertain. Nevertheless, a few of the data have been plotted in Figure 1 and are in excellent agreement with Equation 6 at low Reynolds numbers.

Claassen (*2*) in 1918, desiring to test the assumptions of certain theories of heat transmission, studied the flow of water, of molasses, and of 25 per cent sodium chloride solution down the outer vertical walls of a polished, an unpolished but bright, and a rough steel pipe. The outside diameter of the first pipe was 5.0 cm. and its wetted length 135.0 cm.; for the other pipes the diameter was 4.0 cm. and the wetted length, 196.0 cm. The holdup, from which the average layer thickness could be computed, was determined by stopping the flow, weighing the drainage, and adding to the weight thus obtained the weight of the liquid adhering to the surface. The latter quantity was found by wiping the surface with a tared towel and reweighing the towel. Unfortunately, in more than half of his runs, Claassen either used molasses of unrecorded viscosity or operated at such a high inlet temperature that cooling by evaporation vitiated the results. Hence it is permissible to show but few of his data in Figure 1. They are not very consistent with themselves, but six of the nine points are close to the theoretical curve.

In 1920 Schoklitsch (*8*), in the course of an extensive series of experiments on the flow of both clear and muddy water in shallow streams, repeated and extended the experiments of Hopf. He used a trough 25.5 cm. wide with a plate glass floor and varnished wood sides. The data are reported only in the form of a small graph in which the depth is plotted against the mean velocity. The slopes ranged from 0.0042:1 to 0.0340:1. A number of points have been read from the graph and transferred, after the necessary computations, to Figure 1. In judging these data, possible errors due to the method of transcription must be taken into account.

In 1928 Chwang (*1*), with an apparatus (Figure 2) similar to that of Hopf, measured layer thicknesses and rates of flow over a flat glass plate for slopes between horizontal and 0.23:1. Both water and a viscous hydrocarbon oil were used. The plate was about 25 cm. wide. To avoid edge effects, the measurements were made only for a narrow strip near the center line of the plate. The data at low velocities with zero angle of plate inclination are plotted in Figure 1. End effects make the runs at high velocities incomparable with the other data under consideration.

Willey (*3*), in collaboration with one of the present authors, studied the flow of dilute sulfuric acid down the inside wall of a vertical glass tube 1.134 cm. in diameter and 63.5 cm. high (Figure 3). The holdup was measured by stopping the flow, draining, washing out the adhering liquid, and determining the acid in the combined drainage and washings by titration. These data are plotted in Figure 1. They cover the range of Reynolds numbers from 1.53 to 192 and are in rough agreement with Equation 6.

Warden (*9*), in 1930, employed an apparatus (Figure 4) similar to that of Cooper and Willey. Water was the liquid studied, and the holdup was determined by a modification of the method of Claassen (*2*). The viscosity of the water was varied by controlling its temperature, which for the data presented here ranged from 20° to 50° C. The Reynolds number ranged from 278 to 7330. Warden used a glass tube with a diameter of 6.35 cm. and a length of 73.2 cm., and a brass tube with a diameter of 6.18 cm. and a length of 76.4 cm.[2]

Examination of Figure 1 shows that the data of the various observers, taken as a whole, support the theoretical Equation 6 for *Re* less than about 1500; and this limit may be raised to

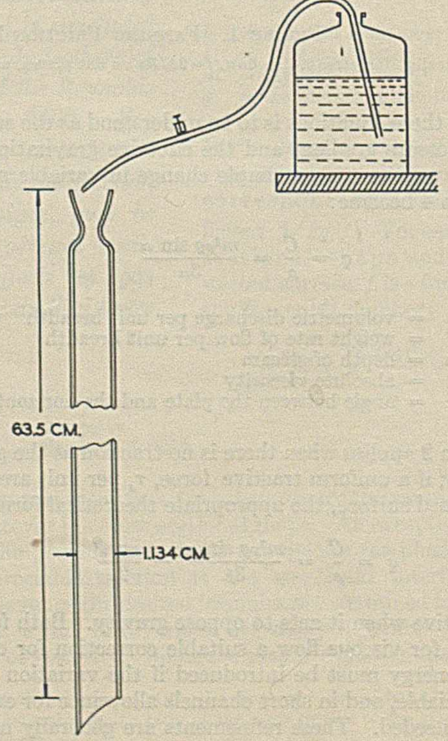

Figure 3. Apparatus of Cooper and Willey

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[2] The detailed data of these three investigations will appear in *Trans. Am. Inst. Chem. Engrs.*

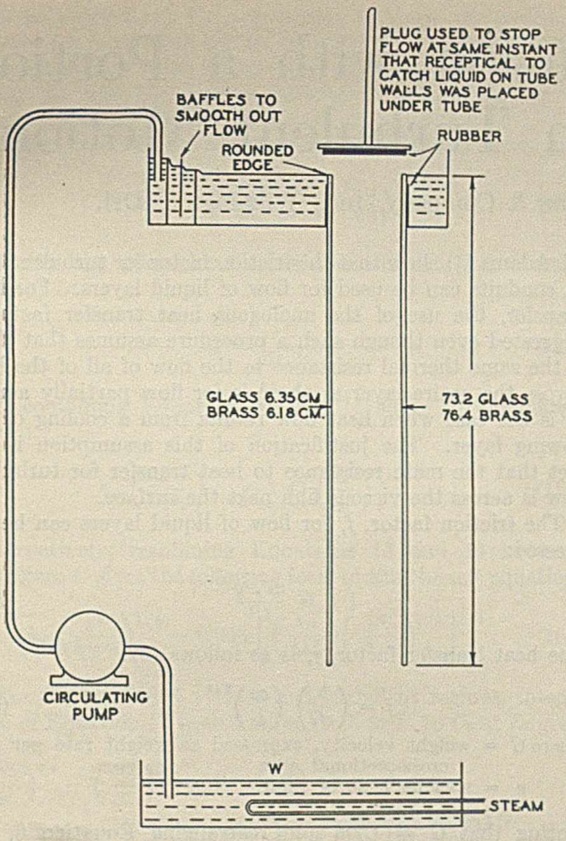

Figure 4. Apparatus of Warden

2100, the lower Reynolds criterion in circular pipes, without doing violence to any of the more pertinent measurements. For larger values of *Re* the friction factor curve given by Drew, Koo, amd McAdams (*4*) for smooth round pipes is a fair approximation for the data. The precision of the data at present available in the turbulent flow range is believed insufficient to warrant the presentation of a separate curve for flow on plates. It may therefore be concluded that for *Re* less than 2100 the theoretical viscous flow formulas may be used, while for *Re* greater than 2100 the Fanning equation together with the usual friction factor curves should give results of sufficient precision for many purposes. There is no indication from the data available that gas traction at the interface between gas and liquid has any appreciable effect on the flow of the liquid film. However, since in the experiments discussed no positive gas velocity was used, the absence of such an effect in other cases can by no means be assumed. In fact, it is well known that a sufficiently high gas velocity will entirely stop the flow of a liquid film.

NOMENCLATURE

Any consistent set of units may be employed; those of the C. G. S. system are given for illustration.

C = weight rate flow per unit breadth, grams/(sec.)(cm.)
f = friction factor, dimensionless
g = acceleration due to gravity, 981 cm./(sec.)(sec.)
h = drop in head, cm.
L = length of channel over which h is measured, cm.
m = hydraulic depth, cm.
q = volumetric rate of flow per unit breadth, cc./(sec.)(cm.)
Re = Reynolds number $4mV\rho/\mu = 4C/\mu$
u = local linear velocity, cm./sec.
V = mean linear velocity, cm./sec.
y = perpendicular distance from bottom of channel, cm.
α = angle of inclination to horizontal
ρ = density, grams/cc.
μ = absolute viscosity, grams/(cm.)(sec.)
τ = tractive force exerted by gas on interface, positive when opposing gravity, grams/sq. cm.

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Received December 8, 1933. Presented before the session on Principles of Chemical Engineering at the meeting of the American Institute of Chemical Engineers, Roanoke, Va., December 12 to 14, 1933; abridged.

Exhibit of U. S. Steel Corporation at Fourteenth Exposition of Chemical Industries

Calculation of Condensation with a Portion of Condensate Layer in Turbulent Motion[1]

Allan P. Colburn, E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

The paper by Kirkbride (*5*) attacks the problem of film-forming condensation by dimensional analysis, whereas it is felt that the complications of the case warrant an attempt at a more exact solution. Such a solution requires the determination of an expression for the condensation rate at each point down the length of the vertical condenser, and then an integration of the total condensation for the apparatus. Both steps are complicated for cases where the condensate layer becomes so thick near the lower end of the condenser that a portion of it flows in turbulent motion, but an attempt will be made to carry them out with several simplifying assumptions.

Point Condition Values of Heat Transfer Coefficient and Condensation Rate

For viscous flow of the condensate layer, the heat transfer coefficient at any point is equal to the quotient of the thermal conductivity, k, of the fluid divided by the layer thickness, m. This statement assumes that the amount of heat abstracted from or added to the condensate layer in passing the point is negligible compared to the heat conducted across the layer resulting from condensation. Nusselt (*7*) showed that, since for viscous flow the thickness is expressed,

$$m = \left(\frac{3C\mu}{\rho^2 g}\right)^{1/3} \tag{1}$$

where C = rate of flow of liquid layer, expressed as weight per unit time and unit periphery
μ = viscosity of liquid
ρ = density
g = acceleration due to gravity

the heat transfer coefficient for viscous flow, h, at any given point on a vertical surface is equal to:

$$h = \frac{k}{m} = k\left(\frac{\rho^2 g}{3C\mu}\right)^{1/3} \tag{2}$$

Rearranging and multiplying both sides by $\mu^{2/3}$:

$$h\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \left(\frac{\mu}{3C}\right)^{1/3} \tag{2a}$$

The differential rate of condensation, dC, over a differential length, dL, can be expressed:

$$dC = h\Delta t\, dL/\lambda \tag{3}$$

where λ = latent heat of vaporization
Δt = temp. drop across condensate layer

Substituting the value of h from Equation 2a in Equation 3:

$$dC = \left(\frac{\Delta t\, dL}{\lambda}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3}\left(\frac{\mu}{3C}\right)^{1/3} \tag{4}$$

For turbulent flow of the condensate layer the evaluation of the heat transfer coefficient is not so simple. In the absence of experimental data it is possible to make use of an analogy with the case of heat transfer between a fluid and the walls of a rectangular conduit with a large aspect ratio—i. e., ratio of width to heighth. Cooper, Drew, and McAdams (*4*) show that the friction factor for turbulent flow in conduits can be used for flow of liquid layers. For heat transfer, the use of the analogous heat transfer factor is suggested even though such a procedure assumes that there is the same thermal resistance to the flow of all of the heat across the entire layer as there is for flow partially across, as is the case when heat flow results from a cooling of the flowing layer. The justification of this assumption is the fact that the main resistance to heat transfer for turbulent flow is across the viscous film next the surface.

The friction factor, f, for flow of liquid layers can be expressed:

$$\tfrac{1}{2}f = \frac{m^3\rho^2 g}{C^2} \tag{5}$$

The heat transfer factor, j, is as follows (*3*):

$$j = \left(\frac{h}{cG}\right)\left(\frac{c\mu}{k}\right)^{2/3} \tag{6}$$

where G = weight velocity, expressed as weight rate per unit cross-sectional area
c = specific heat of fluid

Noting that $G = C/m$ and rearranging Equation 6, the following is obtained:

$$h = \frac{jcC}{m(c\mu/k)^{2/3}} \tag{7}$$

For turbulent flow in conduits it has been shown (*3*) that $\frac{1}{2}f = j$. Substituting this equality in Equation 5 and solving for m gives:

$$m = \left(\frac{jC^2}{\rho^2 g}\right)^{1/3} \tag{8}$$

Substituting Equation 8 in 7 and collecting variables into dimensionless groups:

$$h\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \left(\frac{j}{2}\right)^{2/3}\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{4C}{\mu}\right)^{1/3} \tag{9}$$

By analogy with turbulent flow in conduits,

$$j = a\left(\frac{4C}{\mu}\right)^{-n} \tag{10}$$

The constants a and n are tentatively taken as 0.027 and 0.2; then,

$$h\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 0.056\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{4C}{\mu}\right)^{0.2} \tag{11}$$

The differential rate of condensation for turbulent flow becomes:

$$dC = 0.056\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{\Delta t\, dL}{\lambda}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3}\left(\frac{4C}{\mu}\right)^{0.2} \tag{12}$$

Integration of Total Condensation and Determination of Average Heat Transfer Coefficient

An exact general integration of Equations 4 and 12 over their respective ranges is difficult, since the thermal properties and temperature difference usually vary along the length of the condenser. An exact integration of a particular problem

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[1] Presented as discussion of the three preceding papers at the session on Principles of Chemical Engineering at the meeting of the American Institute of Chemical Engineers, Roanoke, Va., December 12 to 14, 1933.

can be carried out by a graphical method. Sufficient accuracy for most work can be achieved by taking the thermal properties at a mean temperature (*3*) and assuming a constant Δt, and the general integration will be carried out assuming them constant.

For viscous region, integration of Equation 4 gives:

$$C^{4/3} = \frac{4}{3}\left(\frac{\Delta t L}{\lambda}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3}\left(\frac{\mu}{3}\right)^{1/3} \qquad (13)$$

Defining the mean heat transfer coefficient, h_m, over the length, L:

$$h_m = \frac{\lambda C}{\Delta t_m L} \qquad (14)$$

and combining Equations 13 and 14 so as to eliminate L gives:

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 1.47\left(\frac{4C}{\mu}\right)^{-1/3} \qquad (15)$$

Alternatively, combining Equations 13 and 14 so as to eliminate C gives the following form of the Nusselt equation:

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = 0.945\left[\left(\frac{\lambda\mu}{\Delta t L}\right)\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}\right]^{1/4} \qquad (16)$$

For the combined viscous and turbulent regions, integration of Equation 12 from a value of C_c at L_c to C_b at L_b gives:

$$\left(\frac{4C_b}{\mu}\right)^{0.8} - \left(\frac{4C_c}{\mu}\right)^{0.8} = 0.18\left(\frac{c\mu}{k}\right)^{1/3} \left[\left(\frac{\Delta t L_b}{\lambda\mu}\right) - \left(\frac{\Delta t L_c}{\lambda\mu}\right)\right]\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} \qquad (17)$$

The critical Reynolds number, $4C_c/\mu$, at which the type of flow changes from viscous to turbulent may vary over quite a range, as for flow in pipes. While the value is not known accurately, it will be tentatively assumed as follows:

$$4C_b/\mu = b = 1600 \qquad (18)$$

The value of $\Delta t L_c/\lambda\mu$ is obtained from Equation 13 when the above equality for $4C_c/\mu$ is substituted, giving:

$$\left(\frac{\Delta t L_c}{\lambda\mu}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} = \frac{1}{4}\left(\frac{3b}{4}\right)^{4/3} = 3200 \qquad (19)$$

Substituting Equations 18 and 19 in 17 gives:

$$\left(\frac{4C_b}{\mu}\right)^{0.8} - 364 = 0.18\left(\frac{c\mu}{k}\right)^{1/3}\left[\left(\frac{\Delta t L_b}{\lambda\mu}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} - 3200\right] \qquad (20)$$

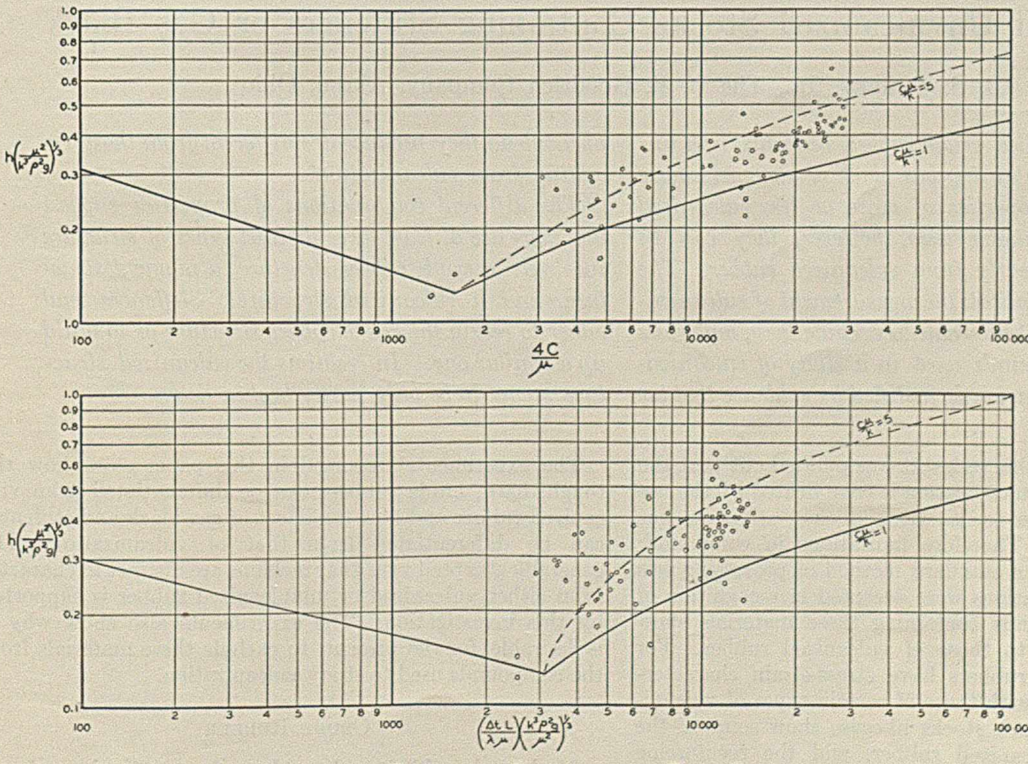
Combining Equation 20 with 14 so as to eliminate L gives:

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \frac{4C_b/\mu}{\frac{22}{(c\mu/k)^{1/3}}\left[(4C_b/\mu)^{0.8} - 364\right] + 12{,}800} \qquad (21)$$

Alternatively, combining Equation 20 with 14 so as to eliminate C:

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \left(\frac{\lambda\mu}{\Delta t L_b}\right)\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}\left[0.059\left(\frac{c\mu}{k}\right)^{1/3} \left(\frac{\Delta t L_b}{\lambda\mu}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} - 190\left(\frac{c\mu}{k}\right)^{1/3} + 120\right]^{1.25} \qquad (22)$$

Equations 21 and 22 can also be expressed generally by including the constants a and b from Equations 10 and 18, respectively, rather than substituting numerical values, as follows:



A. When number and diameter of tubes are assumed

B. When length of tubes is assumed

FIGURE 1. CONDENSATION FILM COEFFICIENT

c = specific heat of condensate, P. c. u./lb.
C = condensate, lb./(hr.)(ft. perimeter of tubes), at bottom of condenser
g = acceleration of gravity, 4.18×10^8 ft./(hr.)(hr.)
h = condensing vapor-film heat transfer coefficient, P. c. u./(hr.)(sq. ft.)(° C.).
k = thermal conductivity of condensate, P. c. u./(hr.)(sq. ft.)(° C./ft.).
L = length of tubes, ft.
Δt = temp. difference between vapor and tube surface, ° C.
λ = latent heat of vaporization, P. c. u./lb.
μ = viscosity of condensate, lb./(hr.)(ft.).
ρ = density of condensate, lb./cu. ft.
(Any other set of self-consistent units may also be used.)

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \frac{4C_b/\mu}{\left[\frac{1.25}{(a/2)^{2/3}(c\mu/k)^{1/3}}\right]\left[(4C_b/\mu)^{0.8} - b^{0.8}\right] + \left(\frac{3b}{4}\right)^{4/3}} \quad (23)$$

$$h_m\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3} = \left(\frac{\lambda\mu}{\Delta t L_b}\right)\left(\frac{\mu^2}{k^3\rho^2 g}\right)^{1/3}\left[1.25\left(\frac{a}{2}\right)^{2/3}\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{\Delta t L_b}{\lambda\mu}\right)\left(\frac{k^3\rho^2 g}{\mu^2}\right)^{1/3} - 0.26\left(\frac{a}{2}\right)^{2/3}\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{3b}{4}\right)^{4/3} + \left(\frac{b}{4}\right)^{0.8}\right]^{1.25} \quad (24)$$

Figure 1*A* shows plots of Equations 15 and 21 and data on condensing diphenyl (*1*). While the data scatter considerably, they show, in general, fair agreement with the predicted line for the turbulent region for a value of $c\mu/k = 5$. Inasmuch as the value of $c\mu/k$ of water is equal to 1.8 at 100° C. and 1.0 at 190° C., data on condensing steam (under film-forming conditions rather than dropwise) would be expected to lie near the lower curve shown on the figure. This plot is convenient to use where the number and diameter of tubes can be conveniently assumed, thus fixing the value of $4C/\mu$ and the length is left variant. Alternatively, Figure 1*B* shows a plot of Equations 16 and 22 and the same data. This plot is convenient to use where the condenser length is fixed, and the number and diameter of tubes are left variant. In the latter case it is necessary to estimate the mean temperature difference across the condensate layer, which may require cut-and-try calculations, based on the value for the over-all logarithmic mean temperature difference. Since condenser lengths are more often fixed than the number and diameter of the tubes, Figure 1*B* will be preferred by many engineers.

High vapor velocities in a downward direction will decrease the film thickness and increase the heat transfer coefficient thereby; they may also cause a transition from viscous to turbulent flow before the value of $4C/\mu$ becomes 1600. It is emphasized also that these equations do not hold under conditions causing drop-forming condensation (*6*), but the evidence available indicates that film-forming condensation predominates with organic materials. It is therefore believed that the figures presented make possible a conservative determination of the heat transfer surface.

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Received January 20, 1934. This paper is Contribution 142 from the Experimental Station of E. I. du Pont de Nemours & Company, Inc.

The Chemistry of Soft Rubber Vulcanization

III. Comparison of Vulcanized Rubber with Unmilled Crude Rubber Reclaims, and Unvulcanized Stocks Containing Stiffeners or Gas Black

B. S. Garvey, Jr., The B. F. Goodrich Company, Akron, Ohio

Tough unmilled crude rubber, reclaims, and uncured stocks containing gas black or stiffeners have some of the properties of more or less vulcanized rubber. By suitable tests, however, they can be differentiated clearly from vulcanized rubber. The similarities complicate the measurement of vulcanization and make it desirable to exclude these materials from the compounds used in a study of vulcanization. This exclusion is justified by evidence that the phenomena they produce are different from those resulting from vulcanization.

The different combinations of properties suggest that there are at least three distinct types of structure involved: a crude rubber structure, a pigment structure, and a vulcanized structure. Stiffeners tend either to retain the crude rubber structure or to build up a similar one. In reclaims the vulcanized structure seems to be only partly broken down.

In Part I (*1*) of this series[1] it was pointed out that the measurement of vulcanization is complicated by the use of unmilled rubber (e. g., latex stocks), stiffeners, gas black, and reclaims. Therefore limitations in compounding were accepted and a standard method of processing was adopted. These limitations were accepted in recognition of the fact that compounds containing these materials show some properties akin to those of vulcanized rubber. For example, some crude rubbers have stress-strain characteristics almost identical with those of certain types of vulcanizate. Uncured gas black stocks likewise show some of the characteristics of vulcanized rubber, and the reënforcing action of gas black is sometimes spoken of as a sort of vulcanization (*2*). Such limitations are desirable only if it can be shown that the phenomena excluded are different from those being studied.

The experiments[2] reported in this paper show how the tough, hard, crude rubbers can be differentiated from vulcanized rubber and how the effect of gas black and stiffeners can be differentiated from that of vulcanization. The generally accepted view that reclaims are distinct in character from either vulcanized or unvulcanized rubber is supported by this investigation. The experiments also show why it is desirable, for the present, to exclude these materials from the compounds used to study vulcanization.

Crude Rubber

Moderately milled crude rubbers showed no signs of vulcanization by any of these tests. They gave results similar to those of unvulcanized rubber-sulfur compounds (*1*). With tough crude rubber which was unmilled, or only slightly

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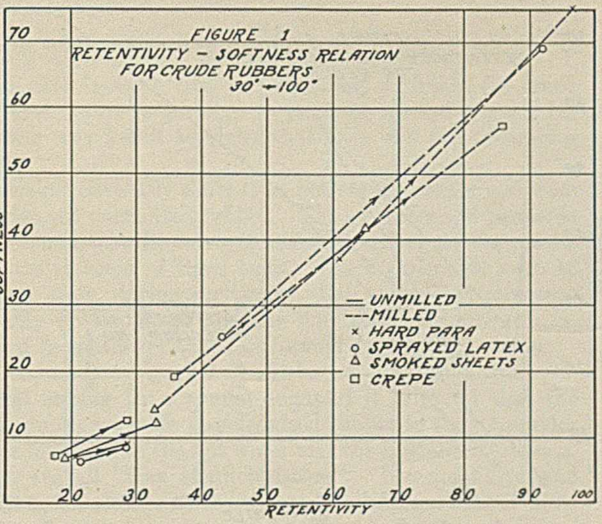
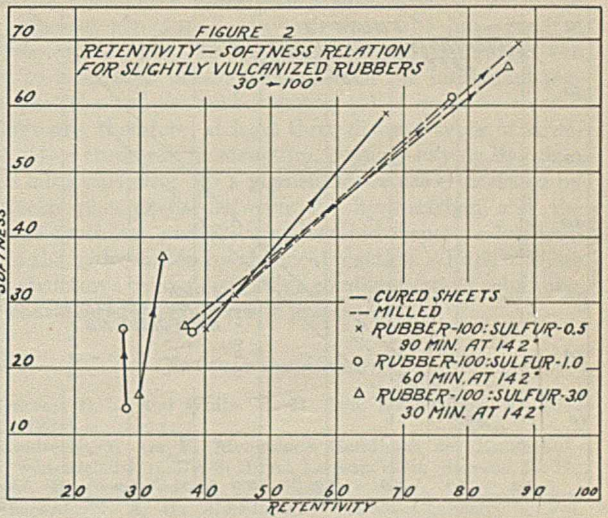
[1] Part II appeared in Ind. Eng. Chem., 25, 1292 (1933).

[2] The tests used were described in detail in the previous paper (*1*).





milled, the properties were in some respects very similar to those of milled rubber which had been slightly vulcanized. The test data for four such rubbers are given in Table I.

In the hot water test, crude Para and sprayed latex did not break. After slight mastication all crude rubbers broke in this test. On the mill, tough crude and very slightly vulcanized milled rubbers behaved much the same although differences were readily detected in samples in which vulcanization had progressed a little farther. The values for thermoplasticity, hysteresis set, and hysteresis/set modulus for crude rubber are about the same as those for very slightly vulcanized rubber. The tensile strength and modulus figures for crude rubber, on the other hand, sometimes reach values which can be attained with milled rubber only after a rather high degree of vulcanization. In fact some stocks which were fairly well vulcanized when judged by all other tests showed tensile values lower than those for crude hard Para or sprayed latex rubber. Apparently tough crude rubbers cannot be distinguished from slightly vulcanized rubbers by any of these tests.

The retentivity softness relations at 30° and 100° C., however, differentiate sharply between tough crude and scorched rubbers. This is shown by Figures 1 and 2. The slope of the curve for crude rubber is considerably less, and it increases when the rubber is milled. The slope of the curve for the slightly vulcanized sheets is considerably greater and it decreases when the rubber is milled.

By this relation tough crude rubber can be classified positively as unvulcanized in spite of the similarity of some of its properties to those of scorched, milled rubber.

STIFFENERS

Stiffeners, such as benzidine and magnesia, were added to crude rubber with varying degrees of milling. The following compounds were tested:

1. First latex crepe, 100; benzidine, 1. The stock was mixed on the mill with light mastication of the rubber. It was also tested after remilling for 10 minutes.
2. Smoked sheets No. 1, 100; benzidine, 1. The stock was mixed on a very hot mill with minimum mastication of the rubber and a tensile sheet molded 30 minutes at 105° C.
3. Smoked sheets No. 1, 100; light calcined magnesia, 1. The stock was mixed in an internal mixer with minimum mastication of the rubber. It was also tested after being remilled for 10 minutes.
4. Smoked sheets No. 1, 100; light calcined magnesia, 1. The stock was mixed on a very hot mill with minimum mastication of the rubber and a tensile sheet molded 30 minutes at 105° C.

TABLE I. VULCANIZATION TESTS ON UNMILLED CRUDE RUBBER

	QUALITATIVE TESTS				PLASTICITY TESTS							HYSTERESIS TESTS					STRESS-STRAIN TESTS			
													Modulus at 300%		Set/modulus		Modulus at 500%		Ultimate tensile	
RUBBER	Ice water	Hot water	Milling	Solubility	R_{30}	R_{100}	S_{30}	S_{100}	P_{30}	P_{100}	$\frac{P^2_{100}}{P_{30}}$	Set	*Kg./cm.²*	*Lb./in.²*	*Kg.*	*Lb.*	*Kg./cm.²*	*Lb./in.²*	*Kg./cm.²*	*Lb./in.²*
Hard Para	0	1	1	2	20.5	28.4[a]	6.7	8.7	1.4	2.5	6.25[a]	90[a]	4.5	64[a]	20.2	1.41[a]	10.5	150[a]	79	1125[a]
Smoked sheets	0	0	1	1	18.9	33.0[a]	6.4	11.9	1.2	3.9	12.7[a]	130[a]	4.9	70[a]	19.5	1.37[a]	3.5	50[a]	14.6	208[a]
Crepe	0	0	1	1	17.3	28.4[a]	7.0	12.6	1.2	3.6	10.8[a]	100[a]	4.2	60[a]	26.4	1.85[a]	3.5	50[a]	31.4	446[a]
Sprayed latex	0	1	1	1	21.3	28.5[a]	6.2	8.6	1.3	2.5	6.7[a]	100[a]	5.1	73[a]	23.8	1.67[a]	8.8	125[a]	88	1250[a]

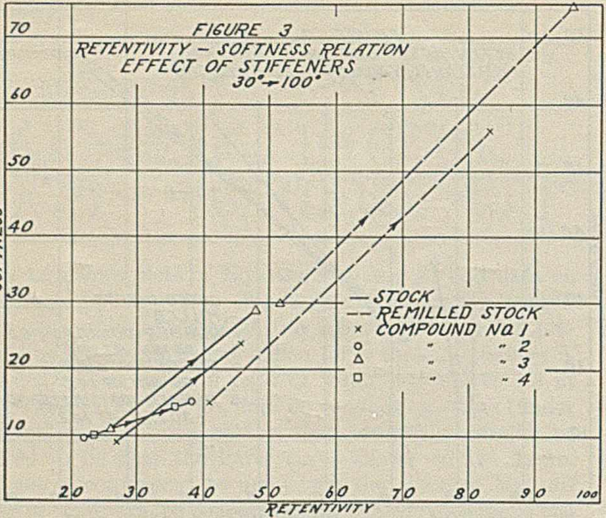
[a] Measurements suitable for use without the others.

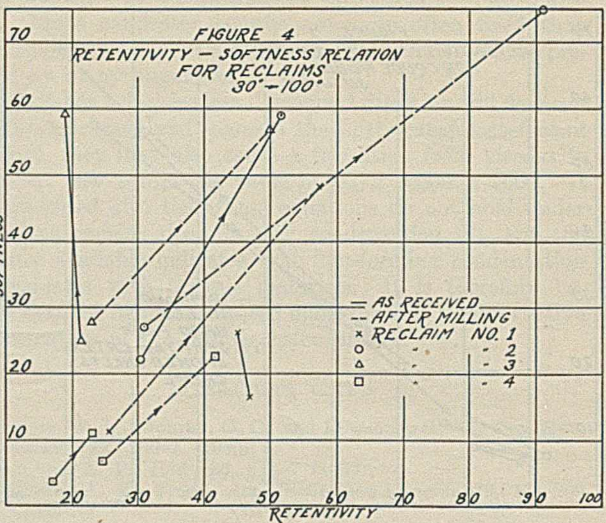
TABLE II. VULCANIZATION TESTS ON GAS BLACK STOCKS

(A, rubber 100, gas black 50, factory mixed; B, rubber 100, gas black 50, sulfur, 3)

		QUALITATIVE TESTS				PLASTICITY TESTS							HYSTERESIS TESTS					STRESS-STRAIN TESTS			
														Modulus at 300%		Set/modulus		Modulus at 500%		Ultimate tensile	
STOCK	CURE AT 142° C.[a]	Ice water	Hot water	Milling	Solubility	R_{30}	R_{100}	S_{30}	S_{100}	P_{30}	P_{100}	$\frac{P^2_{100}}{P_{30}}$	Set	*Kg./cm.²*	*Lb./in.²*	*Kg.*	*Lb.*	*Kg./cm.²*	*Lb./in.²*	*Kg./cm.²*	*Lb./in.²*
A	None	0	0	0	4	33.9	41.8[b]	3.7	10.9	1.2	4.6	17.6[b]	...	...	..	..	..	..	...	..	..
	30	0	0	0	4	37.4	37.0[b]	5.7	11.8	2.15	4.4	9.0[b]	195[b]	9.1	130[b]	21.4	1.50[b]	19.3[b]	275	28	400[b]
	120	0	0	0	4	36.5	39.0[b]	4.9	9.2	1.8	3.8	7.2[b]	185[b]	12.2	174[b]	15.1	1.06[b]	21.9[b]	325	30	425[b]
	240	0	0	0	4	37.5	34.0[b]	4.6	8.0	1.8	2.8	4.3[b]	160[b]	18.4	262[b]	9.1	0.64[b]	28.1[b]	400	35	500[b]
B	None	0	0	0	4	38.4	42.3[b]	6.8	26.1	2.6	11.0	46.5[b]	...	...	..	..	..	..	...	..	..
	30	0	1	2	4	30.7	29.8[b]	4.0	6.6	1.23	1.99	3.2[b]	125[b]	18.1	248[b]	7.1	0.50[b]	45.7[b]	650	56.2	800[b]
	60	0	1	3	4	39.8	30.5[b]	2.7	5.6	1.16	1.70	2.5[b]	100[b]	23.9	340[b]	4.1	0.29[b]	..	[c]	63.3	900[b]
	240	2	1	4	4	19.4	18.4[b]	2.0	2.4	0.40	0.46	0.46[b]	0.35[b]	44	625[b]	0.85	0.06[b]	..	[c]	140.6	2000[b]

[a] 142° C. = 287° F. = 40 pounds steam pressure.
[b] Measurements suitable for use without the others.
[c] Stock broke at 480 per cent elongation.





In all the tests these stocks gave results like those obtained with crude rubber which has been milled to some extent. Since the most sensitive test for vulcanization appears to be retentivity-softness curve, this is shown in Figure 3 for several stocks with stiffeners added. It will be noted (compare with Figures 1 and 2) that these curves are those for crude and not for vulcanized rubber.

Gas Black

With low loadings of black the stocks did not resemble vulcanized rubber but with higher loadings they did in some respects. In Table II data are given for a factory-mixed master batch containing 50 parts by weight of black on 100 of rubber. In the ice water, hot water, and milling tests the behavior was that of milled crude rubber. The solubility was that of a well-vulcanized rubber. The plasticity data were confusing and showed only that, if the gas black had any vulcanizing action, it was very small. The hysteresis set values were in the range given by milled crude rubbers. The modulus at both 300 and 500 per cent elongation was considerably higher than those found for any crude rubber and the tensile strength was much above that of milled crude rubber.

The same gas black master batch was then heated with 3 parts of sulfur so as to vulcanize the rubber slightly. The testing data are given in Table II. As compared with the unvulcanized master batch, marked differences were noted in the hot water test, the behavior on the mill, plasticity factors, set, modulus, and tensile strength.

Reclaims

Four types of reclaim were tested: (1) whole tire reclaim, alkali process, rubber value (estimated rubber content) 50 per cent; (2) tube reclaim, heater process, rubber value 62 per cent; (3) tube reclaim, special process, rubber value 68 per cent; and (4) boot and shoe reclaim, acid process, rubber value 38 per cent. The testing data are given in Table III.

The ice water test and solubility indicate a fairly high degree of vulcanization. In the hot water test these reclaims were similar to unvulcanized rubber. In the milling test a special class, 6, was necessary for the classification of reclaims. They behaved quite differently from crude rubber. They were all sticky, especially on a hot mill, and were either grainy and short or rough and nervy. The plasticities and thermoplasticities were mostly in the range of crude rubbers or slightly vulcanized rubbers. The hysteresis set and set/modulus values are in the range of slightly vulcanized rubbers as are the values for modulus and tensile strength.

The retentivity-softness relations were different from those for either vulcanized or unvulcanized rubber as is shown by the curves in Figure 4.

Discussion

Some of the tough crude rubbers resemble milled rubber with a rather high degree of vulcanization with regard to tensile and modulus characteristics. However, their behavior on the mill, solubility, plasticity, and hysteresis set are similar to those of milled rubber which has been only slightly vulcanized. Behavior on the mill, hysteresis set, and plasticity are all similar in that they involve what might be called the "flow characteristics" of the rubber. Comparing milled vulcanized rubber with tough, unmilled, crude rubber it is seen that the relation between the solubility and flow characteristics and the tensile properties are quite different. It has been shown that the two types can be sharply differentiated by the retentivity-softness relations. In the case of the slightly vulcanized rubber the effect of raising the temperature is predominantly to increase the softness with comparatively little effect on the retentivity. With crude rubber, on the other hand, raising the temperature causes a considerable increase in the retentivity.

In the earlier paper (*1*) the characteristics of vulcanized rubber were attributed to a mechanical structure developed by chemical reactions in the hydrocarbon. Similarly the pe-

Table III. Vulcanization Tests Applied to Reclaims

	Qualitative Tests				Plasticity Test							Hysteresis Tests					Stress-Strain Tests			
													Modulus at 300%		Set modulus		Modulus at 500%		Ultimate tensile	
No.	Ice water	Hot water	Milling	Solubility	R_{30}	R_{100}	S_{30}	S_{100}	P_{30}	P_{100}	$\frac{P^2_{100}}{P_{30}}$	Set	*Kg./cm.²*	*Lb./in.²*	*Kg.*	*Lb.*	*Kg./cm.²*	*Lb./in.²*	*Kg./cm.²*	*Lb./in.²*
1	3	0	6	3	47.0	45[a]	16.5	26.5	7.7	11.9	77[a]	110[a]	6.6	94[a]	16.6	1.17[a]	6.7[a]	96	6.7	96[a]
2	2	0	6	3	30.5	51.5[a]	22.0	59.2	8.6	30.5	108[a]	105[a]	4.0	57[a]	26.2	1.84[a]	4.5[a]	64	8.0	115[a]
3	2	0	6	3	21.6	19.0[a]	25.0	59.0	5.5	11.2	22.8[a]	60[a]	4.0	57[a]	15.0	1.05[a]	8.4[a]	120	17.5	250[a]
4	2	0	6	3	17.0	23.0[a]	3.7	10.8	0.66	2.5	9.5[a]	125[a]	11.25	160[a]	11.1	0.78[a]	...	[b]	14.0	200[a]

[a] Measurements suitable for use without the others.

[b] Broke at 375 per cent.

culiar properties of unmilled rubber may be attributed to a "crude rubber structure." This structure appears to be essentially different from the vulcanized structure.

The data indicate that stiffeners help to retain the crude rubber structure or possibly to build up a similar one. No evidence was found to show that they act as vulcanizing agents.

Reclaims obviously differ from both crude rubber and from unreclaimed vulcanized rubber. The softeners and pigments present undoubtedly have considerable effect on the results obtained in some of these tests. The experiments seem to indicate that, during reclaiming, the vulcanized structure is partly broken down and the flow characteristics are increased by softeners added or formed during the process.

When uncured gas black stocks are compared with vulcanized rubber in a similar manner, it is found that the black stocks resemble unvulcanized rubber in their behavior on the mill, and in the hot water and the hysteresis set tests. These are all "flow characteristics." The solubility and modulus are similar to those of well-vulcanized rubber while the tensile strength is similar to that of slightly vulcanized rubber. Here is a combination of properties which is different from that in either vulcanized or crude rubber. It seems, therefore, that there exists here a third type of structure, the "pigment structure." Investigators who have studied the reënforcing action of gas black generally attribute the effect to interfacial phenomena between the individual pigment particles and the rubber matrix (*3*).

There are, therefore, at least three distinct types of structure: (1) a crude rubber structure, possibly having its origin in the latex particles; (2) a pigment structure established by interfacial phenomena between the hydrocarbon and the pigment particles; and (3) a vulcanized structure built up within the hydrocarbon by chemical reaction. Each of these three structures causes distinctive combinations of solubility, flow characteristics, and tensile properties.

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Received September 28, 1933.

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IV. Vulcanizing Agents Other than Sulfur

The vulcanizing action of sulfur chloride, m-dinitrobenzene, selenium, tetramethylthiuram disulfide, and benzoyl peroxide has been investigated by the use of a set of tests developed for measuring the degree of vulcanization with sulfur-cured compounds. These tests show that all of these materials are true vulcanizing agents. Comparison of the various vulcanizates with different types of unvulcanized rubber shows that the outstanding characteristic of the vulcanized structure is its resistance to flow under a wide variety of conditions. The vulcanized structure appears to be a composite one which varies with the rate of a reaction catalyzed by the vulcanizing agent, the rate of combination of the vulcanizing agent, the nature of the addition product, and possibly with differences in the nature of the catalyzed reaction.

PREVIOUS papers in this series have covered the development of a set of tests for measuring vulcanization (*10*) and the use of these tests for studying the function of sulfur during vulcanization (*9*), and for comparing vulcanized rubber with unmilled rubber and uncured gas black stocks (*8*). This report covers the use of the same set of tests for a comparison of vulcanization by sulfur with that by other materials generally accepted as vulcanizing agents.

The recipes for the compounds used are as follows:

Sulfur Chloride

Compound 1. First latex crepe was calendered in the laboratory to 0.038 cm. (0.015 inch) and cured in the factory by the vapor process followed by treatment with ammonia.

Compound 2. First latex crepe was calendered and cured (vapor process) in the factory; the sheet was 0.023 cm. (0.009 inch) thick.

Compound 3, *m*-Dinitrobenzene

[Cures: 10, 20, 30, 45, 60, and 120 min. at 142° C. (287° F.)]

First latex crepe	100
Litharge	10
Gas black	10
m-Dinitrobenzene	3
	123

Compound 4, Selenium

[Cures: 15, 30, 60, 120, 240, and 480 min. at 149° C. (300° F.)]

First latex crepe	100
Vandex (selenium)	28
β-Naphthylamine	4
Paraffin wax	4
Litharge	25
Zinc oxide	50
	211

Compound 5, Tetramethylthiuram Disulfide

[Cures: 5, 10, 20, and 30 min. at 142° C. (287° F.)]

First latex crepe	100
Tetramethylthiuram disulfide	4
Zinc oxide	5
	109

Compound 6, Benzoyl Peroxide

[Cures: 5, 10, 15, 30, and 45 min. at 135° C. (275° F.)]

First latex crepe	100
Benzoyl peroxide	4
	104

The dinitrobenzene compound is based on a formula used by Fisher and Gray (*7*); that for selenium is based on a recommendation by Boggs (*5*). The mixing, curing, and testing procedure was the same as that described in detail in the earlier paper (*10*). In Table I are given the testing data for each compound on the uncured stock and on the cured sheet having the highest tensile strength in the range selected.

Discussion of Results

Comparison of these data with the corresponding data on sulfur compounds, reported in the earlier paper, shows that all of these compounds have undergone the changes characteristic of vulcanization with sulfur. Therefore, according to the criteria used here, the materials tested are true vulcanizing agents.

A comparison of the properties of the different types of vulcanized rubber with each other and with tough crude rubber and uncured gas black stocks shows that all of the vulcanizates have a marked resistance to flow in all of the tests. On the other hand, both the gas black stocks and crude rubber show a comparatively small resistance to flow in one or more of the following tests: hot water, milling, retentivity, thermoplasticity, hysteresis set. With regard to tensile and modulus, both of these types give values as high or higher than do some types of vulcanizate. Uncured gas black stocks, like vulcanized rubber, show low solubility in benzene. In ice water, some vulcanized, high accelerator–low sulfur compounds freeze as badly as crude rubber. It is thus apparent that the outstanding characteristic of the vulcanized structure is its resistance to flow under a wide variety of conditions, especially at high temperatures.

Vulcanization, then, is a reaction which primarily sup-

Table I. Vulcanization Tests on Compounds Cured with Various Vulcanizing Agents

Compound	Cure	Qualitative Tests				Plasticity Tests							Hysteresis Tests					Stress-Strain Tests			
		Ice water	Hot water	Milling	Solubility	R_{30}	R_{100}	S_{30}	S_{100}	P_{30}	P_{100}	$\frac{P^2_{100}}{P_{30}}$	Set	Modulus at 300%		Set Modulus		Modulus at 500%		Ultimate tensile	
	Minutes													Kg./cm.²	Lb./in.²	Kg.	Lb.	Kg./cm.²	Lb./in.²	Kg./cm.²	Lb./in.²
1	....	4	1	5	4	8.1	9.0[a]	4.5	6.3	0.37	0.56	0.85[a]	20[a]	15.5	220[a]	12.7	0.89[a]	77.3	1100[a]	109	1550[a]
2	....	2	1	5	4	Too thin to measure							70[a]	41.9	597[a]	1.7	0.12[a]	91.4	1300[a]	126.5	1800[a]
3	None	0	0	0	2	46.9	86.0[a]	15.8	65.2	7.4	56	424[a]	..	..	...	...	...	...	...	...	...
	45 at 142° C.[b]	4	1	5	4	6.8	5.8[a]	4.4	5.2	0.30	0.30	0.30[a]	30[a]	23.9	340[a]	1.28	0.09[a]	91.5	1300[a]	130	1850[a]
	120 at 142° C.	4	1	5	4	5.7	11.0[a]	4.2	4.8	0.24	0.53	1.17[a]	30[a]	30.6	435[a]	1.0	0.07[a]	116	1650[a]	134	1900[a]
4	None	0	0	0	0	53.2	93.7[a]	15.6	66.4	8.3	62.2	466[a]	..	..	...	...	...	...	...	...	...
	120 at 149° C.[c]	0	1	3	4	12.6	16.0[a]	5.2	5.9	0.66	0.94	0.13[a]	45[a]	12.4	177[a]	3.5	0.25[a]	28.1	400[a]	112	1600[a]
	480 at 149° C.	4	1	5	4	10.4	12.7[a]	7.5	7.7	0.79	0.98	0.12[a]	40[a]	11.4	162[a]	3.5	0.25[a]	18.3	260[a]	42	600[a]
5	None	0	0	0	0	38.5	78.6[a]	11.2	46.5	4.3	37.0	318[a]	..	..	...	...	...	...	...	...	...
	30 at 142° C.[b]	3	1	5	4	0	5.7[a]	4.5	3.9	0	0.23	0[a]	15[a]	18.8	267[a]	0.85	0.06[a]	36.6	520[a]	225	3200[a]
6	None	0	0	0	0	75.6	Too soft	51.5	Too soft	39.0	Too soft	Too soft	..	..	...	...	...	...	...	...	...
	10 at 135° C.[d]	3	1	4	4	12.8	10.3[a]	11.8	12.1	1.52	1.26	2.0[a]	40[a]	4.1	58[a]	9.8	0.69[a]	...	...	24	340[a]

[a] Measurements suitable for use without the others.
[b] 142° C. = 287° F.
[c] 149° C. = 300° F.
[d] 135° C. = 275° F.

presses the flow characteristics of uncured rubber. This change always seems to be accompanied by a marked decrease in solubility and by an increase, to a greater or less extent, in the tensile strength and modulus.

Theoretical Discussion

In these compounds the several properties change at different relative rates. Where similar differences were observed in the case of accelerated sulfur compounds, they were attributed to differences in the vulcanized structure depending on the relative rates of two structure-forming reactions, sulfur addition, and a reaction catalyzed by sulfur (*9*). The extension of this explanation to the nonsulfur vulcanizing agents is in agreement with the chemical evidence available.

With sulfur chloride there is an addition reaction which probably results in bridge formation between double bonds of the hydrocarbon (*1, 11–14, 19*). With nitro compounds the reagent is destroyed during cure, and there appears to be a small amount of some sort of addition product formed (*2, 6, 15, 18*). Selenium apparently combines to a limited extent with rubber (*3, 4*). Benzoyl peroxide forms some addition or substitution product and probably also causes some bridge formation by dehydrogenation of the rubber (*17*). Tetramethylthiuram disulfide probably decomposes and liberates a small amount of very active free sulfur (*16*). In all of these cases the amount of addition product is small, either because of low tendency of formation or because of the small amount of reagent available. With sulfur alone there is reason to believe that amounts of combined sulfur up to one per cent are not sufficient to cause more than a very slight vulcanization (*9*). This is probably also the case with equivalent amounts of addition product of these other reagents. It seems probable, therefore, that in all of these cases a catalyzed reaction of the hydrocarbon plays an important part in the vulcanization. In the case of selenium (*4*), nitro compounds (*7*), and benzoyl peroxide (*7*), as with sulfur, there is evidence that this catalyzed reaction is not one involving a change in unsaturation.

Thus there appears to be in all of these cases the probability of at least two reactions: (1) a combination of vulcanizing agent with rubber and (2) a reaction of the hydrocarbon catalyzed by the vulcanizing agent. The product of the combination would, of course, be different with different reagents. Possibly, also, there are differences in the nature of the catalyzed reaction, though in most cases it seems to be one which does not involve a change in the unsaturation of the hydrocarbon. The catalytic activity of the vulcanizing agents undoubtedly depends on the initial composition and also on the stability, and thus varies considerably among the different reagents.

The vulcanized structure seems to be a composite one built up by the catalyzed reaction and modified more or less by the addition reaction.

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Received November 23, 1933.

Benzene Exports and Production Higher. Exports of benzene from the United States in 1933 totaled 8,439,456 gallons, valued at $1,594,075, compared with 3,241,317 gallons, valued at $611,656, in 1932, according to the Department of Commerce. Benzene, an important industrial chemical product obtained in the distillation of coal tar, is used extensively as a motor fuel constituent. Other consuming outlets are explosives, dyes, plastics, and a number of other finished coal-tar products.

Some shifts have occurred in the markets for American benzene. Shipments to the Central and South American area increased 20 per cent compared with 1932, Argentina taking 71,000 gallons of a total of 130,000 gallons shipped to that area. Consignments to the Far East practically quadrupled in 1933 compared with the preceding year, the largest Far Eastern purchaser being Japan.

Extraction by Immiscible Solvents

THEODORE W. EVANS, The Shell Development Company, Emeryville, Calif.

In the extraction of a solute by immiscible solvents such that the partition law holds, the degree of solute removal is conditioned mainly by the relative volumes of the solvents. While use of several small portions is preferable to one combined portion, excessive subdivision is unjustified, since a limiting percentage removal exists for every ratio of solvent volumes. At least 94 per cent of this maximum removal of which a given volume of solvent is capable is achieved by division into five portions, so that in practice it is scarcely worth while to divide the extracting solvent into more than five portions.

SEVERAL excellent articles (*2*) have appeared recently dealing with the extraction of a solute from a solution by means of a second immiscible solvent. For the laboratory worker the case of greatest interest is that ordinarily encountered—i. e., repeated shaking of the solution with fresh portions of solvent in a separatory funnel. Ordinarily a predetermined total volume of extracting solvent is taken, and this solvent used in several successive portions, the portions being of equal size for greatest efficiency. (For a proof that equal subdivision is superior to unequal, see citation *3*.) While it is generally recognized that the larger the number of portions used (keeping the total volume constant) the better the extraction, no particular attention seems to have been given to the maximum extraction obtainable in this way, although the impression is given that by sufficiently increasing the number of subdivisions any required percentage of the solute may be recovered with a given total volume of extracting solvent (*1*, *2*).

In the following, this last conception will be shown to be erroneous, the limits of extraction determined, and a practical value set upon the number of portions into which the solvent should be divided.

Suppose a solvent of volume L liters contains m grams of solute. This solute is to be extracted by a total volume U liters of an immiscible solvent, the solutions being such that the partition coefficient is a constant. Assume U to be divided into n equal portions and L extracted successively with these n portions. Let x_i be the amount of solute remaining in the ith portion of the second solvent, and y_i similarly the amount of solute left in the first solvent at the end of the ith extraction:

$$\frac{x_i \div \frac{U}{n}}{y_i \div L} = k;\ \frac{x_i}{y_i} = \frac{kU}{nL} = \frac{K}{n}$$

where $$K = \frac{kU}{L}$$

$$x_1 + y_1 = m;\ x_1 = m - y_1$$

$$\frac{x_1}{y_1} = \frac{m - y_1}{y_1} = \frac{K}{n};\ y_1 = \frac{m}{1 + \frac{K}{n}}$$

Hence $$y_n = \frac{m}{\left(1 + \frac{K}{n}\right)^n}$$

Now let n approach infinity; i. e., let the solvent be divided into an infinite number of portions, thus securing the greatest possible extraction:

$$\underset{n \to \infty}{\text{Limit}}\ y_n = \underset{n \to \infty}{\text{Limit}}\ \frac{m}{\left(1 + \frac{K}{n}\right)^n} = \frac{m}{e^K} = me^{-K} = me^{-k\frac{U}{L}}$$

Consequently, once the relative volumes of the two solvents are fixed, the maximum percentage of the solute which can be removed is also fixed; it is given by:

$$(1 - e^{-K})\ 100 \text{ per cent}$$

This formula leads to several interesting results. Suppose the original solution is extracted in a perfect[1] countercurrent tower. Then, since the solution leaving the tower is in equilibrium with that entering (once the steady state is reached), for a volume L of solution there is required a volume $U = L/k$ of solvent to extract completely the entering volume L.

Now, if instead of employing the ideal countercurrent extraction, the same L/k liters were used in consecutive small amounts, $K = \frac{kU}{L} = \frac{k(L/k)}{L} = 1$, the percentage removal would be $(1 - e^{-1})$ 100 per cent, or 63 per cent as contrasted with 100 per cent in the tower. It should be remembered, of course, that in the infinite tower we assume the steady state to be already established.

It is of particular interest to examine the effect of increasing n on the total percentage extracted, since this effect should determine the practical choice of the number of extractions made.

Table I shows the percentage of the solute removed for various values of n and K. The value of K is fixed by the value of k and the relative volumes of the two liquids. It is increased by increasing the amount of extracting solvent used, doubling this amount doubles K, etc. The figures show clearly that, in order to achieve an extraction of 80 per cent, or better, sufficient solvent must be used to give a value of K of from 2 to 10, depending on the recovery desired. Thus, if $k = 1$—i. e., the two liquids are equal solvents for the solute—then at least two volumes of extracting solvent should be used for each volume of solution. As to the number of portions into which the solvent should be subdivided, it seems that 5 is generally sufficient, the labor of further subdivision being scarcely justified by the additional amount of solute recovered.

To investigate this choice of five subdivisions as a practical maximum, the ratio of the recovery for $n = 5$ to $n = \infty$ should be considered, since this ratio gives the relative efficiency of the process for five subdivisions. These values have been tabulated as the final column in Table I. This ratio passes through a minimum of approximately 0.94, indicating that by five subdivisions one always secures at least 94 per cent of the maximum solute removal, of which the given volume of solvent is capable, when used in the batch extraction. To fix this figure more definitely, the minimum of this function $(n = 5)/(n = \infty)$ may be approximated as follows:

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[1] By this expression is meant a tower consisting of an infinite number of perfect plates. In the present case the choice of volumes makes $K = 1$. For this value of K, n perfect plates will achieve a removal of $\frac{100n}{n+1}$ per cent of the solute.

$$\frac{n = n}{n = \infty} = f(K, n) = \frac{1 - \left(\frac{n}{n+K}\right)^n}{1 - e^{-K}}$$

$$\left(\frac{\delta f}{\delta K}\right)_n =$$

$$\frac{(1 - e^{-K})\left[n\left(\frac{n}{n+K}\right)^{n-1}\frac{n}{(n+K)^2}\right] - \left[1 - \left(\frac{n}{n+K}\right)^n\right]e^{-K}}{(1 - e^{-K})^2}$$

$$= \frac{\left(\frac{n}{n+K}\right)^{n+1} - e^{-K}\left[\left(\frac{n}{n+K}\right)^{n+1} - \left(\frac{n}{n+K}\right)^n + 1\right]}{(1 - e^{-K})^2}$$

For a minimum, $\left(\frac{\delta f}{\delta K}\right)_n = 0$. The values of this function for different values of K with $n = 5$, are:

K	$\left(\frac{\delta f}{\delta K}\right)_{n=5}$	K	$\left(\frac{\delta f}{\delta K}\right)_{n=5}$
0.1	−0.1765	3	0.00881
1	−0.0210	5	0.0087
1.6	−0.0009	∞	0
2	0.00602		

Consequently $K = 1.6$ corresponds very nearly to a minimum for $(n = 5)/(n = \infty)$. Using $n = 5$, $K = 1.6$, it is found that 75.05 per cent of the solute is removed, while $n = \infty$ corresponds to a 79.81 per cent removal. The ratio $0.7505/0.7981 = 0.9403$, so that in any case the use of five subdivisions is certain to achieve a removal of solute equal to at least 94 per cent of the maximum of which the given volume of solvent is capable.

In passing, it should be noted that the value $K = 1$ corresponds to the amount of solvent required for 100 per cent extraction in a perfect countercurrent tower, which is roughly one-fifth that demanded for substantial recovery by ordinary laboratory extraction. Unfortunately countercurrent extraction is impractical on a laboratory scale, and hence the above conditions must be met for the ordinary extractions encountered in regular work.

TABLE I. EFFECT OF n AND K ON PERCENTAGE OF SOLUTE REMOVED

K	$n = 1$	$n = 2$	$n = 5$	$n = 10$	$n = \infty$	$\frac{n = 5}{n = \infty}$
	%	%	%	%	%	%
0.1	9.09	9.30	9.43	9.47	9.52	0.99
1	50.00	55.56	59.81	61.44	63.21	0.947
2	66.67	75.00	81.40	83.85	86.47	0.941
3	75.00	84.00	90.46	92.75	95.02	0.953
5	83.33	91.84	96.87	98.27	99.33	0.97
10	90.91	97.22	99.59	99.90	99.99	0.99

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RECEIVED October 13, 1933.

Surgical Catgut Ligatures

X-Ray Diffraction Studies

GEORGE L. CLARK, University of Illinois, Urbana, Ill., R. K. FLEGE, AND P. F. ZIEGLER,
Curity Suture Laboratories, Chicago, Ill.

RESEARCH in the field of surgical ligatures has been steadily progressing for many years. Processing technics, sterilizing technics, and exact tests on products have been rather thoroughly covered by the better ligature manufacturers. In addition, there have been sponsored research programs at universities and medical schools. All of this research, however, has dealt with the macro aspects of the ligature. After reaching a certain point, further knowledge of the products had to await the development of tools and technics that permitted examination of the ultimate structural characteristics of these protein fibers. Such a tool is x-ray diffraction equipment.

X-RAY METHOD OF STRUCTURAL STUDY OF LIGATURES

Knowledge of the chemistry of proteins has been decidedly fragmentary, and definite information as to how protein molecules build themselves into solid animal tissues so as to account for complex behavior is almost entirely lacking. The microscope has been useful in disclosing gross structural features. By splitting up collagen fibers, such as those which constitute catgut sutures, by means of swelling experiments, it has been demonstrated that there are fiber bundles built up from five to ten fibers; each fiber is built up from about a hundred fibrils. These tiny fibrils are the real collagen units, and yet the microscope is able to say nothing as to the still smaller and more fundamental units which comprise the fibril.

The experimental technic for x-ray diffraction analysis of ligatures is comparatively simple. A monochromatic beam of x-rays defined by small pinholes (about 0.025 inch, or 0.635 mm., in diameter) is passed through a ligature specimen perpendicular to the fiber axis. A photographic plate is adjusted at a fixed distance (usually 5 cm.) behind the specimen. After development of the film the characteristic pattern appears and, in accordance with straightforward principles, is measured and interpreted in terms of ultimate constitution and structure so that a model can be constructed.

DIFFRACTION PATTERNS FOR CATGUT LIGATURES

Upon the basis of typical diffraction patterns for cellulose, silk fibroin, and keratin fibers which have been extensively studied and interpreted, it is possible to approach intelligently the interpretation of patterns for ligatures which have not been subjected to any appreciable amount of study. An average diffraction pattern for a commercial catgut ligature is reproduced in Figure 1*A* and a graphical representation which may be somewhat more easily described in Figure 2*A*. The principal features of the ligature patterns, proceeding from the center out, are as follows:

1. The amorphous scattering or fogging near the undiffracted beam which indicates truly amorphous matter may vary from practically zero intensity to a very marked blackening of the film, showing an almost continuous variation between specimens containing little or no amorphous matter to those which are almost completely broken down—for example, by heating or by digestive processes.
2. The innermost sharp ring, corresponding to a spacing of 11.9 Å. of all features of the pattern, is most sensitive to variations in specimens which appear to be very similar. The arcs which appear ordinarily on the equator of this inner ring may be so long actually as to form a continuous ring as in Figure 1*B*. In this case the molecular organized units responsible for this

The structural characteristics of surgical catgut ligatures and sutures as revealed by the monochromatic Kα-ray of copper and the effect of conditions of process on that structure are discussed.

Catgut rendered plastic by immersion in certain swelling agents gives an x-ray pattern indicating that it is almost wholly amorphous. Patterns obtained from the same specimen after application of tension, or drying at constant length, show the presence of a definitely organized or crystalline substance, indicating that tension has caused a parallel arrangement of micelles into long chains.

Quality in catgut, to a large extent, is shown to reside in structural units.

Tension-dried raw catgut has a more preferred orientation than any specimen following further processing. Elevated temperatures required for sterilization and certain tubing fluids employed tend to lower the degree of orientation of the original pattern more or less.

The formula of Mark which relates tensile strength after stretching with micellar dimensions is shown to be applicable in the case of catgut ligatures; new formulas are deduced for tensile strength and micellar dimensions.

interference would be distributed at random in much the same way as cellulose crystallites are arranged in brush-heap fashion in Cellophane. On the opposite extreme these arcs may actually be so sharp and short that they appear simply as spots lying on the equator of the pattern as in Figures 1*C*, 2*B*. In this case the units must be oriented in a nearly perfect preferred direction parallel to the axis of the fiber.

Between the two extremes described, every possible arc length might easily be observed in different specimens. It is evident, therefore, that the length of these arcs is definitely a measure of the degree of the preferred orientation of the crystalline particles or colloidal micelles which build up the protein collagen fibril. Different ligature specimens can be compared, therefore, by relative measurement of arc lengths. This comparison may be made strictly quantitative by a new method worked out by Clark and Sisson (*5*). A microdensitometer with rotating stage is employed. The film is adjusted so that it may be rotated with this inner circle in focus, and successive readings can be made of the actual density of the photographic emulsion which is plotted as a function of an angle. A curve can thus be drawn whose width is a quantitative measure of the length of the arc. Figure 3 illustrates the corrected curves obtained for the ligature patterns. These curves may be treated mathematically to give definite numerical values, expressing the perfection of orientation of the micelles. These numerical values are highly significant in that they run parallel with measured physical properties such as tensile strength. (See last section of paper.) Other things being equal, the shorter and sharper these arcs, indicating high degree of preferred orientation, the greater is the tensile strength of the fibril. The fact that it is possible with any given ligature specimen to change these arc lengths by suitable chemical and mechanical methods has given to this x-ray research method an even greater practical significance.

3. Running somewhat parallel with the inner arcs, the halo, due to a part of the collagen which is essentially amorphous, may vary from a continuous band of uniform width, representing random distribution, to a high degree of preferred orientation even for this imperfectly organized material. In this latter case the equator of the band becomes very broad in marked bulges while the polar parts of the band become narrow and quite faint.

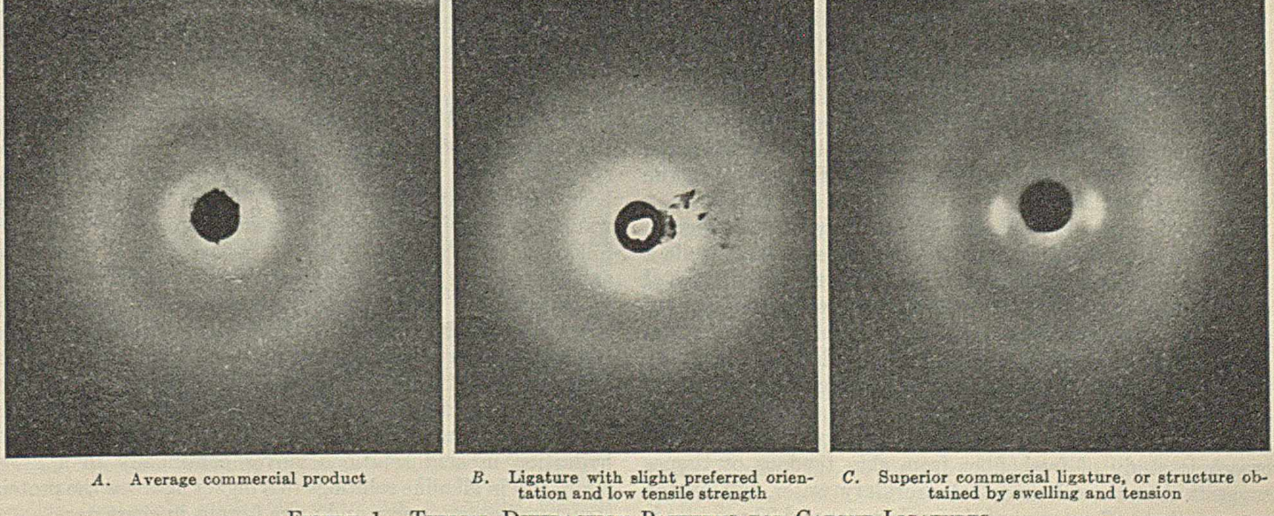
4. The lengths of the arcs on the outer sharp ring appearing at the poles may also vary from a continuous circle to short lengths, as preferred orientation improves. The spacing is 2.8 Å.

5. It is significant that variations in the widths of the two principal sharp rings and the halo may also be observed, as well as variations in lengths. The widths of the interferences are conditioned by the size of the crystalline particles or micelles. The broader these maxima, the smaller both in length and cross section are these colloidal particles. If collagen is built up in some fashion from long chains similar to the construction of cellulose, then it follows that any rupturing of these chains, or breaking down into shorter molecules and smaller colloidal particles, would be manifested by increase in width of the lines or spots which appear upon the pattern.

6. A significant variation in patterns is the appearance or nonappearance of an additional diffraction ring which appears simply as four sharp arcs between the inner ring of small diameter which is always present and the broad halo. The appearance of these new spots is always associated with the shortest and sharpest arc lengths for the other interferences—in other words, with the highest degree of fibering (Figures 1*C*, 2*B*). In general, the appearance of these new interferences would indicate sutures of unusual quality, especially as regards tensile strength. They appear only occasionally in ordinary commercial specimens of raw catgut or of finished sutures, but it is significant that they can be made to appear by stretching a specimen while in a plastic condition. This process will be considered in a later section of the paper.

RELATION OF LIGATURE DIFFRACTION PATTERNS TO X-RAY RESULTS ON COLLAGEN AND GELATIN

The catgut ligature pattern is in general agreement with that of collagen and gelatin which have been known for several years (*3*, *4*, *7*, *8*, *9*, *12*, *13*).



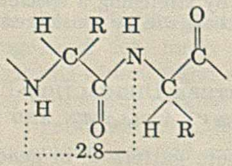
A. Average commercial product *B.* Ligature with slight preferred orientation and low tensile strength *C.* Superior commercial ligature, or structure obtained by swelling and tension

FIGURE 1. TYPICAL DIFFRACTION PATTERNS FOR CATGUT LIGATURES

Thus for a dried block of gelatin there are observed two sharp rings corresponding to crystal dimensions of 11.9 and 2.8 Å. [considered by Astbury (*1*) to be the length of a single amino acid residue in the direction of the main chain] and a broad halo for an amorphous part with the spacing 4.3 Å., exactly as found for fibrous catgut and collagen. Furthermore, gelatin may be stretched as much as 200 per cent, yielding a fiber pattern with the new additional four spots (Figure 2*B*) between the innermost ring and the broad halo which is practically indistinguishable from that of catgut or fibrous collagen. An additional spacing, the identity period along the fiber axis, may now be determined from the layer line diagram. This is 9.5 Å.

COMPARISON WITH SWELLING PHENOMENA AND FUNDAMENTAL CONCLUSIONS ON PROTEIN STRUCTURE

Natural silk fibers formed from the protein fibroin were the first studied by x-ray methods to give a clue as to the problem of the structure of the protein molecule as a whole. Natural silk does not give such a complete fiber diagram as that of cellulose, but Meyer and Mark applied to it principles learned from the latter and suggested that the fibrils in crystallites also were no other than bundles of long molecular chains. Just as the long chains in cellulose consist of a repeating unit of the dehydrated glucose residue, so the protein chain is built up from units mainly joined through peptide linkages. The remarkable studies on stretched wool and hair by Astbury (*1*) give further definite confirmation to this conception. More recently Katz and de Rooy (*9A*) have found that blood fibrin can be drawn into fibers which yield typical diffraction patterns similar to those of keratin and thus produce additional evidence of a fundamental underlying structure which is generally common for fibrous proteins. The result is a long polypeptide chain with the length of the repeating unit usually 3.5 Å., although this varies somewhat with the protein and is probably 2.8 Å. in gelatin and collagen. This is illustrated diagrammatically as follows:



In this diagram R represents any side group attached to the main backbone chain. These groups differ from one protein to another and serve to distinguish the behavior, particularly as regards swelling in water of various types of proteins. The diffraction pattern for catgut ligature or collagen fibers then relates itself directly to the more definitely crystalline patterns for silk and stretched keratin. Poor as the photographs are when judged by standards of ordinary crystalline analysis, the fact that any pattern at all is obtained suggests that in the more perfectly organized or "crystalline" part of the fiber substance, the sequence of amino acid residues cannot be extremely irregular.

As has been observed frequently in this work, the diagram for a colloidal sol indicates an amorphous structure, while a jelly has usually well-defined rings characteristic of crystal structure. Jelly formation is therefore due to development of some degree of organization. Knowledge of an actual structural constitution of a catgut fibril is aided materially by studies of swelling of these fibers. In comparing the swelling of such systems with that of gelatin jellies, the fact remains that water may pass either into or between the fibrils. Microscopic study of fresh fiber from skin tendons or tissues suggests that there is little interfibrillary water, but on the average about 67 per cent of tissues is water and 33 per cent is solid matter almost entirely collagen. Consequently, according to Lloyd (*10*), fresh collagen materials may be compared with the behavior of 33 per cent gelatin jellies, and any discrepancies are to be ascribed to histological structure and to molecular organization. The swelling of collagen fibers resembles gelatin in many ways, although the degree of swelling is much less. The resemblances are as follows:

1. They show swelling in acid solutions, which begins at pH values less than the isoelectric point of the protein and rises to a well-defined maximum, afterwards falling off with decreasing pH value. For volume increase, width increase, and length decrease of fresh fibers, as measured by Lloyd, Marriott, and Pleass on skin collagen and confirmed in this work on catgut, the maxima appear at pH 2.5 to 2.6, and for dried fiber at 1.8.
2. They show swelling in alkaline solutions which does not begin at pH values immediately greater than the isoelectric point but appears at pH 9.5. There is a swelling maximum at pH 10 followed by great volume increase at higher pH because of destructive action of the alkali.
3. They show swelling in salt solutions at pH values near the isoelectric point.
4. When both are dried, the power of swelling is considerably reduced, except possibly in strongly alkaline solutions.

Collagen fibers differ from gelatin jellies in the following features:

1. Under the same external conditions, swelling is always less than in a gelatin jelly set at the same concentration of protein.
2. There is not a sharp minimum of swelling corresponding to the isoelectric point but a well-marked stability zone from pH 5.5 to 9 (4 to 10 for dry fibers) over which fiber width, length, and volume are constant.
3. Swelling in acid and alkaline solutions is generally accompanied by contraction along the axis of the fiber. The first stages of swelling show splitting into fibrils.
4. Swelling in salt solutions at pH values near the isoelectric point is due to splitting of the fiber into fibrils.

These observations, together with the x-ray studies, suggest that the collagen fibril is composed of a bundle of protein molecules arranged with backbones parallel to the long axis of the fiber and held together by coördinate links between backbones of adjacent molecules. The R groups terminating in charged centers ($—NH_2^+$ or $—COOH^-$) are arranged so that some are situated within the fibril, but a large number are located on the outer surface. It is by virtue of these groups that the fibrils are held together in the fiber. These strong cohesive forces act to reduce the swelling of collagen to a very much lower value than that of equally concentrated gelatin jelly under the same external conditions.

Gelatin shows marked swelling in water alone, and the x-ray diffraction measurements made in this laboratory several years ago indicate the process clearly in the following data:

Water content, %	Dry	25	50	100	200
Ring diameter, mm.	13.9	11.8	11	10.2	9.2
Lattice spacing, Å.	11.1	13.1	14	15.7	16.2

Solubility and hydration of proteins are greatly affected by the closeness of packing of the molecules into organized structures with cross linkages between molecules. It has been demonstrated by Lloyd (*10*) that the ability to hold water by protein materials decreases progressively in the following series: gelatin, muscle, collagen, wool, horsehair, and fibroin (silk gut). X-ray patterns by the present writers indicate for this series progressively a more fibrous structure. Fibrous proteins, particularly those with a preponderance of residues of short-chain aliphatic amino acids, are the most resistant to solvents. With the development of oriented structure in proteins, a stability range towards hydrating influence appears (pH 4 to 8), and the pH value at maximum hydration in acid solutions moves continually to a lower figure and in alkaline solutions to a higher figure as the protein structure becomes more and more fibrous in character.

It follows then that the swelling and dehydration, as well as other physical properties for the same protein, will be conditioned by the degree of fibering. If, for example, in catgut ligatures this degree of fibering can be controlled, the practical behavior also should be subject to control. Experimental results on this point are presented in a later section of this paper.

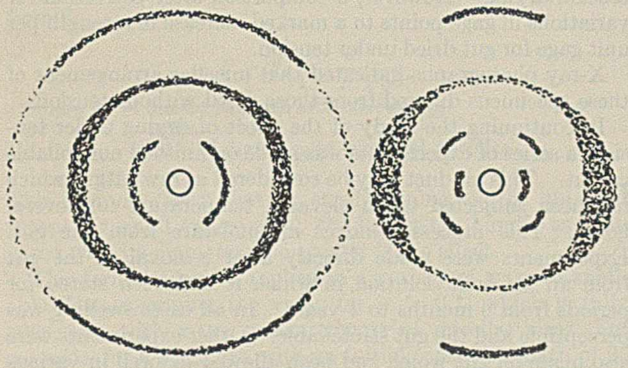

A. Average commercial product (Figure 1*A*)
B. Superior product (Figure 1*C*)

Figure 2. Diagrams of Diffraction Patterns for Catgut Ligatures

Summarizing, the x-ray diagram indicates, therefore, that catgut is composed of highly polymerized protein molecules or micelles which are easily oriented into an organized condition by virtue of long bundle form, and of weakly polymerized protein material (shorter and varied lengths) which has essentially amorphous properties but may show a tendency towards preferred orientation. The expectation would be that this noncrystalline portion of the catgut would be most readily attacked chemically or by biological fluids, and this is found to be true.

This protein material may be pictured as composed of micelles built up of uniform long molecules arranged in lattice fashion (the crystal-like portion); and of an amorphous part of irregular chains which might be bundled into micelles but would possess no lattice arrangement. These might be called "mixed micelles" by analogy with mixed crystals. The micelles tend to hold each other in position by virtue of active chemical groups on the surface of the particles which are extensions from the backbones. Even the fibrils in a fiber exercise certain attractive forces upon each other which materially affect the ability to absorb water or other reagents. These micelles or bundles may be pictured as somewhat elastic or wormlike rods because of the nature of the protein chain. The x-ray spacings correspond to a definite direction along the chain or to the cross section of a bundle of chains.

Comparison of Raw Catgut and Finished Ligatures from Various Sources

All raw catgut and finished ligature specimens yield diffraction patterns characteristic of protein collagen with dimensions noted above. Specimens are differentiated from each other, however, with great sensitiveness by the degree of preferred orientation of the micelles with respect to the long axis of the fiber. This is measured especially well by the length of innermost equatorial arcs which correspond to the 11.9 Å. dimension.

The following general conclusions may be derived from a large number of x-ray studies:

1. Raw catgut has a higher degree of preferred orientation than any specimen following further processing, provided tension and stretching are not applied. Elevated temperatures and swelling treatments invariably disarrange a parallel micellar arrangement to a greater or less extent.

2. Commercial finished samples are distinguished chiefly by the lengths of arcs on the inner sharp diffraction ring. A rating on performance as to tensile strength, uniformity, and absorption time in the tissues can be and has been made from patterns. In general, the shorter and sharper the arcs on the inner interference ring, and the narrower the corrected microdensitometer curve, the stronger is the ligature, other things being equal. X-ray patterns show remarkable differences between ligatures from different manufacturers, and in some cases in different lots from the same manufacturer, while other commercial ligatures are remarkably consistent. Variations in raw material and the slightest differences in any chemical or physical treatment change the structure and the controlling x-ray pattern.

Correlation with Observations with Polarizing Microscope

The anisotropic structure of gut ligatures is easily disclosed by the polarizing microscope. The fiber structure can be studied by its extinction effect. The more highly fibered sections of a given ligature showed good extinction while the unoriented material appeared dark in all positions. Cross sections of specimens were especially interesting since they appeared spotted on the field. Being oriented in different directions in the horizontal plane, the spots did not show extinction at the same angles but became dark consecutively as the field was changed. Between these spots were areas of unoriented material which remained dark in all positions. Examination of the ligatures lengthwise showed nonhomogeneous portions which remained dark. These spots were marked with ink and the specimen was used for x-ray diffraction and breaking tests. These spots showed invariably a lack of orientation in the patterns. Several specimens were subjected to tensile tests, and in nearly all cases the break occurred at one of the marked points.

Effect of Tension on Catgut

If the structure pictured for catgut is true (and it explains all known facts of behavior), it should be possible by suitable tension on the catgut fiber, rendered plastic by swelling agents, to pull the micelles into still more perfect alignment. The x-ray diffraction pattern proves this to be the case, for the pattern not only shows sharper fiber intensity maxima but four new intensity maxima symmetrically arranged between the inner crystal ring and the amorphous halo.

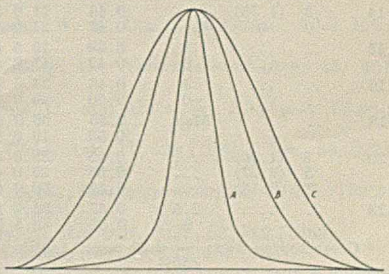


Figure 3. Microdensitometer Curves for Inner Diffraction Arcs in Patterns in Figure 1

A (Figure 1*C*); *B* (Figure 1*A*); *C* (Figure 1*B*)

This diagram indicates a degree of symmetry superior to that observed for the ordinary commercial catgut; there is distinctly an axis of orientation parallel to the direction of tension and stretching, and the structure approaches that of a well-oriented crystalline substance. The new intensity points enable accurate calculation to be made of the identity period along the fiber axis—namely, about 9.5 Å. In other words, some combination of atoms along the complex polypeptide chains repeats itself. Another dimension is the 11.9 Å., deduced from the inner spots. Such a pattern, however, is obtained only under these conditions of swelling and tension. Further processing into final sterile ligatures always tends to remove this evidence and to leave less perfect orientation.

Relationship between Structure and Tensile Strength

Experiments on rayon indicated that, when the cellulose filament was regenerated from solution under tension, the micelles were more perfectly aligned than in ordinary varieties, as indicated by a far more highly fibered diffraction pattern, and the tensile strength was considerably enhanced. The surface forces of the micelles were able to bind the micelles into a strong unit as compared with a brush-heap micellar arrangement. Similarly, cotton which has been swollen and stretched in the solid phase, becomes stronger by 50 per cent or more.

Bergmann and Jacobi (*2*) have shown for a band of gelatin the following:

	Kg./sq. mm.
Gelatin unstretched	4.4
Gelatin stretched 300%	9.3

For tendons or fibrous collagen the following data have been obtained:

Tendon (swine)	11.0
Same heated and shrunk at 80° C. (x-ray fiber pattern disappears)	3.0
Stretched again to original length	10.6

The shrunk and stretched tendons are thus exactly analogous to rubber. That the chains on the stretched tendons lie in the fiber direction can also be shown by freezing. There is a marked cleavage in the fiber axis, while the shrunk tissue breaks into clumps. By heat treatment, therefore, the principal valence chains change their form and become rolled up, and the x-ray pattern disappears.

Table I. Effect of Tension Drying on Strength of Raw Catgut

Run	Drying Tension	Elongation	Av. Diam.	Tensile Strength: As detd.	Tensile Strength: Cor. to constant diam.[a]	No. of Tests
	Lb. (kg.)	*%*	*Mm.*	*Lb./sq. in. (kg./sq. cm.)*	*Lb./sq. in. (kg./sq. cm.)*	
12	7 (3.18)	..	0.41	15.0 (1.05)	23.2 (1.63)	2
	0 0	..	0.40	12.0 (0.84)	19.0 (1.34)	2
14	3 (1.36)	..	0.46	21.0 (1.48)	26.6 (1.87)	4
	0 0	..	0.47	21.0 (1.48)	24.7 (1.74)	4
15	.. ...	3	0.39	19.5 (1.37)	33.4 (2.35)	3
	.. ...	0	0.42	17.0 (1.20)	25.0 (1.76)	3
16	.. ...	3	0.46	24.0 (1.69)	30.3 (2.13)	4
	.. ...	0	0.50	20.0 (1.41)	20.0 (1.41)	3
18	..	Max.	0.55	26.0 (1.83)	20.8 (1.46)	7
			0.55	19.0 (1.34)	15.3 (1.08)	7
20	3 (1.36)	...	0.55	29.0 (2.04)	25.0 (1.76)	..
	5 (2.27)	...	0.55	29.0 (2.04)	25.0 (1.76)	..
	7 (3.18)	...	0.55	30.0 (2.11)	25.7 (1.81)	..
23	.. ...	2.5	0.57	35.5 (2.50)	28.4 (2.00)	7
	.. ...	0	0.55	32.5 (2.28)	27.8 (1.95)	13

[a] Corrected to diam. = 0.50 mm.; tensile strength corrected = tensile strength actual × $\frac{(50)^2}{(\text{av. diam.})^2}$.

The x-ray pattern of catgut ligatures should therefore be an indication of tensile strength—the more strongly fibered or perfectly oriented, the stronger they are in general. Hence, the appearance of the four new interference points (the most sensitive and accurate criterion) should be accompanied by changed mechanical properties and enhanced strength.

Tensile strength is obviously a function of gage or diameter, strength increasing with gage. If it were possible to decrease the gage of any given strand of gut without causing a change in tensile strength, in effect the ratio of strength to gage would be increased. With this in mind, a series of experiments was carried out to determine if improvement in tensile strength could be effected by drying catgut while the length was maintained constant (which in effect introduces tension) or even with the maximum tension possible. To this end a number of strands of raw catgut representative of a production lot were selected and thoroughly plasticized. One-half of each original strand was then allowed to dry under room conditions while the other half was maintained under identical conditions except that tension was applied. Data obtained in experiments with raw catgut are presented in Table I.

Table I shows that on the average the application of tension caused a reduction in gage or diameter over that of gut dried without tension. A direct comparison of strength data as obtained indicates that strength is only slightly improved by tension-drying. However, a comparison after correction for variations in gage points to a marked increase in strength per unit gage for gut dried under tension.

X-ray photographs indicated that micellar arrangement of these specimens differed from those dried without tension.

In continuing the study of the effect of drying under tension, a series of experiments was made on finished nonboilable catgut. This product may be considered as raw catgut which has been subjected to an elevated temperature for several hours. This process removes all moisture from the gut. Experiments were made directly after removal of the gut from an alcoholic solution in which it had been stored for periods from 6 months to 4 years. In all cases swelling was perceptible and the gut stretchable. Other experiments were also made on gut which had been allowed to swell in various media. All data obtained are given in Table II.

Table II. Effect of Tension Drying on Strength of Finished Catgut

Run	Drying Tension	Av. Diam.	Tensile Strength: As detd.	Tensile Strength: Cor. to constant diam.[a]
	Lb. (kg.)	*Mm.*	*Lb./sq. in. (kg./sq. cm.)*	*Lb./sq. in. (kg./sq. cm.)*
1	5 (2.27)	0.51	18.5 (1.30)	18.5 (1.30)
	5 (2.27)	0.49	19.0 (1.34)	20.2 (1.42)
	0 0	0.55	19.0 (1.34)	16.6 (1.17)
2	5 (2.27)	0.52	15.0 (1.05)	14.4 (1.01)
	0 0	0.55	17.0 (1.20)	14.6 (1.03)
	0 0	0.56	14.5 (1.02)	12.5 (0.88)
	0 0	0.55	14.0 (0.98)	12.2 (0.86)
8	5 (2.27)	0.52	20.0 (1.41)	19.2(1.35)
	0 0	0.53	17.5 (1.23)	16.4 (1.15)
9	7 (3.18)	0.62	24.0 (1.69)	16.4 (1.15)
	0 0	0.64	26.0 (1.83)	15.2 (1.07)
10	10 (4.54)	0.51	18.5 (1.30)	18.5 (1.30)
	0 0	0.57	18.5 (1.30)	14.8 (1.04)
	10 (4.54)	0.52	19.5 (1.37)	18.7 (1.31)
	10 (4.54)	0.49	20.0 (1.41)	21.6 (1.52)
11	5 (2.27)	0.68	28.0 (1.97)	15.8 (1.11)
	0 0	0.71	28.0 (1.97)	14.4 (1.01)
	7 (3.18)	0.60	28.0 (1.97)	20.2 (1.42)
	7 (3.18)	0.60	27.0 (1.90)	19.5 (1.37)
	0 0	0.64	25.5 (1.79)	16.2 (1.14)
4	5 (2.27)	0.52	21.5 (1.51)	20.5 (1.44)
	0 0	0.51	17.0 (1.20)	17.0 (1.20)
7	5 (2.27)	0.48	21.5 (1.51)	24.2 (1.70)
	0 0	0.52	19.5 (1.37)	18.6 (1.31)

[a] Corrected to diam. = 0.50 mm.

Here, as with raw catgut, the application of tension to gut while swollen and its maintenance under that condition while drying resulted in improved tensile strength.

Mechanism of Deformation Resulting in Micellar Orientation and Enhancement of Tensile Strength

The process of stretching catgut with resulting improved orientation and enhanced tensile strength suggests the cold-drawing of metallic wires in which gliding on crystallographic planes occurs. However, in protein fibers and cellulose there is good reason to assume that the micelles remain intact during deformation, and they flow as if they were soft wormlike bundles. There is no decrease in micellar size during the extension detectable from increasing widths of x-ray diffraction interferences. Hence the micelles must be oriented as a whole without being broken or torn during the plastic extension. Under these assumptions it is possible to make a quantitative approach to the problem of connecting the amount of orientation of long rodlike bundles with the amount of extension. Eckling and Kratky (*6*) deduced the formula:

$$N(\alpha) = N_0 \frac{v^3}{[1 + (v^3 - 1)\sin^2 \alpha]^{3/2}}$$

where $N(\alpha)$ = number of particles per unit angle, whose long axis forms an angle with the direction of stretching
N_0 = number before stretching
v = amount of extension, given by $v = l/l_0$, where l_0 = initial length and l = final length of sample

From this, Mark (*11*) derived the useful approximation formula:

$$F = F_0 \frac{v^3}{1 - \rho + \rho v^3}$$

where F = tensile strength after stretching
F_0 = initial value
ρ = ratio of diameter to length of micelles

This formula shows that no strengthening can be obtained except for small values of ρ; the longer the bundle as compared with its diameter, the greater is the effect.

This formula can be applied in a variety of ways to available data, assuming the value for $\rho = 0.1$, which is fully consistent with x-ray measurements of micellar size. For example, for a specimen with an initial tensile strength of 25 pounds per square inch (1.76 kg. per sq. cm.) and an elongation of 3 per cent:

$$F = \frac{1.76(1.03)^3}{0.9 + 0.1(1.03)^3} = \frac{1.76 \times 1.10}{0.9 + 0.11} = 1.93 \text{ kg. per sq. cm.}$$

This is in excellent agreement with experimental values. In order to double the tensile strength of a ligature with an initial value of 15.0 pounds per square inch (1.05 kg. per sq. cm.), a 120-cm. length of gut would have to be elongated to 156 cm.

There are some further related calculations which can be made for the tensile strength of the ligatures. In Figure 3, curves of arc lengths for three catgut specimens are converted to a common height. By a method of summation, a value is obtained which should be proportional to the sine of the average angle over which the protein crystallites are distributed. The distribution values obtained by this method actually may vary from 0° to 90°. When the average distribution angle determined by this method for several specimens is plotted against the tensile strength, the curve so obtained has the general type equation:

$$xy = K$$

For this particular case:

$$T = \frac{K}{\sin \alpha + k} \qquad (1)$$

The object of k is to prevent the tensile strength values from reaching infinity as the distribution angle approaches 0°. Preliminary results indicate that the equation holds for variations in catgut fibers, and in general for variations within any particular type of fiber such as cotton. Of course, each type of fiber may have a different constant.

It is now of interest to discover more specific meanings of the constants. If the distribution of micelles is the most important factor contributing to tensile strength, the tensile strength should be expressed by the equation:

$$T = AK^1$$

where A = area of contact
K^1 = a constant of cohesion

For cylindrical rodlike particles the contact surface is simply given by:

$$A = \frac{b^2}{\sin \alpha + b/l}$$

where b and l = respectively, breadth and length of micelles
α = angle between micellar axes

Hence

$$T = \frac{b^2 K^1}{\sin \alpha + b/l}$$

By reference to Equation 1,

$$b^2 K^1 = K;\ b/l = k$$

Hence, in the empirical equation K is a cohesion constant multiplied by the cross-section area of a micelle; and k is the ratio of width to length (or the shape) of the micelle. Substituting the experimentally found values of T (Tables I and II) and sin α for two catgut ligatures, and assuming α is approximately the same as the distribution angle used above, it is possible to solve for b/l. The average experimental value is 0.1, which was used above. In general, these approximation formulas express the fundamental relationships in catgut ligatures, as well as in all varieties of cellulose and other protein fibers remarkably well.[1]

An even more intriguing phase of the relationship between structure and physical properties is that centering around the absorption characteristics of ligatures in their surgical use. Work along this line is already in progress and will be reported later.

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RECEIVED November 7, 1933. Presented before the Division of Leather and Gelatin Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

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[1] A special application to rayon by W. A. Sisson gives values $b = 41$, $l = 305$ for viscose; and $b = 35$, $l = 700$ for cuprammonium rayon, while for the original native cellulose $b = 60$ and $l = 750$ Å. For viscose, Meyer and Mark found by another method $b = 54$, $l = 346$. Hence, the micelles are evidently half as long in certain viscose rayons and half as thick in certain cuprammonium rayons as in native cellulose.

IMPROVEMENT IN FRANCE'S RUBBER INDUSTRY. Notable improvement was registered in the French rubber manufactures industry during 1933, according to a report to the Commerce Department from Paris. Imports of raw rubber totaled 710,000 quintals, compared with 470,000 quintals in 1932. Production indices in 1933 showed the best average for any post-war year.

The French tire business reacted to the upturn of the automobile trade. Several large manufacturers claim to have sold from 10 to 15 per cent more tires in 1933 than in 1932. However, as competition was very keen, prices remained low and profits, if any, were small. The demand for rubber articles, other than tires, remained steady and prices were remunerative.

Salmon Liver and Salmon Egg Oils

Vitamin Content, and Chemical and Physical Properties

Charles F. Lee and Chester D. Tolle, Bureau of Fisheries, Washington, D. C.

At present there is no commercial production of salmon liver or salmon egg oil. However, the quantity of these oils that could be produced is quite large. The catch of salmon in the United States and Alaska amounts to about 500,000,000 pounds annually. Of this amount, approximately 2 per cent constitute livers and 3 per cent eggs. The livers contain from 5 to 8 per cent of oil and the eggs from 10 to 12 per cent.

From the results obtained by the Schmidt-Nielsens (*6*) who reported that salmon liver oil contained 10,000 units of vitamin A per gram, and by Tolle and Nelson (*8*) who reported that salmon cannery waste was rich in vitamin A, it appeared that salmon liver offered a possibility of producing a vitamin-carrying oil rich in vitamin A particularly. Salmon egg oils were also considered since they are high in oil and could be easily separated from the other cannery waste if found sufficiently high in vitamin content to justify such a selection.

Because of the apparent demand for an oil rich in vitamins and the possibilities offered by salmon liver and salmon egg oils from the standpoint of availability and possible vitamin potency, these products have been studied. The investigations herein reported were designed to obtain information with respect to the vitamin potency, chemical, and physical properties of salmon liver and salmon egg oils, and the vitamin A potency of the oil obtained from the different parts of the Chinook salmon.

Source of Material

Samples of oil were prepared from canned livers and eggs of five species of salmon. The samples from the Columbia River and Puget Sound were prepared by Norman D. Jarvis, U. S. Bureau of Fisheries, and those from the Fraser River were prepared by Harry R. Beard, The Canadian Fishing Company, Ltd., Vancouver, Canada, in the following manner: The livers and eggs were taken from fresh fish from different localities and placed in tin cans. The cans were given a mechanical exhaust and then heated in a retort for varying lengths of time at different temperatures. The oils prepared are shown in Table I, by number, indicating the source of the fish, the origin of the oil, the time heated, and the temperature at which the cans were heated. The oils will be referred to hereafter by number.

The different parts of the Chinook salmon were prepared after the same manner as the eggs and livers and are also shown in Table I. The liver oils were obtained from the canned material by solvent extraction, and the egg oils and oils from the different parts of the Chinook salmon were obtained by pressing and centrifuging.

The cod liver oils used for comparison in these studies were representative of the average medicinal cod liver oil in vitamin D potency but varied considerably in vitamin A potency.

Biological Assays

Vitamin A tests were carried out in the manner described by Tolle and Nelson (*8*). The vitamin A storage of the animals had been controlled by the technic described by Nelson (*3*). Albino rats weighing 40 to 45 grams were placed upon the following ration until they showed distinct signs of vitamin A deficiency:

	Parts
Casein extracted with hot alcohol	18
Osborne and Mendel's (*4*) salt mixture IV	4
Agar	2
Cooked cornstarch	67
Peanut oil	1
Yeast	8

One-sixteenth of the yeast used had been exposed to ultraviolet light, and the vitamin D potency of this product has been shown to be adequate to supply sufficient quantities of that vitamin in the ration.

The rats were then divided into groups of six animals each, comparable as to size, sex, and parentage. One group of animals in each series received no vitamin A and served as a control to show that the animals were depleted of the vitamin in question. The control group in each series, represented by Figures 1 to 6, is indicated by N. C. The remaining groups in each series received the amount and kind of oil indicated in the figures. The dotted portion of the curve represents the growth response during the depletion period prior to the feeding of the oil. The vertical lines crossing the curves indicate the point at which an animal died.

Table I. History and Characteristics of Oils Tested

Sample	Source of Fish	Origin of Oil	Time Heated	Temperature		Sp. Gr. (25°/25° C.)	Refractive Index (20° C.)	Iodine No. (Hanus)	Saponification Value	Acid Value	Unsaponifiable Matter
			Hours	*° F.*	*° C.*						
1*L*	Columbia River	Chinook livers	5	212	100	0.9280	1.4791	168.0	178.3	5.50	3.19
1*E*		Chinook eggs	5	212	100	0.9258	1.4859	217.8	180.2	0.77	2.10
3*L*		Blueback (Sockeye) livers	5	212	100	0.9232	1.4834	169.6	174.4	5.17	5.97
3*E*		Blueback eggs	5	212	100	0.9294	1.4862	219.2	184.4	1.29	2.19
4*L*	Puget Sound	Chum livers	1	228	108.9	....	....	...	...	..	..
4*E*		Chum eggs	1	228	108.9	0.9292	1.4849	206.4	185.0	0.80	1.68
5*L*		Chum livers	5	210	98.9	0.9399	1.4786	162.3	159.7	48.90	8.46
5*E*		Chum eggs	5	210	98.9	0.9174	1.4860	206.5	176.6	5.47	2.88
6*L*		Sockeye livers	1	228	108.9	....	....	...	...	..	..
6*E*		Sockeye eggs	1	228	108.9	0.9295	1.4847	210.8	183.5	0.51	1.71
7*L*		Sockeye livers	5	210	98.9	0.9234	1.4822	167.8	169.0	8.98	6.44
7*E*		Sockeye eggs	5	210	98.9	0.9249	1.4843	208.9	179.5	2.08	2.41
8*L*		Coho livers	1	228	108.9	....	....	...	...	...	..
8*E*		Coho eggs	1	228	108.9	0.9299	1.4869	223.5	182.5	0.93	2.46
11*L*	Fraser River	Humpback livers	1	228	108.9	I. S.[a]	1.4822	205.4	176.8	I. S.	I. S.
11*E*		Humpback eggs	1	228	108.9	0.9300	1.4880	228.7	178.6	0.85	2.38
1*X*	Columbia River	Chinook trimmings	5	212	100	0.9154	1.4734	113.0	191.2	0.86	0.72
1*N*		Chinook trimmings (without livers)	5	212	100	0.9191	1.4760	135.3	189.1	1.75	0.91
1*F*		Commercial canned Chinook	5	212	100	0.9177	1.4756	133.6	191.5	0.41	0.63
1*C*		Whole-fish canned Chinook	5	212	100	0.9161	1.4747	121.8	191.0	0.45	0.73
1*S*		Chinook milt (sperm)	5	212	100	....	....	...	...	..	..
C. L. O. Medicinal		Cod liver				....	....	...	..	..	..

[a] I. S., insufficient sample.

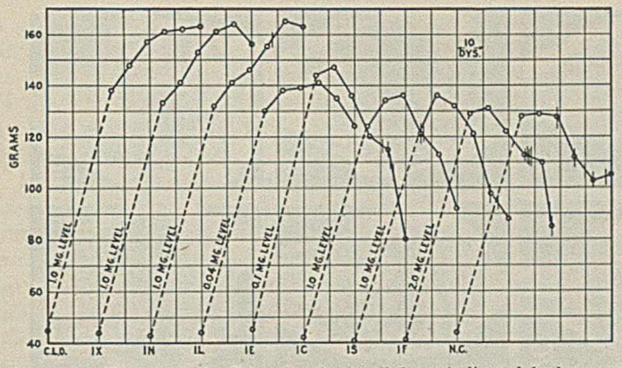

Figure 1. Vitamin A in Chinook salmon oil from indicated body parts

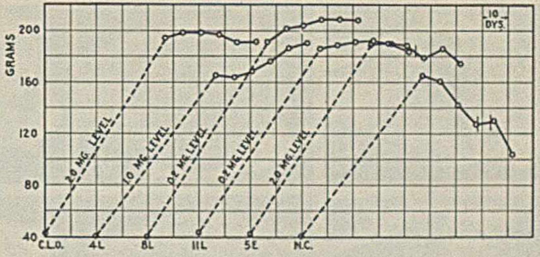

Figure 2. Vitamin A in salmon liver and egg oils

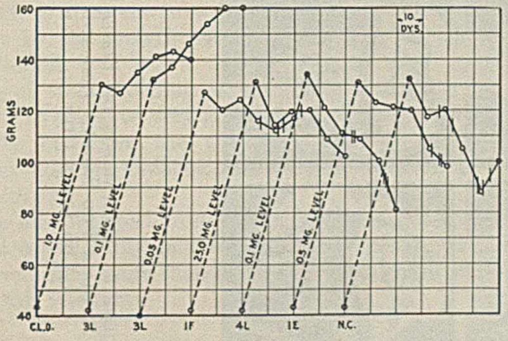

Figure 3. Vitamin A in salmon oils

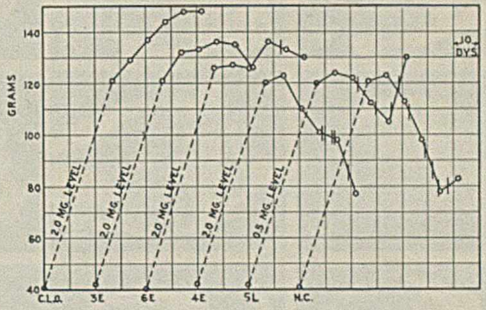

Figure 4. Vitamin A in salmon egg and liver oils

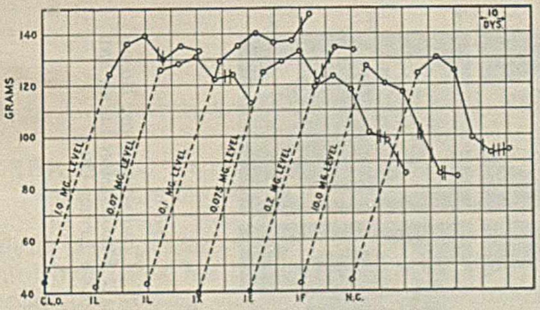

Figure 5. Vitamin A in salmon oils

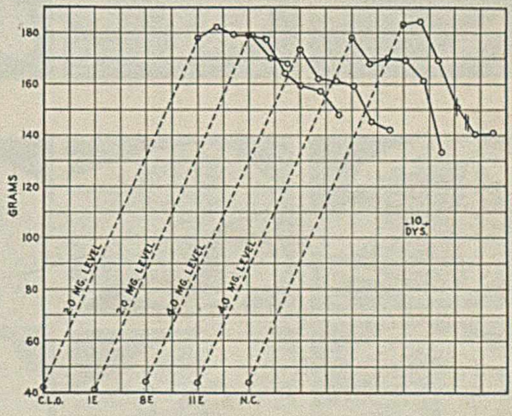

Figure 6. Vitamin A in salmon egg oils

FIGURES 1 TO 6. COMPOSITE GROWTH CURVES OF ANIMALS FED SALMON OILS

Figure 7 gives photographs of the distal ends of radii which were split longitudinally and stained with silver nitrate. They show the degree of healing induced by various levels of salmon liver oils as compared with a standard medicinal cod liver oil. *A* is a normal bone, and *B* shows the degree of rickets produced in 30 days by the basal diet. From the three animals on salmon liver oil and the three on cod liver oil used in each test, one bone was selected as typical of the healing produced by each oil. Photographs 1*L* to 11*L* correspond to the numbers used in Table I. The affixed letter *C* refers in each case to the cod liver oil control. 3*L* was fed at two levels, 0.03 and 0.05 per cent. All the other liver oils were fed at 0.05 per cent in comparison with cod liver oil at 0.1 per cent.

Figure 8 shows sectioned radii stained with silver nitrate, indicating healing induced by salmon egg oils. Oil 3*E* was fed at 0.15 per cent. Oils 1*E*, 5*E*, 6*E*, 7*E*, 8*E*, and 11*E* were fed at 0.2 per cent. Oil 4*E* was fed at 0.25 per cent. Oil 11*E* was also fed at 0.1 per cent. Cod liver oil was fed at 0.1 per cent in all comparisons.

The procedure used in determining the vitamin D potency of the oils was the same as that described by Manning, Nelson, and Tolle (*2*) for menhaden oils. Albino rats weighing from 60 to 70 grams were fed the Steenbock and Black (*7*) ration No. 2965 for 23 to 25 days. They were then segregated and the desired quantity of oil was incorporated in the ration. After 10 days the animals were killed and their bones examined for healing of rachitic metaphyses. In all cases comparisons were made between salmon liver or egg oil and a medicinal cod liver oil fed to litter mate animals. In each case a given level of salmon oil was compared with 0.1 per cent of cod liver oil in the ration.

CHEMICAL AND PHYSICAL CHARACTERISTICS OF SALMON OILS

The more important chemical and physical characteristics of the salmon oils were determined. The results obtained are shown in Table I.

A note concerning the source of raw material may explain to some extent the high results obtained under the acid value of the oils. Table I shows that the acid value for sample 5*L* is very high in comparison with the acid value for the other liver samples. The same is true in the case of sample 5*E*. According to N. D. Jarvis, the fish from which these samples were taken were approximately 48 hours old and the livers were stale when received. After the livers and eggs

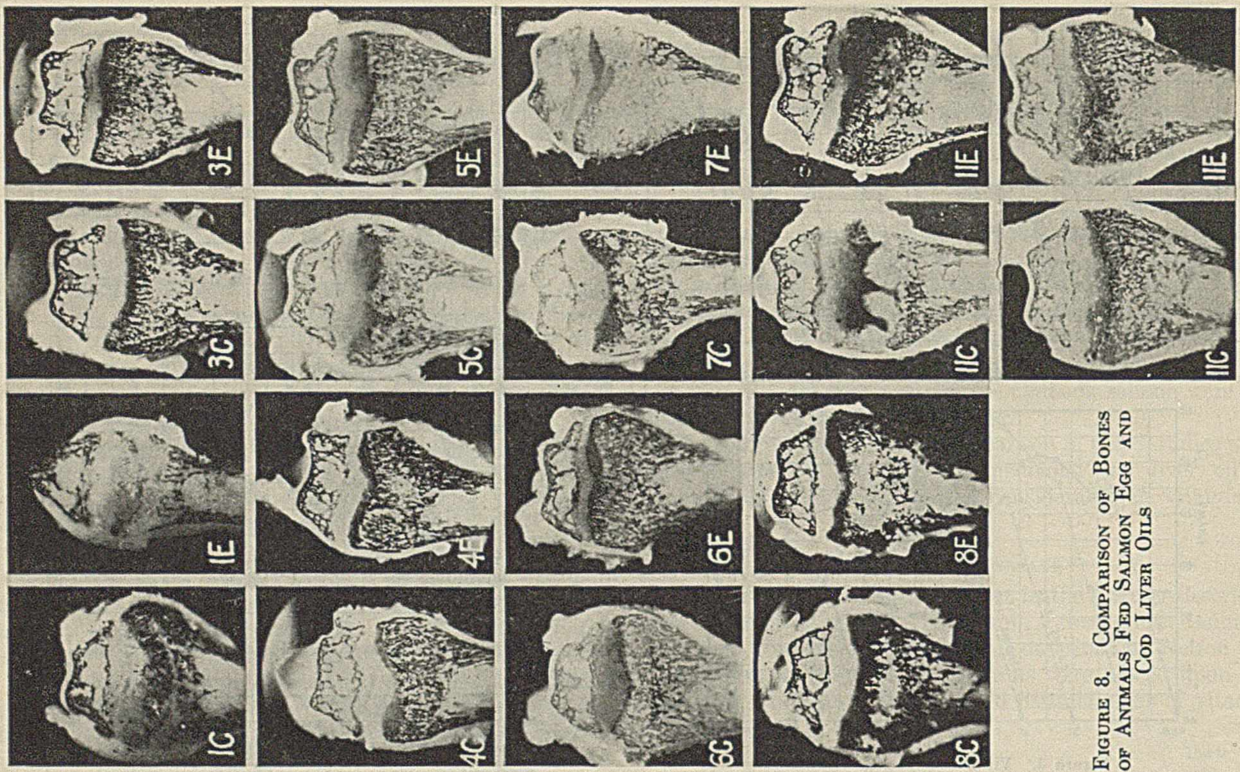

FIGURE 8. COMPARISON OF BONES OF ANIMALS FED SALMON EGG AND COD LIVER OILS

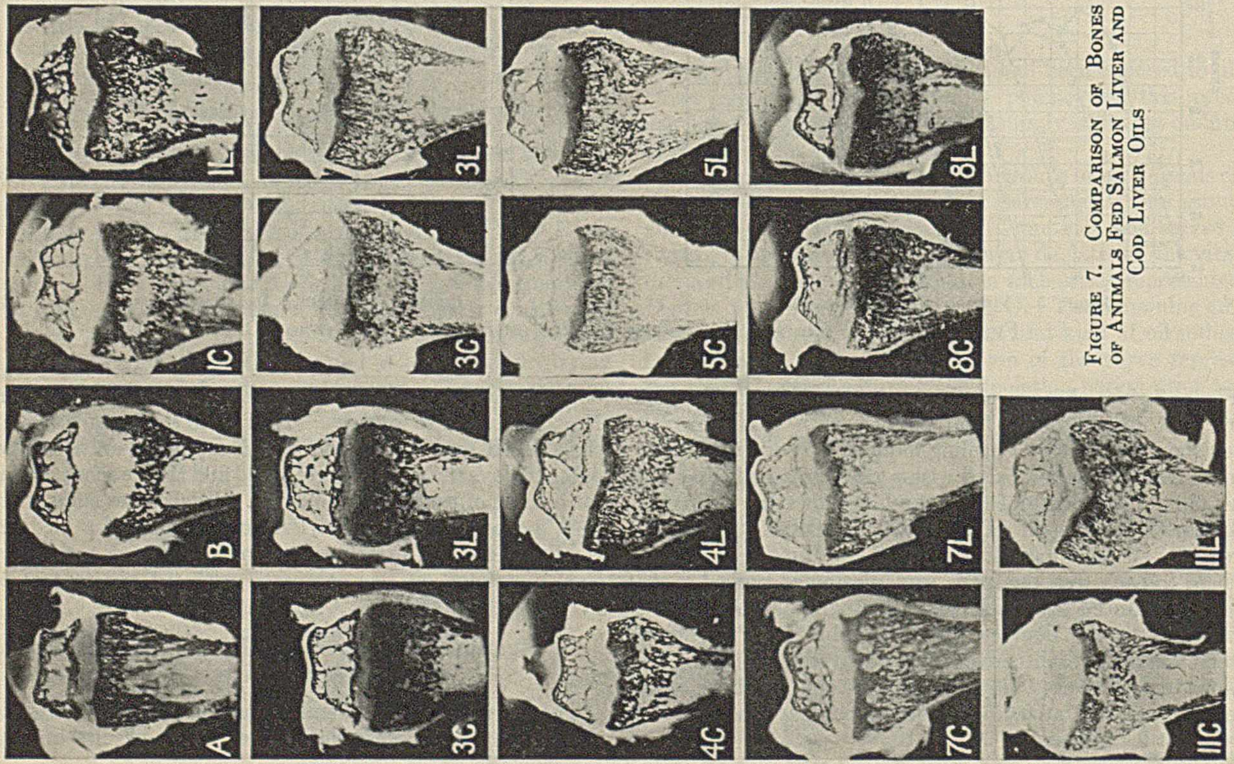

FIGURE 7. COMPARISON OF BONES OF ANIMALS FED SALMON LIVER AND COD LIVER OILS

were packed in the cans, they were given a heat exhaust before sealing by heating the cans in boiling water for one hour. This may account for the high acid values.

DISCUSSION

The weight criterion was followed in deciding the vitamin A potency of the oils. This assay is based upon the estimation of the minimum amount of cod liver oil necessary to meet specific growth-promoting requirements in a standard test animal (*5*).

According to Holmes (*1*) the vitamin potency of cod liver oil shall be expressed in units per gram of oil, the unit to be the minimum daily amount (in milligrams) of cod liver oil required to cause, in 60 per cent of the animals in any one group, a gain in weight of at least 12 grams within a period of 28 days under the conditions of growth and diet specified in this assay. The maximum weight must be attained at the end of the test, and the eye condition must be corrected by an amount of cod liver oil not to exceed three times the minimum growth factor.

In this study, a 35-day test period was used, and in many cases the oils were not fed at high enough levels to produce minimum growth. However, the object of the investigation was not to determine the vitamin A content per gram of the oil but to determine the relative potency. The results obtained as indicated by Figures 1 to 6 show that salmon liver oils are approximately 5 to 20 times as potent in vitamin A as cod liver oil. As previously stated by Tolle and Nelson (*8*), medicinal cod liver oils vary appreciably in vitamin A potency, and this is apparent from the results shown in the different figures by the growth curve of the group which received cod liver oil.

The oil from the Chinook trimmings, both with and without the livers, gave very good results, as indicated in Figure 1. The oils from the whole Chinook, the commercially canned, and the Chinook milt (sperm) were low in vitamin A potency.

The oils obtained from the eggs of the different species varied considerably in their vitamin A potency and in no case were they more than equal to a good grade of cod liver oil in this vitamin.

The results of the vitamin D tests are given in Figures 7 and 8. As shown in Figure 7, the liver oils from the five species of salmon studied were twice as potent in vitamin D as a good grade of medicinal cod liver oil. Oil 3*L* from the livers of Columbia River Blueback or Sockeye salmon was fully three times as potent in vitamin D as the cod liver oil used as a control.

Figure 8 shows the results obtained with the salmon egg oils. These oils showed considerable variation in their vitamin D potency. They range from 40 to 100 per cent as potent as a good grade of medicinal cod liver oil.

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Received October 1, 1933.

Apple Juice Concentrate

D. C. Carpenter and E. C. Smith, New York State Agricultural Experiment Station, Geneva, N. Y.

The production of apple juice concentrate for use in carbonated beverages is studied in small-scale equipment in which esters originally present in the juice are returned to the concentrate. On the basis of comparison used and within the experimental errors involved, a high recovery of esters is found.

Reconstituted juice prepared from concentrate by dilution with water compares favorably with the original juice in organoleptic tests.

It appears probable that apple juice concentrate may be handled by bottlers for the production of carbonated beverages with little or no change in bottling operations or equipment.

THE demand for natural fruit flavors for use in the beverage industry, chiefly for the production of carbonated fruit juices, has made necessary the working out of methods of preparing fruit juice concentrates that would possess all the aroma and flavoring substances originally present in the natural juice. In the case of apple juice, Carpenter and Walsh (*2*) have shown that a carbonated beverage may be satisfactorily prepared by carbonation of the whole juice after the proper processing and filtration to remove suspended colloidal material has taken place. It is desirable however that an apple concentrate be prepared so that the bottler may follow his usual technic of preparing carbonated beverages—namely, that of placing in the bottle a small amount of a concentrate or sirup containing the desired flavoring material and filling the remainder of the bottle with carbonated water. The production of such a concentrate would make available to the public an apple beverage throughout the entire year instead of only during the fall and winter months, to which production is at present limited. The experiments described here have been carried out for the purpose of producing such a concentrate that would contain to a large degree the aroma and flavoring substances of the original apple juice.

According to the work of Power and Chestnut (*8*) the principal odorous constituents of apples are the amyl esters of formic, acetic, and caproic acids, respectively, together with furfural and acetaldehyde. These authors were unable to confirm the statement often found in textbooks designating isoamyl isovalerate as "apple oil," even though the odor of this ester is much like the characteristic aroma from apples.

It is obvious that the removal of water from apple juice and the concentration of the soluble ingredients may be accomplished (1) by freezing out water as ice, from which the concentrate may be separated in a centrifugal, or (2) through the evaporation of water by the application of heat. Gore (*4*) proposed the freezing process some years ago.

If the concentration of apple juice is to be effected by the use of heat, it is obvious that evaporation *in vacuo* is necessary to avoid caramelization of the sugar contained in the juice by exposure to high temperatures. Whether vacuum is applied or not in the evaporation process, the bulk of the esters and other volatile flavoring materials will be volatilized along with the water vapor removed, and a concentrate will result which has little or no volatile material remaining. It is clear that some means must be employed by which the desired volatile substances may be condensed and returned to the concentrate. To this end The Pfaudler Company has designed a fruit juice concentrator having an ester impregnating unit (*12*), and it has been chiefly with a small model of this machine that the work reported here has been done.

PROCESSING OF THE JUICE

Before concentration of the juice can be attempted, the suspended colloidal material must be removed so that a sparkling clear juice is delivered to the concentrator. In processing the apple juice for these experiments, the flash heating process, described by Carpenter and Walsh (*2*), has been used:

> This consists essentially in passing the freshly pressed juice through a tubular heater so that its temperature may be rapidly raised to 82.2° C. (180° F.) to coagulate the colloidal material. Before leaving the heater and being exposed to the air, the juice is cooled to room temperature by passing through coils cooled by running water so that little or none of the aroma substances is lost. The juice is then mixed with Filter-Cel and filtered through a frame filter press. A second filtration through asbestos and paper pulp gives a brilliant, clear product, but this is unnecessary at this stage of the process for juice that is to be concentrated, as it is believed to be better practice to filter the finished concentrate just before bottling.

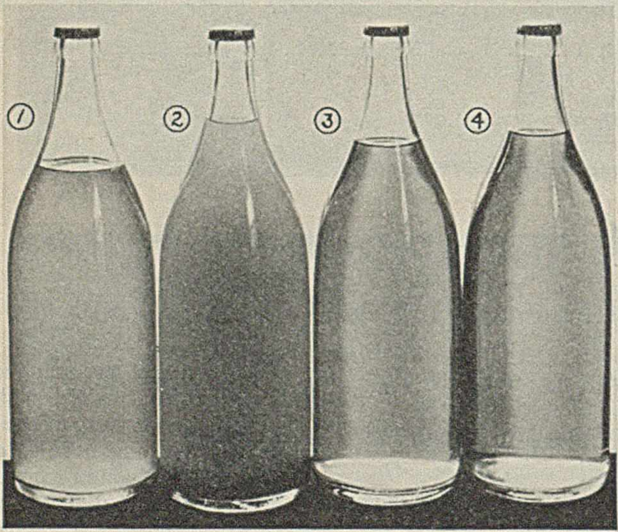

FIGURE 1. STAGES IN PROCESSING OF ROME BEAUTY APPLE JUICE BY FLASH HEATING METHOD

In Figure 1 is shown a series of samples of Rome Beauty apple juice at various stages in the processing. Bottle 1 shows the raw juice as pressed; 2 after the flash heating at 82.2° C. (180° F.) to coagulate the colloidal material which may be seen to be largely deposited at the bottom of the bottle; 3 after filtration through Filter-Cel; and 4 after filtration through the Seitz filter, which not only gives a sparkling clear product, but one which is also sterile (*1*).

The chemical analysis of juice from Rome Beauty, Russet, and Northern Spy apples has been carried out by the methods previously used in this laboratory and the results are given in Table I for the raw juices as pressed and after processing to give a clear product, respectively. In commercial plants it is common practice to estimate total solids by refractive index, assuming that the established relationship between refractive index and sugar concentration applies (*9*). As will be seen from the data, the total solids in apple juice as estimated by refractive index are somewhat high as compared with figures actually obtained by drying. In the case of Rome Beauty, Russet, and Northern Spy, the solids obtained by drying are, respectively, 96.7, 97, and 94.6 per cent of the values given by the refractive index method. On the whole it may be said that for apple juices the total solids actually approximate about 96 per cent of the solids as determined by refractive index methods. The latter is obviously a valuable factory control method.

TABLE I. COMPOSITION OF APPLE JUICES

(In per cent)

	ROME BEAUTY		RUSSET		NORTHERN SPY	
	Raw	Filtered	Raw	Filtered	Raw	Filtered
pH	3.34	3.37	3.32	3.37	3.54	3.54
Density	1.054	1.054	1.071	1.0706	1.055	1.054
n_D^{20}	1.3525	1.3534	1.3593	1.3596	1.3525	1.3534
Solids (Schönrock)	13.1	13.5	17.2	17.4	13.1	13.5
Solids (by drying)	...	13.09	...	16.88	...	12.75
Volatile acidity[a]	...	0.04	...	0.14	...	0.06
Total acidity[b]	0.27	0.26	0.73	0.70	0.45	0.42
d-Fructose	...	5.76	...	4.56	...	5.83
d-Glucose	...	3.62	...	3.20	...	3.15
Sucrose	...	2.29	...	5.63	...	2.22
Nitrogen	0.0086	0.0056	0.0118	0.0096	0.0057	0.0036
Calcium pectate	0.145	0.132	0.162	0.165	0.139	0.094
Tannin	0.013	0.012	0.033	0.021	0.032	0.018
Nontannin	0.055	0.066	0.081	0.100	0.065	0.085
Total astringency	0.068	0.078	0.114	0.121	0.097	0.103

[a] Volatile acidity calculated as acetic acid.
[b] Total acidity calculated as malic acid.

Eoff (*3*) found that fructose was the predominant sugar in a number of apple varieties. The present results are in harmony with his conclusion except in the case of the Russet variety in which the writers have found that sucrose exceeds the fructose content.

In accord with other results from this laboratory, the principal changes in composition of the juice brought about by filtration are the removal of part of the protein, pectin substances, and tannin, changes which improve rather than detract from the flavor of the juice.

DETERMINATION OF THE GELLING CONCENTRATION

A juice containing pectin, sugar, and acid in the right amounts will form a jelly when concentration of the juice has progressed far enough. For producing juice concentrates that are to remain fluid, we are therefore under certain limitations as to how far the concentration operation can be carried without setting up the juice to a jelly in the evaporator. In the absence of fundamental data from which to predict the gelling concentration of the various juices, this point has been established experimentally by the evaporation *in vacuo* of 300-cc. tests samples, interrupting the evaporation at intervals, and transferring samples to test tubes to observe when the gelling point has been reached. The concentration of the series of samples is then determined by refractive index and reference to Schönrock's table, and the gelling property recorded, to serve as a measure of the concentration that can be attained in the evaporator without complications due to gel formation.

TABLE II. GELLING CONCENTRATION OF APPLE JUICES

	ROME BEAUTY		RUSSET		NORTHERN SPY	
SAMPLE	n_D^{20}	Total solids	n_D^{20}	Total solids	n_D^{20}	Total solids
		%		%		%
1	1.4158	48.0	1.3935	36.8	1.3960	38.1
2	1.4220	51.0	1.4232	51.5	1.4175	48.8
3	1.4250	52.4	1.4285	54.0	1.4266	53.1
4	1.4272	53.4	1.4305	54.9	1.4325	55.8
5	1.4315	55.4	1.4348	56.85	1.4424	60.2
6	1.4325[a]	55.8[a]	1.4368[a]	57.8[a]	1.4525	64.7
7	1.4335[a]	56.3[a]	1.4387[a]	58.6[a]	1.4675	71.0

[a] Samples gelled in 2 to 3 hours at room temperature.

In Table II are given the results of several of the gelling tests with various apple juices. These indicate that Rome Beauty and Russet juice may be concentrated to around 55 per cent total solids before difficulties are encountered due to gel formation. Northern Spy juice did not gel even at 71 per cent total solids and therefore presented no difficulties. From Table II, the ratios of sugar to pectin in Rome

Beauty and Russet juice are 88 to 1 and 81 to 1, respectively, while in Northern Spy juice the ratio is 119 to 1. It is probable that the higher pH of the Northern Spy juice is responsible for the fact of not gelling, although the ratio between sugar and pectin is considerably greater than in the other juices.

CONSTRUCTION OF EVAPORATOR AND ESTER IMPREGNATOR

The evaporator and ester impregnator were constructed of large cylinders of Pyrex glass fitted by means of rubber gaskets to other parts of the equipment which were principally of glass-lined steel. Heating was done by steam passing through a heavily silver-plated coil inserted near the base of the evaporator. The evaporator was equipped with a sampling device whereby samples of the concentrate could be withdrawn at any time without disturbing the evaporation. Vacuum was maintained in the evaporator by a water pump actuated in turn by a motor-driven centrifugal pump forcing water at a constant pressure of 0.84 kg. per sq. cm. (12 pounds per square inch) through the water pump. On the ester impregnator side, the concentrate was circulated by a motor-driven pump through cooling coils surrounded by running water so that efficient condensation of the esters in the cooled concentrate was to be expected. In the vapor outlet lines from the evaporator, two balanced check valves were installed, permitting the passage of fluid or vapor in only the outgoing direction. Regulation of the two large monel metal valves in the vapor outlet line permitted collection of vaporized material in the impregnator or its escape to the drain. The evaporator was supplied with an accurately calibrated vacuum gage and thermometers recording the temperature of vapor and liquid phases, respectively. The set-up is shown in Figure 2.

OPERATION OF EVAPORATOR AND ESTER IMPREGNATOR

After the installation had been carefully checked for air leakages and these had been eliminated, the system was washed out with water and was ready for operation.

The necessary valves were closed, cutting off the impregnator and closing the evaporator except to the vacuum line. The vacuum pump was then started, and, when the vacuum gage registered about 51 cm. (20 inches), apple juice was admitted to the evaporator. A charge of 37.85 liters (10 gallons) of juice was accommodated at one time in the evaporator. The intake valve was then closed and steam admitted to the heating coil. The temperature of the juice rose until the boiling point was reached, depending, respectively, on the vacuum produced and the concentration of dissolved solids in the juice. Boiling was continued until samples drawn from the evaporator showed that the gelling point of the juice had been nearly reached, as described before. When the end point had been reached, the steam valve was closed, the vacuum line cut off, and air gradually admitted to the evaporator.

The concentrate left in the evaporator at this stage was practically devoid of the flavor and aroma substances originally present in the juice. The esters are a complete loss in the first batch concentrated in the evaporator. It is necessary, however, to produce the deësterized concentrate in order to have material with which to charge the ester impregnator.

The thick deësterized concentrate was transferred from the evaporator to the impregnator unit by opening a valve in the base of the former and starting the pump on the impregnator side of the set-up. When the concentrate was all transferred to the impregnator, the valve in the base of the evaporator was closed and the concentrate circulated through the cooling coils on the impregnator side.

A fresh charge of 37.85 liters (10 gallons) of apple juice was drawn into the evaporator, the evaporator was evacuated to the desired degree, and the valves in the vapor lines were set so that vapors given off from juice in the evaporator would pass to the impregnator unit. Heat was again applied to the evaporator, and the volatile aroma substances were driven off and condensed in the cold deësterized concentrate which was continually circulated. Samples were removed from the evaporator from time to time and subjected to organoleptic tests to determine when the aroma substances had been practically volatilized. Of course some water vapor was transferred along with the aroma substances to the impregnator side. This tended to dilute the finished esterized concentrate but it was entirely possible to start esterification of a concentrate containing 55 to 56 per cent total solids and have a finished esterized concentrate having 49 to 50 per cent total solids without material loss of esters.

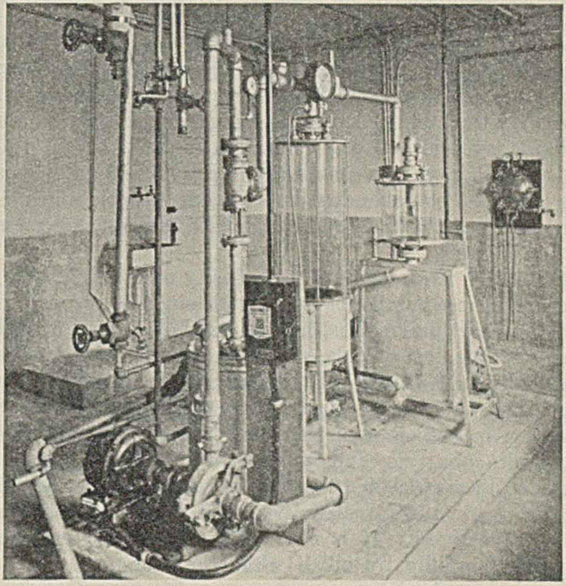

FIGURE 2. EXPERIMENTAL MODEL OF PFAUDLER FRUIT JUICE CONCENTRATOR AND ESTER IMPREGNATOR

At this stage the valve in the vapor line connecting the evaporator and impregnator was closed, the valve in the vapor line from the evaporator to the drain was opened, and the evaporation of the juice in the evaporator continued as described until the gelling point was almost reached. While evaporation was going on, the esterized concentrate was pumped out of the impregnator unit and stored in a carboy or other receptacle until it received the final filtration before bottling. The impregnator unit was then ready to receive a fresh charge of deësterized concentrate from the evaporator, and the cycle of operations was repeated.

The esterized concentrate is viscous and filtration is slow. Filtration is desirable, however, to give a brilliant, clear product for the bottler. If the final filtration is made through the Seitz E. K. filter, the product is sterile and may be filled directly into sterile bottles. If filtration is made through an ordinary beer filter, the filtrate may be pasteurized at 76.6° C. (170° F.) for 15 minutes after bottling. Pasteurization at higher temperatures or for long periods, in the authors' experience, resulted in the deposition of a brown sediment in the bottled goods. However, the sediment clung to the bottom of the container well and was not easily dislodged; it would probably introduce no complications to the experienced bottler but it may be avoided. If cold storage facilities are available, the concentrate may be stored for long periods with no sterilization, without complications due to bacterial spoilage.

ESTIMATION OF ESTERS

The classical reaction for the estimation of esters is saponification with alkali, and it is on this reaction that we must depend for quantitative results. In order to use the reaction on complex mixtures such as fruit juices, it is necessary that the esters be separated from the other materials before the reaction can be applied. The means of separation of the esters are limited to the use of immiscible solvents and to distillation. The former would be preferable to the latter on account of the fact that, during distillation (even steam distillation as recommended by Wilson, *13*) changes in the carbohydrates take place which yield volatile substances that undergo the saponification reaction with alkali. The writers have tried a number of immiscible solvents—benzene, heptane, ether, isoamyl alcohol, and carbon tetrachloride—for shaking out the esters of apple juice and have found carefully purified carbon tetrachloride to be fairly satisfactory. Considerable difficulty has been encountered, however, in effecting good separations of the liquid phases in the separatory funnel. The addition of salt to the water phase helped break the emulsion and drive esters and free acid into the carbon tetrachloride layer. Removal of the carbon tetrachloride layer without the removal at the same time of traces of the juice layer was practically impossible; for this reason the idea has been abandoned of using immiscible solvents as a means of separation, and steam distillation has been employed instead.

Olsson (*7*) has examined the velocity of saponification by alkali of a large number of esters. Although he experimented with no amyl derivatives, his results showed that for ethyl esters of the fatty acids, the velocity constant decreased materially as the length of the acid chain increased and was somewhat less for iso acids than the normal type. For instance, in the cases of the ethyl esters of formic, acetic, propionic, *n*-butyric, and *n*-valeric acids, the velocity constants (k_a) were 21,300, 100, 89.6, 52.5, and 50.0, respectively; for isobutyric and isovaleric acids the values were 49.2 and 25.3, respectively. It is clear that the simpler esters are saponified rapidly by alkali while the more complex ones proceed more slowly.

TABLE III. DETERMINATION OF CONDITIONS OF SAPONIFICATION

(0.0858 gram isoamyl isovalerate)

EXPT.	SOLVENT	0.1 *N* KOH ADDED INITIALLY	BOILING PERIOD	0.1 *N* KOH USED IN SAPONIFICATION	AMOUNT SAPONIFIED
		Cc.	*Hr.*	*Cc.*	%
1	200 cc. H_2O	20.00	1	0.71	14.3
2	200 cc. H_2O + 80 cc. C_2H_5OH	20.00	1	3.51	70.5
3	200 cc. H_2O + 80 cc. C_2H_5OH	10.00	1	2.47	49.6
4	Same	20.00	1	3.51	70.5
5	Same	30.00	1	4.09	82.2
6	200 cc. H_2O + 80 cc. C_2H_5OH	30.00	1	4.09	82.2
7	Same	30.00	2	4.38	88.0
8	Same	30.00	3	4.66	93.7
9	100 cc. H_2O + 100 cc. C_2H_5OH	30.00	1	4.08	82.0
10	Same	30.00	2	4.58	92.1
	Theoretical			4.98	100.0

While isoamyl isovalerate has not been found in apples, this ester has been used here in saponification tests to determine in general the kind of solvent, boiling period, and amount of excess alkali—tests which would give an indication of the procedure required for saponification. In view of Olsson's work it is believed that the esters actually present in apple juice would be saponified much more readily than the ester chosen for these tests.

In Table III are listed a number of saponification tests with isoamyl isovalerate. It is clear that the presence of alcohol is required and that a large excess of alkali is desirable if the saponification is to be anywhere near complete within a reasonable boiling period. From these results the conditions given under experiment 7 for conducting the saponification have been empirically chosen. These conditions are saponification at the boiling point with 30 cc. of 0.1 *N* potassium hydroxide for 2 hours in a solvent composed of 200 cc. water and 80 cc. ethyl alcohol, all of which is subsequent to neutralization of the volatile acid with alkali. Under these conditions, saponification of isoamyl isovalerate has proceeded to an extent of about 88 per cent.

As regards the recovery of known amounts of isoamyl isovalerate by steam distillation, it appears from Table IV that about 87 per cent was recovered in the first 200 cc. of steam distillate and that further recovery was very slow and tedious by steam distillation. Quantitative recovery of esters by steam distillation from fruit juices appears to be out of the question owing to the great falling off of the ester recovery with successive fractions as shown above, and the opposing factor which produces saponifiable substances because of the breakdown of sugars by the action of heat, as has been mentioned before. The recovery of isoamyl isovalerate by steam distillation, followed by saponification as above, would indicate values in the neighborhood of 76 per cent of the actual amounts present. It is believed that the recovery would probably be greater on the esters present in the apple than have been found here for isoamyl isovalerate for the reason that the latter is a more complex ester than those so far identified in the apple.

TABLE IV. RECOVERY OF ISOAMYL ISOVALERATE BY STEAM DISTILLATION

(0.0858 gram ester and 200 cc. water, steam-distilled)

FRACTION	VOL. OF FRACTION	SOLVENT	INITIAL ALKALI ADDED	BOILING PERIOD	0.1 *N* KOH USED IN SAPONIFICATION	RECOVERY
	Cc.		*Cc.*	*Hours*	*Cc.*	%
1	200	200 cc. H_2O + 80 cc. C_2H_5OH	30.00	2	4.34	87.0
2	200	Same	30.00	2	0.23	4.6
Total	...	....	...	.	4.57	91.6
Theoretical	...	....	...	.	4.98	100.0

In Table V are recorded some experiments on the production of saponifiable materials during steam distillation of sugar solutions. The sugars were taken from samples previously carefully purified in this laboratory for solubility determinations. Three per cent solutions were made of *d*-glucose and *d*-fructose, 200-cc. samples of each were submitted to steam distillation, and several fractions of 200 cc. each of distillate were collected and saponified. It is clear that *d*-fructose is broken down much more than *d*-glucose, and it appears probable that separation of the esters from fruit juices by steam distillation is made difficult, at least partly, by decomposition of fructose during the operation. These data show the futility of an absolute determination of the esters present in fruit juices. In the case of apple juice, saponifiable substances continue to steam distill even after five fractions have been collected.

TABLE V. DECOMPOSITION OF SUGARS BY STEAM DISTILLATION

(200 cc. of 3.00 per cent sugar soln.)

200-CC. FRACTION	0.1 *N* KOH REQUIRED TO SAPONIFY DISTILLATE	
	Glucose	Fructose
1	0.12	0.17
2	0.03	0.25
3	0.10	0.39

On account of the foregoing difficulties the writers have concluded that the fairest comparison of the esters contained in apple juice as compared with the esters in the finished concentrate will be obtained when the latter is diluted with water to its original concentration of total solids and comparisons made on the esters contained in the first 200 cc. of steam distillate obtained from 200-cc. samples of the original and the reconstituted juice, respectively.

Carrying out the ester estimation on this basis, the data given in Table VI have been obtained. While the agreement between duplicate results is oftentimes not as good as would be desired, it must be remembered that the esters are present only in traces, and their estimation is thereby subjected to greater errors in individual experiments. The data indicate a satisfactory recovery of esters in the concentrate. This conclusion was borne out by organoleptic tests on the original juice and the diluted concentrate, between which it was impossible to distinguish by taste or aroma. It will be noted that Rome Beauty juice contains a greater amount of esters than the other juices examined.

Table VI. Comparison of Esters Present in Filtered Apple Juice and in Concentrate[a]

		Rome Beauty	Russet	Northern Spy
Esters in filtered juice		0.24	0.19	0.21
		0.24	0.19	0.20
		0.25	0.16	0.19
	Mean	0.247	0.18	0.20
Esters in concentrate		0.28	0.23	0.18
		0.25	0.16	0.22
	Mean	0.265	0.195	0.20

[a] Results expressed in cubic centimeters of 0.1 *N* potassium hydroxide required to saponify the first 200 cc. of steam distillate, respectively, from 200-cc. samples of apple juice and of reconstituted juice prepared from apple concentrate by dilution with required amount of water to give equivalent total solids.

Estimation of Acetaldehyde

Power and Chestnut (*8*) concluded that acetaldehyde occurred in apples in greater quantities than the various esters. If this is the case, determination of the aldehyde could perhaps be applied as a measure of at least part of the aroma substances occurring in the juice. Accordingly, samples of a blended apple juice have been subjected to steam distillation, collecting the distillate in 200-cc. fractions and, after neutralizing the volatile acid of the distillate with alkali, the aldehyde was estimated with 0.1 *N* sodium acid sulfite reagent as described by Kleber (*5*). These data are given in Table VII, and, while good agreement is shown between duplicates and the titration is sharp, steam distillation appears to be inefficient either in the early or the complete separation of aldehyde, or else aldehyde substances are formed continuously by the breaking down of substances in the juice during the distillation. In either case the aldehyde determination can give little definite evidence concerning the aroma substances of fruit juices.

Table VII. Steam Distillation and Estimation of Acetaldehyde in a Blended Apple Juice

(300-cc. sample, steam-distilled)

Fraction	Vol. of Steam Distillate	Vol. 0.1 *N* Sulfite Reagent Required			CH_3CHO
		Trial A	Trial B	Mean	
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Mg.*
1	200	0.28	0.28	0.28	1.23
2	200	0.24	0.22	0.23	1.02
3	200	0.25	0.28	0.26	1.14

Viscosity of Final Esterized Concentrate

The common practice of carbonated beverage manufacturers in the bottling operation is to place a small volume of sirup containing the desired flavoring material in the bottle in the "siruper," then to fill the bottle with carbonated water and close with a crown seal. In the automatic machinery in general use for the siruping operation, the bottle is under the sirup outlet for only a few seconds at most, during which time the charge of sirup must be transferred to the bottle. On account of this procedure the viscosity of the sirup or concentrate has an important bearing on the speed of the operation. Sugar sirups in general use range in density between 28° and 32° Bé., which values correspond to 51.7 and 59.4 per cent sucrose content, respectively.

In Table VIII are recorded the viscosity of the various esterized apple concentrates and of the two sugar sirups mentioned above. The values recorded under relative viscosity were obtained in a pipet viscometer as commonly employed by glue and gelatin manufacturers, and represent the comparative rate at which the respective materials would pass through a pipe in factory practice. The absolute viscosity has also been measured in a MacMichael viscometer and is recorded in centipoises in Table VIII. The MacMichael apparatus was calibrated against a 60 per cent sucrose solution having a viscosity of 56.5 centipoises at 20° C.

If it is assumed that a 32° Bé. sugar sirup handles satisfactorily in the siruping operation, it would appear that Rome Beauty and Northern Spy concentrates would handle at least equally well. Russet concentrate might require the use of a larger sized pipe delivering to the bottle or increased pressure behind the concentrate to deliver the charge more rapidly during the time available for the siruping operation.

Table VIII. Viscosity of Final Esterized Apple Concentrates and of Sugar Sirups at 20° C.

	Relative Viscosity	Viscosity		Relative Viscosity	Viscosity
		Centipoises			*Centipoises*
Water	1.00	1.005	Northern Spy	3.45	13.66
Rome Beauty	16.00	90.8	Sugar sirup, 28° Bé.	4.61	20.25
Russet	24.76	135.9	Sugar sirup, 32° Bé.	14.80	56.5

It is presumable that the high viscosity of the Rome Beauty and Russet concentrates is attributable largely to the interrelation between sugar, pectin, and pH, which is responsible for gelling (*6*, *10*, *11*). It is obvious that blending of Russet juice with Northern Spy would greatly reduce the viscosity in case this property is found troublesome in the siruping operation.

General Characteristics of Concentrates

A summary of certain data collected during the preparation of the deësterized concentrate and the final esterized concentrate is given in Table IX. Of the apple varieties studied, the esters are removed from Russet juice most readily and transferred to the concentrate with the least dilution of the concentrate with water vapor. This is due no doubt to the fact that Russet juice contains less esters than the other juices and perhaps that these esters may be more easily volatilized. The other two juices appear to behave about alike, both carrying considerable water over with the esters during the esterification operation.

Table IX. Data on Apple Concentrates

	Rome Beauty	Russet	Northern Spy
Deësterized concentrate:			
Density at 20° C.	1.2530	1.2545	1.2640
n_D^{20}	1.4272	1.4285	1.4314
Solids (Schönrock), %	53.4	54.0	55.3
Final esterized concentrate:			
Density at 20° C.	1.206	1.231	1.219
Relative viscosity at 20° C. (η/η_{H_2O})	16.00	24.76	3.45
n_D^{20}	1.4113	1.4195	1.4142
Solids (Schönrock), %	45.8	49.75	47.25
Vol. required for 8-oz. split, oz.	2.06	3.04	2.47
(237-cc. split, cc.)	(60.9)	(89.8)	(73.0)

The principal losses in preparing the esterized concentrate are confined to volatile acids removed from the juice while the latter is under straight evaporation and which would not be returned to the esterified product. These losses are relatively unimportant from the standpoints of amount of material and of resulting flavor.

The color of apple juice prepared from apple concentrate by dilution with the requisite amounts of water is about 10 to 15 per cent darker than the original juice. This is probably due to the effect of heat on the various sugars and is of minor importance.

The charge of esterized concentrate required for an 8-ounce (237-cc.) split of carbonated juice has been calculated on the basis of restoring the concentration of solids originally present in the unconcentrated juice and appears in Table IX.

ACKNOWLEDGMENT

The writers are indebted to The Pfaudler Company of Rochester, N. Y., for placing at their disposal the fruit juice concentrator with attached ester impregnating unit used in preparing the concentrates herein described, and to W. D. Pheteplace, Jr., for valuable assistance in carrying out the experiments.

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RECEIVED October 5, 1933. Approved by the director of the N. Y. State Agricultural Experiment Station for publication as Journal Paper 11.

Primary Thermal Dissociation

Velocity Constants for Propane, *n*-Butane, and Isobutane

R. E. PAUL[1] AND L. F. MAREK

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

Propane, n-butane, and isobutane are subjected to limited thermal dissociation in copper and fused-silica tubes under conditions which permit accurate evaluation of the time of contact and temperature for the purpose of determining the velocity constants of the primary thermal dissociation. The extent of dissociation is measured by determination of the olefin content of the product gases by a modified bromide-bromate method.

In the temperature range investigated, the following equations represent the variation of velocity constant with temperature:

$$\text{Propane:}\quad \log_{10} k = 16.60 - \frac{74{,}850}{2.3\,RT}$$

(temp. range 550–650° C.)

$$n\text{-Butane:}\quad \log_{10} k = 17.05 - \frac{73{,}900}{2.3\,RT}$$

(temp. range 530–625° C.)

$$\text{Isobutane:}\quad \log_{10} k = 14.89 - \frac{66{,}040}{2.3\,RT}$$

(temp. range 550–610° C.)

Change of reactor surface to volume ratio, dilution with nitrogen, and change of surface from copper to fused silica are found to have no effect under the experimental conditions.

IN A PREVIOUS paper (*5*) an apparatus for studying the thermal dissociation rates of the lower paraffin hydrocarbons was described. This apparatus permitted accurate control of the cracking temperature and the time of contact through the use of a special electrically heated copper preheater section and a copper-coil reaction chamber of known volume immersed in a lead bath. In the work with ethane and propane, previously reported, analysis of the cracked gases was accomplished with a Burrell gas analysis apparatus in the case of ethane and by low-temperature fractionation followed by gas analysis in the case of propane.

Because of the increasing complexity of the primary dissociation products resulting from the thermal decomposition of paraffin hydrocarbons higher in molecular weight than ethane, it was decided to adopt a different analytical method for the redetermination of the propane dissociation and for the determination of the *n*-butane and isobutane dissociation rates. The method depended upon the fact that, when paraffin hydrocarbons of the molecular weight under consideration break owing to thermal instability, the primary products consist of an olefin plus either hydrogen or a paraffin of lower molecular weight. A determination of the olefin content of the cracked product was, hence, depended upon as a measure of dissociation. Obviously, the method depends upon the exclusion of secondary thermal reactions involving the products of the primary dissociation of the parent hydrocarbon. In the present work, secondary reactions were excluded or limited to insignificant amounts by the restriction of total dissociation of parent hydrocarbon to a low value. In only two runs did the dissociation exceed 9 per cent, and in most of the runs dissociation was below 5 per cent.

APPARATUS AND PROCEDURE

The general arrangement of the experimental apparatus and the method of introducing the hydrocarbon gas were practically the same as in the earlier work (*5*). Two forms of reaction chambers were used in the present work, however. The first (Figure 1) consisted of a copper coil, 14.8 feet (4.51 meters) long, with an internal volume of 38 cc., an internal surface area of 487 sq. cm., and a surface to volume ratio of 12.8. Two-thirds of the runs reported here were made in this copper coil apparatus. The first seven runs were made with a similar coil having a volume of 30 cc. and about the same surface to volume ratio. The reaction coil was heated by immersion in an electrically heated lead bath, the temperature of which was measured by a thermocouple. The second type of reaction chamber consisted of a fused silica tube bent in the form of a U, having one long and one short leg. The short leg of this tube terminated at the upper

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[1] Present address, Humble Oil & Refining Company, Baytown, Texas.

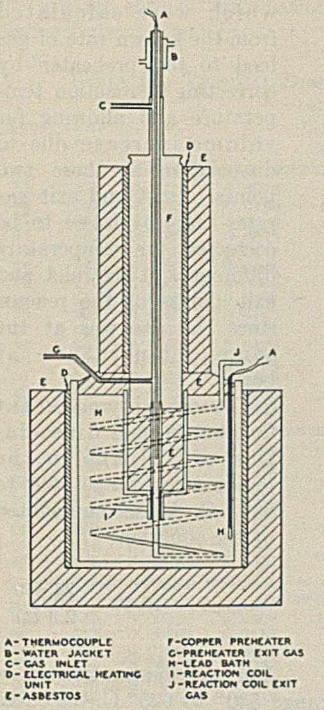

FIGURE 1. EXPERIMENTAL APPARATUS FOR HYDROCARBON DISSOCIATION

surface of the electrically heated lead bath in a thick-walled, fused-silica capillary which served as the exit line. The long leg of this tube extended above the lead bath and served as the preheater section. It was fitted with an electrical heater wound on the outside, a fused-silica thermocouple well which extended to a point below the heater winding and above the upper lead bath surface, and a fused-silica capillary preheater exit line which was sealed in at a point opposite the tip of the thermocouple well, just above the lead bath surface. Both capillary exit lines were fitted with water jackets to insure rapid cooling of the gases and to permit connection to rubber tubing. During the course of the work two of these fused-silica reactors were used. One of these had an internal volume approximating that of the copper-coil reaction chamber and the other had an internal volume only two-thirds as large. Both had surface to volume ratios of nearly 4.5.

During a run the temperature of the preheater was regulated so that the temperature of the gas leaving the preheater and entering the reaction chamber was the same as that of the lead bath.

The hydrocarbon gas was stored in a reservoir, forced out by air-free water, dried with calcium chloride, metered with a calibrated flowmeter, and passed into the preheater and then through the reaction chamber (Figure 2). Samples of the exit gas from the preheater and from the reaction coil were collected in aspirator bottles at atmospheric pressure. Saturated zinc sulfate solution was used as the confining liquid. Gas inlet rates were measured by water displacement and an orifice meter, and were corrected for pressure, temperature, and water vapor in the gas for subsequent calculation of times of contact.

The gas samples were analyzed for olefin content by an adaptation of the bromide-bromate method developed by Francis (*1*). The method used was as follows:

Exactly 25 cc. of approximately 0.02 *N* potassium bromide-bromate solution (restandardized nearly every run) were introduced into a 300-cc. glass-stoppered bottle fitted with a stopcock opening through the stopper and a rubber device for holding the stopper firmly in place. The bottle was evacuated of air by means of a vacuum pump. A sample of the gas to be analyzed, measuring 100 cc. at room conditions, was then introduced from a gas buret with care to prevent the entrance of air. Then 25 cc. of dilute sulfuric acid (27 cc. concentrated sulfuric acid in 2 liters of water) were added. The top of the bottle, including all joints, was then thoroughly coated with melted paraffin wax, and the bottle shaken for 75 minutes in a motor-driven shaker. Sufficient half-saturated potassium iodide solution was added through the stopcock to give an excess over that required to react with the excess bromine. The stopper was then removed from the bottle and the iodine titrated with approximately 0.01 *N* sodium thiosulfate solution (frequently restandardized) with starch indicator. Usual precautions for restandardization of solutions and correction for blanks were taken. Two samples from the preheater and two samples from the reactor were analyzed for each run.

The propane was prepared by fractionating Pyrofax in a low-temperature still. The first and last fractions were rejected and the middle cut was used after scrubbing with concentrated sulfuric acid.

The *n*-butane and the isobutane were obtained from the Ohio Chemical and Manufacturing Company. This material was purified prior to use by low-temperature fractionation, and rejection of the first and last fractions.

RESULTS

The results of the present experimental work are summarized in Tables I to III and presented graphically in Figures 3 to 5. Velocity constants based on the rate of disappearance of the parent hydrocarbon only are plotted. Because of the fact that there is an increase in volume at constant pressure of the gas during dissociation, the parent hydrocarbon drops in concentration at a rate faster than that due solely to disappearance in the dissociation reaction. Consequently, velocity constants based on the change in concentration of the parent hydrocarbon and on the proportion of the original hydrocarbon which disappeared at any given time are not the same. Both of these constants are tabulated.

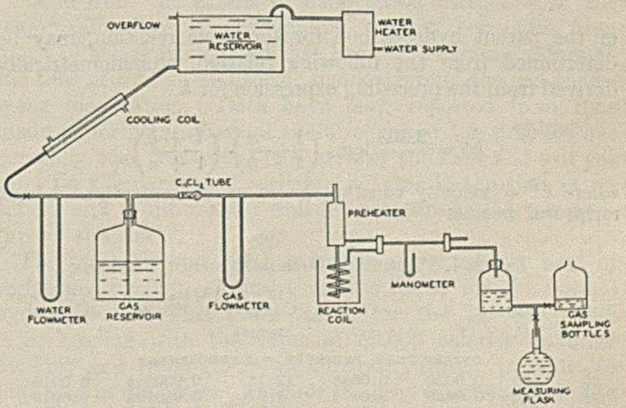

FIGURE 2. FLOW DIAGRAM OF EXPERIMENTAL APPARATUS FOR HYDROCARBON DISSOCIATION

The general velocity equation for unidirectional, first order, homogeneous gas reactions may be written in the integrated form as follows:

$$k = \frac{2.303}{t} \log_{10} \frac{1-a}{1-b}$$

where k = velocity constant based on rate of change of the parent hydrocarbon, reciprocal seconds
t = time of contact, seconds
a = fraction of parent hydrocarbon dissociated in preheater
b = fraction of parent hydrocarbon dissociated in preheater and reactor together

The velocity constant, k, expressed in this way and evaluated by the present data, gives the rate of disappearance of the original hydrocarbon in an isothermal reaction under conditions where the pressure of the parent hydrocarbon remains practically constant. The velocity constants shown by the tables and plots were calculated from the above equation without correction for the effect of reverse reactions. The extent of dissociation was sufficiently remote from equilibrium conditions (*3*) to make correction for the reverse reactions of little importance.

The velocity constant, k', based on change in concentration

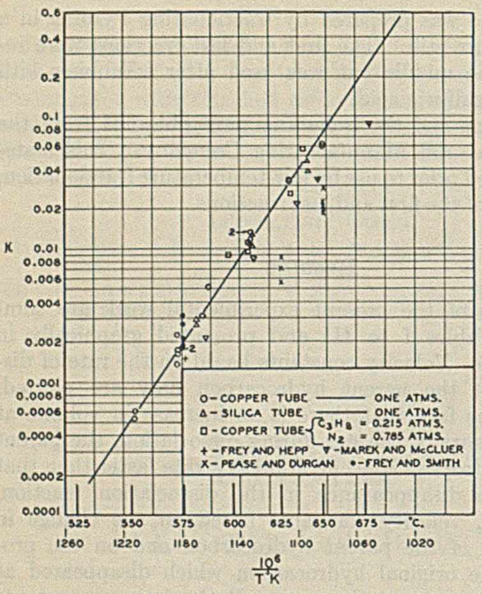

Figure 3. Thermal Dissociation of Propane

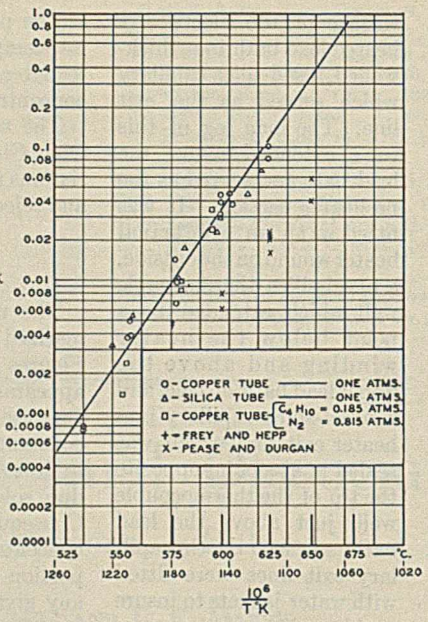

Figure 4. Thermal Dissociation of *n*-Butane

of the parent hydrocarbon for the same reaction, may be determined from the following relation, stoichiometrically derived from the preceding expression for *k:*

$$k' = \frac{2.303}{t} \log_{10}\left(\frac{1-a}{1-b}\right)\left(\frac{1+b}{1+a}\right)$$

where k' = velocity constant based on concentration change, reciprocal seconds

Table I. Thermal Dissociation of Propane

Run	Temp. °C.	*a*	*b*	Time of Contact Seconds	*k*, Basis of Moles	*k'*, Basis of Concn.
			Copper tube, pressure = 1 atmosphere			
30	552	0.0022	0.0086	12.13	0.000534	0.0010
31	552	0.0020	0.0076	8.7	0.000596	0.0012
14	573	0.0046	0.0101	3.58	0.00172	0.00339
16	573	0.0061	0.0140	4.95	0.00164	0.00324
17[a]	573	0.0070	0.0249	8.05	0.00226	0.00445
18	573	0.0040	0.0139	5.82	0.00178	0.00344
19[b]	573	0.0053	0.0182	9.33	0.00138	0.00270
20	585	0.0026	0.0084	1.87	0.00312	0.00620
21	588	0.0012	0.0054	1.234	0.00528	0.00868
22	610	0.0041	0.0216	1.265	0.01380	0.0272
23	610	0.0068	0.0370	2.75	0.01125	0.0220
24	610	0.0038	0.0190	1.27	0.0121	0.0239
25	610	0.0032	0.0158	0.946	0.0138	0.0273
28	631	0.0079	0.0406	0.83	0.0401	0.0784
29	631	0.0115	0.0606	1.156	0.0440	0.0852
26	652	0.0138	0.0729	0.798	0.0772	0.1480
27	652	0.0138	0.0738	0.853	0.0770	0.1446
			Silica tube, pressure = 1 atmosphere			
70	580	0.0052	0.0145	3.1	0.00296	0.00607
71	580	0.0037	0.0101	2.42	0.00270	0.00620
72	610	0.0059	0.0162	0.784	0.01331	0.0253
73	610	0.0046	0.0116	0.543	0.01104	0.0275
74	643	0.0145	0.0422	0.600	0.0477	0.0955
75	643	0.0121	0.0341	0.562	0.0396	0.0731
			Copper tube, propane pressure = 0.215, nitrogen pressure = 0.785 atmosphere			
45	599	0.0069	0.0302	2.54	0.00930	0.01128
47	608	0.0173	0.0633	4.94	0.0097	0.01218
48	610	0.0154	0.0563	3.61	0.0117	0.01355
46	632	0.0115	0.0433	1.217	0.0270	0.0328
49	639	0.0154	0.0700	0.97	0.0586	0.0706

[a] Temperature peak 8° C. above 573° C. occurred during run.
[b] Gas sample stood 60 hours before analysis.

The values of *a* and *b* were determined from the analysis of the exit gases from the preheater and the reactor chamber. Time of contact was calculated from the known volume of the reaction chamber and the average gas rate through the reactor. Average gas rate through the reactor was taken as the arithmetic average of the reactor inlet and exit rates which were calculated from the known rate of gas feed to the preheater by correcting to reaction temperature and allowing for volume increase due to dissociation at these two points. Inlet and exit gas rates did not have to be corrected for temperature differences at the inlet and exit points of the reactor since the gas was at the same temperature at both.

The velocity constant for the thermal dissociation of propane in the temperature range 550° to 650° C. is accommodated by the equation:

$$\log_{10} k = 16.60 - \frac{74{,}850}{2.3\,RT}$$

For the dissociation of *n*-butane in the temperature range 530° to 625° C. the equation takes the form:

$$\log_{10} k = 17.05 - \frac{73{,}900}{2.3\,RT}$$

For the case of isobutane dissociation in the temperature range of 550° to 610° C. the equation becomes:

$$\log_{10} k = 14.89 - \frac{66{,}040}{2.3\,RT}$$

The data of Marek and McCluer (*5*) for ethane recalculated to the present basis for velocity constant evaluation but not corrected for the effect of reverse reactions, and plotted to give least weight to the runs with high dissociation, give the following relations for *k:*

$$\log_{10} k = 16.06 - \frac{77{,}700}{2.3\,RT}$$

The slopes of the equations for the velocity constants, expressed as above, are almost identical for the three hydrocarbons—ethane, propane, and *n*-butane. The heats of activation for these three hydrocarbons lie between approximately 74,000 and 78,000 on the above basis but show a slight progressive decrease in value with increase in molecular weight of the hydrocarbon. The other constant of the equation, however, shows a progressive increase with increase in molecular weight of the hydrocarbon, expressing

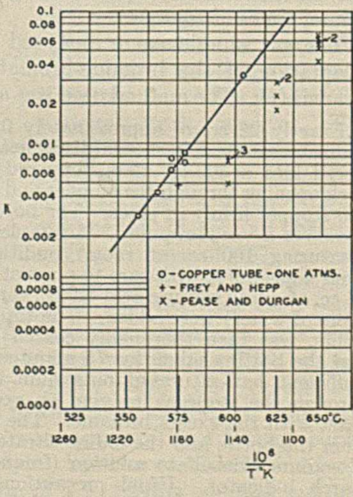

Figure 5. Thermal Dissociation of Isobutane

the greater ease of dissociation of the normal paraffins of higher molecular weight.

Table II. Thermal Dissociation of *n*-Butane

Run	Temp. ° *C.*	*a*	*b*	Time of Contact *Seconds*	*k*, Basis of Moles	*k'*, Basis of Concn.
COPPER TUBE, PRESSURE = 1 ATMOSPHERE						
51	531	0.0021	0.0078	7.7	0.000743	0.00148
52	531	0.0028	0.0148	14.9	0.000791	0.00157
53	554	0.0028	0.0125	2.59	0.00377	0.00750
32	555	0.0062	0.0318	7.58	0.00345	0.00695
33	555	0.0047	0.0217	4.35	0.00387	0.00768
34	577	0.0081	0.0446	4.24	0.00666	0.0171
35	577	0.0072	0.0366	3.07	0.00963	0.01881
54	577	0.0041	0.0187	1.04	0.01435	0.02820
36	601	0.0087	0.0462	0.975	0.0387	0.0780
37	601	0.0077	0.0434	0.806	0.0442	0.0862
38	601	0.0087	0.0472	1.26	0.0311	0.0611
40	606	0.0099	0.0494	1.08	0.0367	0.0715
41	605	0.0089	0.0470	0.877	0.0450	0.0875
42	625	0.0173	0.0930	1.005	0.0801	0.1509
43	625	0.0163	0.0928	0.803	0.1004	0.1900
SILICA TUBE, PRESSURE = 1 ATMOSPHERE						
87	544	0.0078	0.0294	6.64	0.00330	0.00638
86	556	0.0074	0.0274	3.71	0.00536	0.01054
85	578	0.0085	0.0447	3.420	0.01066	0.0206
84	581	0.0078	0.0418	2.035	0.01715	0.0334
82	598	0.0062	0.0305	1.08	0.0230	0.0456
83	599	0.0080	0.0345	0.915	0.0296	0.0579
88	615	0.0069	0.0400	0.767	0.0441	0.0861
89	623	0.0095	0.0551	0.710	0.0664	0.1286
COPPER TUBE, BUTANE PRESSURE = 0.185, NITROGEN PRESSURE = 0.815 ATMOSPHERE						
61	550	0.0038[a]	0.0207	12.4	0.00138	0.00163
60	553	0.0030[a]	0.0168	5.91	0.00236	0.00279
56	581	0.0100	0.0418	4.41	0.00739	0.0087
57	581	0.0080	0.0363	3.22	0.00896	0.01069
58	596	0.0129	0.0557	1.795	0.02380	0.0282
59	596	0.0120	0.0513	1.21	0.03352	0.0397

[a] Estimated, too low to measure with accuracy.

Table III. Thermal Dissociation of Isobutane

Run	Temp. ° *C.*	*a*	*b*	Time of Contact *Seconds*	*k*, Basis of Moles	*k'*, Basis of Concn.
COPPER TUBE, PRESSURE = 1 ATMOSPHERE						
68	556	0.0035	0.0135	3.51	0.00284	0.00564
69	563	0.0031	0.0131	2.30	0.00433	0.0086
64	572	0.0089	0.0366	4.45	0.00636	0.01242
65	572	0.0078	0.0313	3.10	0.00775	0.01517
62	578	0.0134	0.0420	3.90	0.00753	0.01494
63	578	0.0067	0.0272	2.39	0.00872	0.0171
66	608	0.0112	0.0460	1.15	0.0313	0.0610
67	608	0.0099	0.0438	1.07	0.0326	0.0634

The equation for propane given by Marek and McCluer (*5*) shows a slope different from the present equation but was based on a much smaller number of experimental determinations. Of the five runs reported in this previous work, only one was at a total dissociation of less than 5 per cent, and it is noteworthy that at the higher temperature—i. e., above 600° C.—the extent of dissociation in this former work was allowed to increase with the temperature, and that the corresponding values for the velocity constant deviated more widely from the present values as the temperature increased.

The results of Pease and Durgan (*6*) obtained with propane and the butanes yield lower velocity-constant values and a lower heat of activation (65,000 calories) for the dissociations. The results of these workers are shown in Figures 3 to 5 and were obtained in packed and unpacked tubes, and in some instances with a 50 per cent nitrogen dilution. However, decomposition was carried to a much greater extent than in the present case, ranging from 14.7 to 43.8 per cent and being 20 per cent or greater in over half of the runs. As the dissociation of these hydrocarbons was allowed to increase in extent, the velocity of dissociation decreased so that, in the range of dissociation used by these workers, the calculated velocity was considerably lower than in the case where it may be limited to a few per cent. For the case of the dissociation of propane in a silica tube at 575° C. and 760 mm. mercury pressure, the results of Frey and Smith (*4*) showed a progressive decrease in the calculated values for the velocity constant as the extent of dissociation was allowed to increase from 18.1 to 49.9 per cent. Pease and Morton (*7*) have also found in bomb experiments that the apparent dissociation rate dropped off as the reaction proceeded under isothermal conditions in the case of hydrocarbons higher in molecular weight than those under consideration here. Unless it is possible to extrapolate the values of the velocity constants obtained at these high amounts of dissociation to values at zero or low conversions, they should be used with caution in formulating values for heats of activation, general velocity equations, etc.

The results of Pease and Morton (*7*) obtained from the dissociation of *n*-heptane in bomb experiments led to the following relationship for the velocity constant:

$$\log_{10} k = 9.85 - \frac{46,500}{2.3\,RT}$$

The value of 46,500 for the activation energy for *n*-heptane is out of keeping with the values presented here for propane and *n*-butane, but it should be noted that the equation is based on dissociation of 25 per cent and covers a rather narrow temperature range of 30° C.—i. e., from 530° to 560° C.

Aside from the extent of dissociation used, one of the major difficulties in determining velocity constants from much of the previous work has been in assigning values to the time of contact and to the temperature of the gas undergoing dissociation. Data have been reported from runs made under nonisothermal conditions, and the practice has generally been to average in some way the inlet and exit gas rates for the purpose of assigning a value to the time of reaction, and to use reactor wall temperature as the temperature of the gas.

The present results with isobutane show a lower heat of activation (66,000 calories) than was found for the normal hydrocarbons. This lower value for the iso compound is in keeping with the value of 59,000 calories obtained by Frey and Hepp (*2*) in an apparatus similar in effect to that used in the present work for the heat of activation in the case of isopentane dissociation in the range 400° to 575° C.

Values for the velocity constants of the dissociation of propane and *n*-butane obtained from the silica reaction chamber are, in general, within the range of deviation of the values obtained from the copper coil reactor, although the surface to volume ratios varied from 4.5 in the case of the silica tubes to 12.8 in the case of the copper coils. This indicates that the effect of surface is practically negligible in this range of surface to volume ratios, and with these two materials.

The effect of nitrogen dilution on the values of the velocity constants is also indeterminable in the concentrations used. Mixtures by volume of 1 propane to 3.65 nitrogen, and 1 *n*-butane to 4.4 nitrogen gave values of *k* corresponding, respectively, to those obtained with the pure propane and *n*-butane.

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(2) Frey and Hepp, *Ibid.*, **25**, 441 (1933).
(3) Frey and Huppke, *Ibid.*, **25**, 54 (1933).
(4) Frey and Smith, *Ibid.*, **20**, 950 (1928).
(5) Marek and McCluer, *Ibid.*, **23**, 878 (1931).
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Received August 31, 1933.

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Strength in Wood Pulp Papers

Effect of Beating

H. Ainsworth Harrison, Horwich, Lancashire, England

Factors affecting the strength of paper are considered. It is believed that fibrillation in itself is not of such importance in producing strength as is commonly thought. Evidence in favor of this view is advanced. Experiments are given to show the effect of wetting-out agents on the rate of hydration and strength development.

The strength of paper is so deeply involved in numerous factors that to differentiate and assess the importance of each is a difficult problem. Eight of these factors which may be considered of primary importance in their influence on hydration, paper formation, and strength are as follows: felting, fibrillation, surface cohesion, plasticity, pliability, mucilage production, individual fiber strength, and fiber length-diameter ratio. Of course, between some of them there are no definite lines of demarcation.

Felting capacity, for instance, is intimately bound up with fibrillation, cohesion, and plasticity, with fiber length-diameter ratio, and to some extent with the presence or absence of mucilage. Felting, however, is a means to an end, not the end itself. Adequate felting, as indicated by satisfactory sheet formation, simply enables the other factors to become operative. Nakano (*6*) has shown that, although natural silk and asbestos split into fibrils when beaten, the resulting sheets have little strength owing to slippage of the fibers.

Fibrillation

Strachan (*7*) has shown that imbibition is enormously facilitated by increase in specific surface as brought about by fibrillation, and there has arisen a general impression that fibrillation produces strength, probably because they usually occur together in Hollander beating. Although in this article by Strachan no statement is made explicitly that strength is dependent on fibrillation, there is an assumption to that effect, and this relationship is actually maintained in a more recent article (*8*) in answer to a challenge which the author made three years ago (*2*) that the assumption is an entirely erroneous one.

The evidence on which the author first questioned the fibrillation-strength theory is set out at some length (*1*). It is chiefly concerned with the rapid development in strength of unbleached sulfite pulps when beaten in a Lampén mill, and the appearance of the fibers at each stage of beating when photographed at a magnification of 150 diameters. Figure 1 gives these photomicrographs, and Table I the essential strength figures of each pulp. Unbeaten test 1 is that obtained on dry pulp after 4 hours of soaking in water and standard disintegration in the British evaluation apparatus; the other tests have had the same preliminary treatment before the specified beating period.

It is quite certain that fibrillation does occur during beating. Figure 1 clearly shows, however, that such fibrillation by no means coincides with the period of greatest development of strength but commences at a later stage, when, in fact, the strength is remaining constant (the tearing strength is actually decreasing owing to fiber shortening). The air permeability curves (and possibly the drainage time curves also) illustrate the same phenomenon.

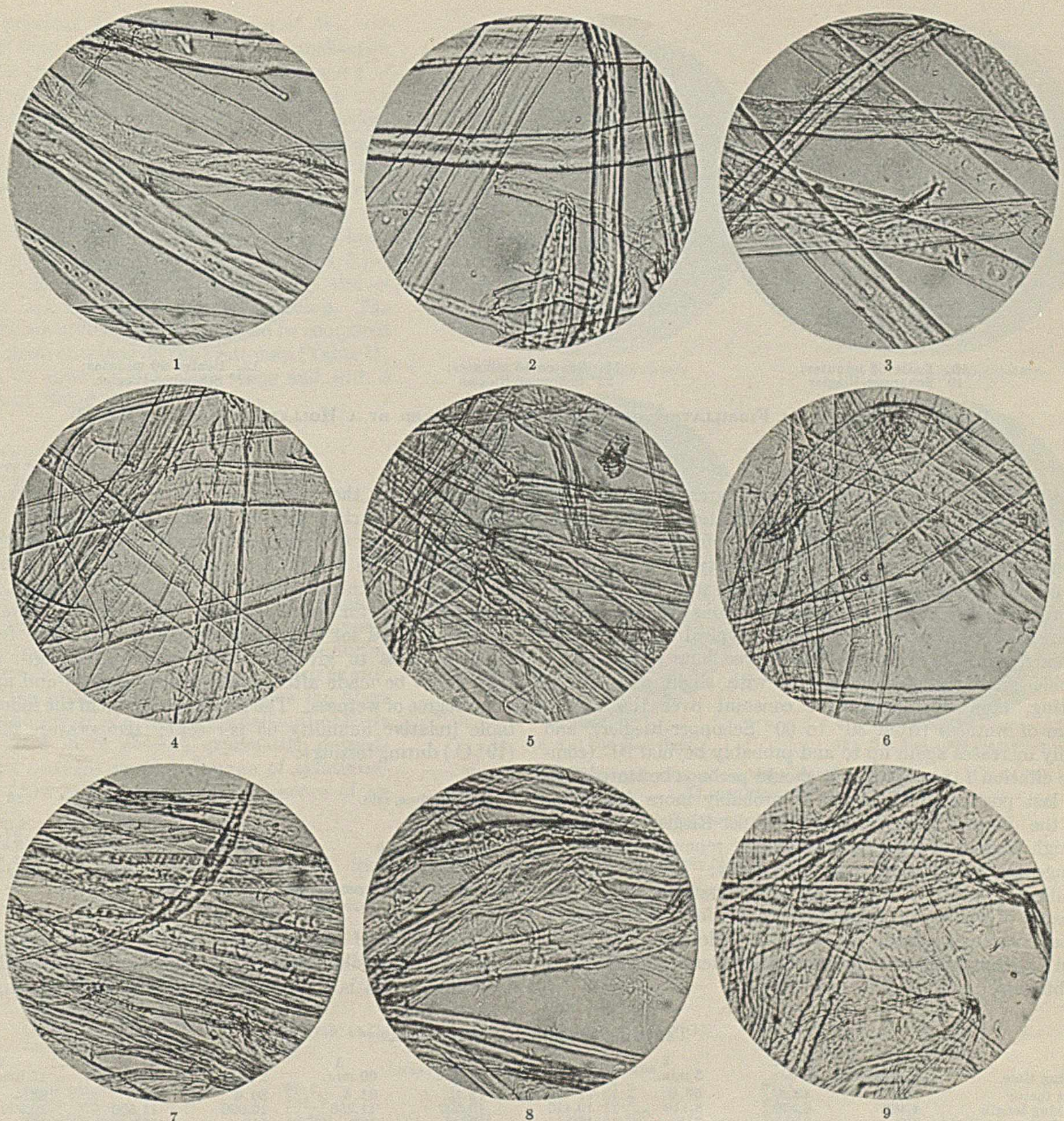
Strachan countered this evidence by seeking to reduce the size of the individual fibrillae from that originally described as being readily discernible under the microscope to about half the wave length of light and by stating that the magnification used by the author (× 150) was therefore not sufficient to identify them. The reply to that argument was fourfold (*3*): In the first place, fibrillae are shown in the later stages of beating under the same magnification. Secondly, "incidental" fibrillation of kraft pulp produced by Hollander beaters is clearly shown in Figure 2 (× 150). The fibers in this series, like those in Figures 1 and 2, were mounted in glycerol jelly, and the lighting conditions (lens aperture, condenser aperture, etc.) were identical throughout. Thirdly, microscopical examination of mechanical pulp, at the same magnification, when beaten for 15 minutes in a Lampén mill, shows marked fibrillation although there is an all-round decrease in strength with increasing wetness from 66° to 75.5° Schopper-Riegler. And in the fourth place, photomicrographs (Figure 3) taken on the original unbleached sulfite pulp, but at 800 diameters and in one case (pulp 16) even at 1000 diameters magnification, still show no signs of fibrillation in the early stages of beating. (The fibers in this case were stained with Safranine and mounted in Hyrax; for pulp 16 a special 8-mm. objective, numerical aperture 0.54, and flattening ocular were used.)

From the foregoing evidence, there can be little doubt that the initial rapid rise in strength occurs in complete absence of fibrillation, and there is an indication that what fibrillation does occur in the early stages of Hollander beating of wood pulp as a result of direct blows from the roll is entirely incidental, perhaps almost accidental; this is characteristic of such beating, no doubt, but is without any significance as far as strength development by facilitating felting is concerned. The absence of fibrillation in strong Swedish kraft papers is considered to be important evidence in favor of this view.

At this stage disagreement should be expressed with the "crystallization theory of strength" originated by W. B. Campbell, at least so far as it has been represented in technical literature available in England. It is an accepted fact among crystallographers that pressure cannot effect appreciable union between two crystalline surfaces unless they are so oriented that their space lattices are congruent. Obviously this can occur only fortuitously and comparatively rarely in a sheet of paper, and the strength so produced can only be a small part of the total strength of the sheet resulting from other causes.

Effect of Beating on Micellar Structure

Regarding the effect of beating on the micellar structure of the cellulose fiber and on the length of the unit chains of glucose residues, the evidence is overwhelmingly in favor of the view that no detectable change in the x-ray photographs is brought about even by excessive beating; this has been confirmed recently by H. Mark of Vienna. So far as the micellar structure is concerned, the bulk of the evidence,



1 2 3 4 5 6 7 8 9

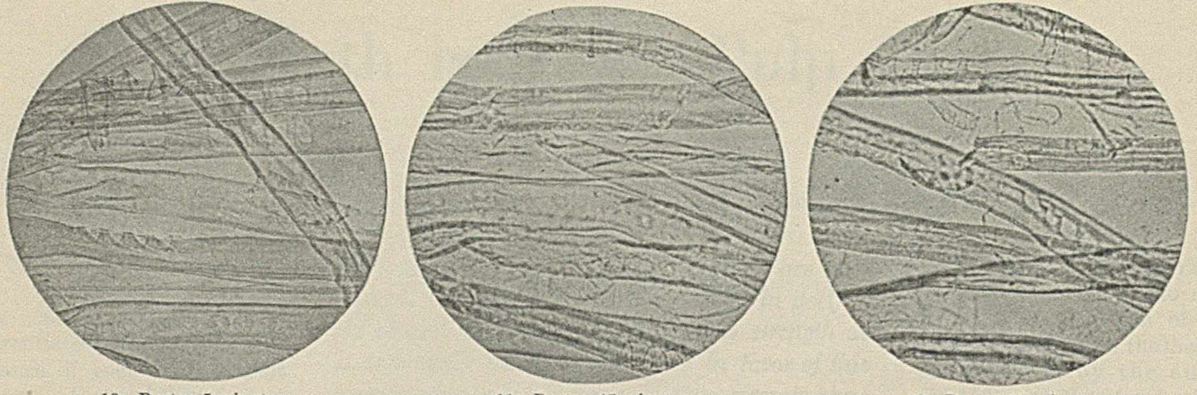
Figure 1. Photomicrographs of Unbleached Sulfite Pulps Beaten in a Lampén Mill (× 150)

(Mounted in glycerol jelly)

mostly from American laboratories, indicates that no micellar breakdown, as indicated by reduction of viscosity in cuprammonium hydroxide, occurs. Kress and Bialkowsky (*4*) have noted slight changes in viscosity on beating wood pulp but attribute this to the fibers being rendered more reactive by the mechanical disintegration. Apparently only in one case has an appreciable decrease in viscosity been recorded—namely, by Nakano (*6*), who observed a 38 per cent decrease when surgical cotton was severely beaten. It appears that with a fiber of this sort, having initially a much larger average micelle size than has wood pulp, excessive beating may produce some micellar detritus and so reduce viscosity, especially if incipient destruction has already occurred during the bleaching process. Nevertheless, the case is exceptional, and, so far as the consideration of wood pulp is concerned, unimportant. The significance of this absence of micellar destruction by beating is that discussion can be limited to considerations of surface change without being concerned in the least with anything more deep-seated.

Surface Cohesion

Consideration will now be given to the most important remaining factor of the eight laid down at the beginning of this article—the cohesion brought about by changes in the colloidal nature of the fiber surface. The physical phenomena which give rise to a surface of this kind are highly complex and are only just beginning to be understood. After the maximum amount of swelling has taken place up to saturation point by immersion in water, further changes brought about by beating include additional imbibition of water by the colloidal envelope of the fiber and a change in the nature of the surface, both promoted by the pressure of the beater roll. These two changes affect the pliability of the fibers, thus enabling the pressures to which the moist web is after-


10. Beaten 5 minutes; 19° Schopper-Riegler

11. Beaten 45 minutes; 22° Schopper-Riegler

12. Beaten 90 minutes; 42° Schopper-Riegler

FIGURE 2. INCIDENTAL FIBRILLATION OF KRAFT PULP PRODUCED BY A HOLLANDER BEATER (× 150)

(Mounted in glycerol jelly)

ward subjected to compress them to a greater extent, and thus forming a denser sheet having a greater area of fiber-to-fiber contact. By plotting the wetness (degrees Schopper-Riegler) against the apparent specific gravity of the laboratory test sheets as given in Table I, all of which were twice pressed according to the British standard conditions of 50 pounds per square inch (3.5 kg. per sq. cm.), a typical cubic curve is obtained, showing in a marked degree how the apparent specific gravity increases rapidly with slight amounts of beating, then remains almost constant over the middle range of wetness (from 30° to 60° Schopper-Riegler), and finally increases again up to and probably beyond 90° (compare citation *1*, page 332). It should perhaps be stated that the last portion of the curve is probably more dependent on the insensitivity of the Schopper-Riegler apparatus at high degrees of wetness than on any renewed rapidity of change in the apparent specific gravity. It may also be significant that on plotting cold copper number (which is a measure of hydration) against air space for a wide variety of papers ranging from blottings to Cellophane and made from different kinds of fibers, an almost identical cubic curve is obtained.

TABLE I. STRENGTH DATA OF PULPS[a]

Pulp	1	2	3	4	5	6	7	8	9
Beating time	Unbeaten	2 min.	5 min.	15 min.	30 min.	60 min.	2 hours	$4^1/_3$ hours	17 hours
Burst factor	28.7	43.5	57.0	71.8	75.0	81.5	80.6	83.7	82.4
Breaking length	4,460	6,460	8,110	10,410	10,520	11,250	10,990	11,500	10,320
Tear factor	202	210	213	180	168	169	158	136	114
Wetness, ° Schopper-Riegler	14	14	15	23	29	45	53	72.5	89
Air permeability (Gurley)	3.1 sec.	6.5 sec.	13.1 sec.	62 sec.	2.25 min.	8.25 min.	14 min.	1.5 hours	9.25 hours
Apparent sp. gr.	0.585	0.625	0.677	0.726	0.740	0.751	0.756	0.791	0.866

[a] Basis weight = g./sq. m.

$$\text{Burst factor} = \frac{\text{av. burst, g./sq. cm.}}{\text{basis weight, g./sq. m.}}$$

$$\text{Breaking length (meters)} = \frac{\text{av. tensile strength, kg.} \times 200{,}000}{\text{basis weight, g./sq. m.} \times 3}$$

$$\text{Tear factor} = \frac{\text{av. grams force to tear } (\times 100)}{\text{basis weight, g./sq. m.}}$$

$$\text{Apparent sp. gr.} = \frac{\text{basis weight, g./sq. m.}}{\text{av. thickness of single sheet, 1/100 mm.}}$$

It might be expected from current theories regarding the nature of wetness and hydration that the presence during beating of a substance which facilitates water penetration would increase the rate of absorption and so facilitate both strength and wetness development. The following experiments indicate that the opposite effect is obtained:

Two lots of a dry kraft pulp (24 grams oven-dry fiber) were each beaten for precisely 60 minutes in a Lampén mill (10-kg. ball model) at 300 r. p. m., consistency 3.0 per cent, as described by the author (*1*). To one lot, however, was added at the start of beating 5 per cent of Perminal W (a wetting-out agent of the alkylnaphthalene sulfonic acid type), calculated on the weight of oven-dry fiber. The wetness of the pulp so obtained was only 19° Schopper-Riegler as compared with 31° for that beaten in the absence of a wetting agent. A third lot of pulp was then beaten alone for 25 minutes so as to give 19°, thus enabling strength comparisons to be made after equal beating periods and at the same degree of wetness. The results are given in the following table [relative humidity 65 per cent; temperature 65° F. (19° C.) during testing]:

Beating time, min.	60	60 in presence of wetting agent	25
Burst factor	83.5	67.0	69.1
Breaking length	10,500	8,600	8,815
Stretch, %	2.9	2.9	2.8
Tear factor	229	261	273
Wetness, ° Schopper-Riegler	31	19	19

Comparison of the first two columns shows that both bursting and tensile strengths are appreciably lower, while the tearing strength is considerably higher when a wetting-out agent is present. These three features, as well as the lower wetness degree, simply show that beating has not proceeded to the same extent. This is confirmed by a comparison of the second and third columns which show that the strength values obtained in presence of the wetting agent used are, within the limits of experimental error, equal to those obtained in the absence of wetting agent at the same wetness. This means that the presence of the wetting-out agent has inhibited wetness development but has not impaired strength at the wetness attained.

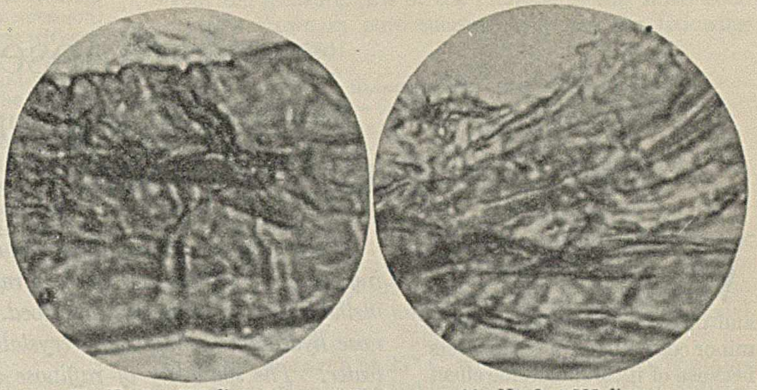
A somewhat more extensive investigation, this time with different percentages of Nekal BX (also an alkylnaphthalene sulfonic acid) on kraft and unbleached sulfite pulps, gave the results shown in Table II.

While the strength and wetness development of the kraft pulp (pH 7.8) were considerably repressed (thus confirming the previous result with Perminal W), the sulfite pulp (pH 5.8) was practically unaffected.

The chief difference during the beating of the two pulps was the formation of froth with the kraft pulp, and the comparative freedom from it with the sulfite, traces of residual acid probably being sufficient to account for this difference. (This froth was of course dispersed before sheet-making.) It was therefore decided to beat another batch of the same kraft pulp for 60 minutes in the presence of 5 per cent Nekal BX but with the addition also of 2 per cent kerosene to prevent frothing. The results are given below and should be compared with those obtained on the kraft pulp (Table II) after 60 minutes of beating alone and with 5 per cent Nekal BX.

Basis weight	61.4
Burst factor	94.0
Breaking length	11,900
Stretch	3.4
Tear factor	230
Wetness, ° Schopper-Riegler	28.5
Drainage time, sec.	5.6 (12.0° C.)
Air permeability, sec.	48

Thus, frothing alone is sufficient to account almost completely for the inability of kraft pulps to develop in strength and hydration during beating when a wetting agent is present. Frothing may, by flotation, remove the fibers from the sphere of action of the ball mill, or there may be a more obscure explanation depending on changes in the degree of gelatinization of the cellulose surface in presence of an air film.


13. No. 1 at 800 diameters 14. No. 3 at 800 diameters

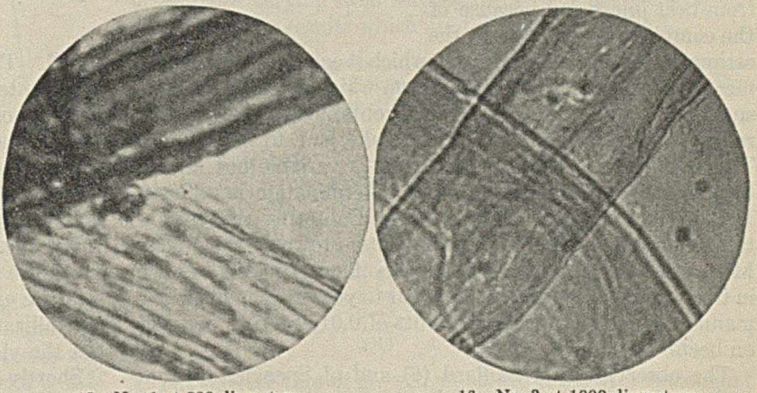

15. No. 6 at 800 diameters 16. No. 3 at 1000 diameters

Figure 3. Photomicrographs of Original Pulps at Greater Magnifications

(Mounted in Hyrax after staining with Safranine)

Table II. Strength Data on Pulps Wetted with Nekal BX

	Wetting Agent				
	Standard	1%	2%	5%	None[a]
			Kraft pulp, beaten 60 minutes		
Basis weight	60.2	61.9	61.8	62.9	60.5
Burst factor	102.6	94.8	90.0	66.0	91.0
Breaking length	12,700	11,420	11,350	8,040	11,400
Stretch, %	3.4	3.5	3.5	3.4	3.5
Tear factor	200	211	216	272	220
Wetness, ° Schopper-Riegler	28	25	21	17.5	21
Drainage time, sec.	5.3 (10.4° C.)	5.4 (11.7° C.)	4.2 (11.4° C.)	3.8 (10.5° C.)	4.2 (11.0° C.)
Air permeability, sec.	54	30	15	4	14
			Kraft pulp, beaten 120 minutes		
Basis weight	60.2	62.4	61.9	61.4	...
Burst factor	104.3	96.3	95.2	80.7	...
Breaking length	13,400	12,100	12,100	9,900	...
Stretch, %	3.2	3.5	3.5	3.5	...
Tear factor	184	205	204	260	...
Wetness, ° Schopper-Riegler	42	36	30	17.5	...
Drainage time, sec.	7.8 (12.0 ° C.)	6.5 (10.5° C.)	5.7 (10.4° C.)	3.9 (9.4° C.)	...
Air permeability, sec.	165	96	58	8	...
			Unbleached sulfite pulp, beaten 60 minutes		
Basis weight	60.2	59.4	60.8	60.2	...
Burst factor	90.7	91.8	89.5	93.3	...
Breaking length	12,520	12,300	12,510	12,280	...
Stretch, %	2.5	2.8	3.0	2.9	...
Tear factor	138.5	149	135	141	...
Wetness, ° Schopper-Riegler	44	42.5	40	39.5	...
Drainage time, sec.	13.8 (8.5° C.)	10.9 (11.4° C.)	10.5 (10.9° C.)	10.4 (11.4° C.)	...
Air permeability, sec.	ca. 14	ca. 14	ca. 14	ca. 14	...

[a] Beaten 35 minutes.

It should again be stressed that these latest results have been forthcoming only at the last moment, and are inserted here in a purely tentative manner.

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Received May 20, 1933.

Raffinose

Preparation and Properties

E. H. HUNGERFORD AND A. R. NEES, The Great Western Sugar Company, Denver, Colo.

The final molasses from the barium desugarizing process is used as the source of raffinose. The method of preparation is described. Pure raffinose hydrate is obtained by crystallization from water. The solubility of raffinose in water has been determined. Other properties are discussed.

WHILE raffinose occurs widely distributed in nature in many grains and plants, it is best known as a minor constituent of sugar beets because of its troublesome effect on the crystallization of sucrose from beet juices and because of the complication it adds to the estimation of sucrose in sirups in which it occurs. Cottonseed meal has been the raw material from which most of the small supply of pure raffinose has been obtained. The yield of raffinose from pressed cottonseed cake is 1 to 3 per cent. The raffinose content in sugar beets is variable but always low, so low in fact that an exact determination is difficult. It is well known that beets grown in California always contain relatively less raffinose than those grown in the Rocky Mountain region. The percentage raffinose in beets grown in the latter locality varies from year to year in an inexplicable manner, usually between the limits of 0.01 and 0.10 per cent on beets.

The observation of Saillard (*6*) and of Spengler (*8*) that raffinose is more abundant in beets grown in wet years does not seem to apply to this region, where irrigation is practiced to such an extent that the effect of the annual rainfall is unimportant.

PREPARATION OF RAFFINOSE

The raffinose is extracted from the beets with the sucrose, passes through the refining process, and goes out in the final molasses, which may contain as little as one per cent at non-Steffen factories and as much as 5 per cent or more at Steffen factories.

Zitkowski (*9*) was able to prepare raffinose from beet molasses of the latter type by a process based on the relative insolubility of lead raffinosate and the relatively high solubility of lead saccharate at high temperatures. However, the concentration of raffinose is too low to make this and other processes feasible in recovering any appreciable part of the 3000 odd tons of raffinose contained in molasses produced annually in the Rocky Mountain region.

One factory at Johnstown, Colo., employs the barium process for desugarizing molasses and uses the discard molasses from the Steffen factories as its source of raw material. About 40 per cent of the raffinose is precipitated with the sucrose by this process and remains in a final molasses which has approximately the following composition:

	%
Dry substance	75.0
Sucrose	66.0 on dry substance
Raffinose	22.0 on dry substance

When this type of molasses first became available, the authors prepared raffinose from it by a method based on the fact that calcium raffinosate is less soluble than is calcium saccharate under the conditions of Steffen cooler operation, and on the further fact that barium raffinosate is more soluble than is barium saccharate. Powdered lime was added to the diluted Johnstown molasses in a Steffen cooler at 10° C. The resulting precipitate containing most of the raffinose and a large part of the sucrose was filtered and washed. Lime was removed from this precipitate with carbon dioxide, and the solution containing little else than raffinose and sucrose was concentrated to about 55° Brix. Twenty-seven per cent barium oxide on dry substance of the 55° Brix sirup was added in the form of a 20 per cent solution at 80° C. This amount of barium oxide was barely sufficient to precipitate the sucrose alone. The barium precipitate, after removal of barium with carbon dioxide, contained 16 per cent raffinose on dry substance, while the filtrate, after removal of barium, contained 32 per cent raffinose on dry substance. This represented a considerable concentration of raffinose, but the loss in the barium precipitate was obviously very large. By concentrating the filtrate to 70 per cent dry substance and adding three volumes of 70 per cent ethanol, raffinose crystallized out and was further purified by two recrystallizations from alcohol. A pure product was obtained, but the yield was small.

Shortly after this work was done, it was observed that raffinose had crystallized spontaneously from a sample of Johnstown molasses after standing several months in the laboratory. It was found that the crystals could be separated from the mother liquor by means of a centrifugal lined with monel metal cloth, and that the crude material could be purified by recrystallization from water. A few pounds of raffinose having a purity of 97.5 per cent were prepared from this molasses. Subsequently about 150 pounds (68 kg.) of pure raffinose hydrate have been prepared in a similar manner.

Spontaneous crystallization of raffinose from the molasses is slow but is accelerated greatly if the molasses is mixed with seed crystals and cooled. In 40 days 78 per cent of the raffinose crystallized from one sample kept at about 20° C. Over 60 per cent crystallized from the same molasses in 20 days when agitated slowly and kept at a temperature of 15° to 18° C. These samples were heavily seeded by the addition of 5 per cent of their weight of an aged molasses containing a very large quantity of crystalline raffinose.

It was soon learned that the crystals could be more satisfactorily separated by filtration than by means of the centrifugal:

The massecuite was diluted to 65 per cent dry substance by cold water, 4° to 5° C., and pumped through a plate and frame filter, dressed with 16-ounce (0.45-kg.) duck under a pressure of 35 to 40 pounds per square inch (2.5 to 2.8 kg. per sq. cm.). One-inch (2.5-cm.) frames were completely filled in 15 to 20 minutes. Satisfactory washing cannot be carried out in the press since the cake channels easily. The best results were obtained by elutriating the unwashed cake with cold water and refiltering. This second cake was superficially washed and blown as dry as possible with compressed air. The crystals obtained in this manner contained 80 to 82 per cent raffinose anhydride on dry substance.

Purification of the crude material was carried out in the following manner: The crystals were dissolved in hot water to form a solution containing 50 to 55 per cent dry substance, to which was added about 3 per cent vegetable carbon. The solution was heated and filtered, and the concentration of filtrate adjusted to 45 per cent dry substance. It was then cooled to 37° C. and seeded with a small amount of pure raffinose hydrate. On further cooling to 20° to 25° C., preferably with constant stirring, a heavy mass of crystals separated, forming a thick suspension, which, however, may be pumped through the filter press without dilution. The crystals are 94.5 to 96 purity. The filtrate is evaporated to 55 per cent dry substance and a second crop of crystals is obtained, which are about 90 purity. The filtrate from this second crystallization contains about 35 per cent raffinose on dry substance or about 10 per cent of the total in the original crude material, and may be concentrated and added to the molasses in the crystallizers.

Raffinose of better than 99 purity can be obtained by the recrystallization of the 94 to 96 purity crystals. One more recrystallization gives a product of practically 100 purity.

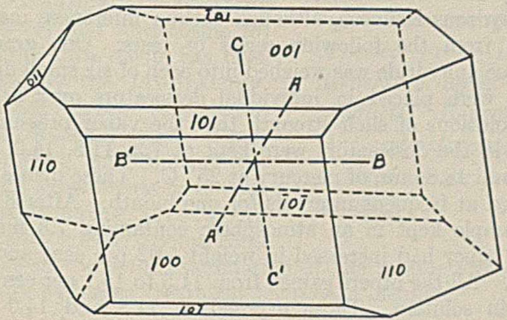

FIGURE 1. "NORMAL" SUCROSE CRYSTAL

The yield of high-purity raffinose is kept quite high by the proper mixing back of "green sirups" and "raw sugar" in the same manner as in a refinery. One ton of molasses will yield about 175 pounds (79.4 kg.) of easily recoverable raffinose hydrate.

PROPERTIES OF RAFFINOSE

EFFECT OF RAFFINOSE ON THE CRYSTAL FORM OF SUCROSE. The peculiar flat crystals of sucrose obtained on crystallization from sirup containing small amounts of raffinose are well known to beet sugar refiners. Slow crystallization of sucrose from such sirups is a problem also familiar to sugar boilers. Quantitative data measuring these phenomena, however, are few. Some results obtained in this laboratory are interesting in that they interrelate slow crystallization and deformed crystals in a roughly quantitative way.

The sucrose crystal is hemimorphic monoclinic. The large faces (Figure 1) intercept the inclined axis, $A-A'$, and are parallel to the plane formed by the intersection of the vertical $C-C'$ axis and the horizontal $B-B'$ axis. Being hemimorphic, the growth of the crystal is dissimilar at the ends of the $B-B'$ axis. Growth is much more rapid at the right end.

In these experiments individual crystals were developed in supersaturated sugar solutions, with and without raffinose, and the growth was measured under a microscope in three directions—namely, along the $B-B'$ axis, along the $C-C'$ axis, and perpendicular to the plane formed by the intersection of the $B-B'$ axis and the $C-C'$ axis. Obviously the latter measurement is not parallel to the $A-A'$ axis since this axis forms an angle of 103°30' with the plane of intersection of the other two axes. It was not possible to grow the crystals in pure sucrose solutions and in sucrose solutions containing raffinose under identical conditions of supersaturation because the influence of raffinose on the solubility of sucrose is not known exactly. It has been shown by Brown and Nees (*2*), however, that the solubility of sucrose in water is reduced by the presence of raffinose. The supersaturation of the solutions containing raffinose used in these experiments was therefore higher by an unknown amount than in those containing no raffinose.

From the measurement of the increase in the dimensions of crystals grown in pure sucrose solutions, the following ratios were obtained:

Tests	Relative Increase in Dimensions $A-A'$	$B-B'$	$C-C'$
38	0.63	1.00	0.85

According to Becker and Rose (*1*) the crystallographic axes bear the following length ratios:

$A-A'$	$B-B'$	$C-C'$
1.2595	1.000	0.8782

Within the limits of error, the growth measured was one axial length along $B-B'$ and $C-C'$ axes and one-half axial length along $A-A'$.

A series of tests run at 25° C. with solutions, each containing 245 grams sucrose per 100 grams water but with quantities of raffinose varying from zero per cent to 5 per cent on sucrose, gave the results which are tabulated in Table I.

TABLE I. RELATIVE INCREASE IN DIMENSIONS OF SUCROSE CRYSTALS GROWN IN SOLUTIONS CONTAINING 245 GRAMS SUCROSE PER 100 OF WATER AT 25° C.

Tests	Raffinose	Growth of $B-B'$	Ratio of Increase to Increase in $B-B'$		
			$A-A'$	$B-B'$	$C-C'$
	% on sucrose	*Mm. per day*			
9	0.00	1.00	0.56	1.00	0.80
2	0.10	1.18	0.47	1.00	0.74
2	0.30	0.89	0.45	1.00	0.71
2	0.50	0.74	0.47	1.00	0.97
2	0.75	0.58	0.50	1.00	1.00
4	1.00	0.51	0.57	1.00	1.16
8	2.00	0.38	0.42	1.00	0.92
8	3.00	0.43	0.07	1.00	0.67
2	4.00	0.38	0.08	1.00	0.61
1	5.00	0.45	0.06	1.00	0.50

The relative rate of growth along the three axes is changed little with concentrations of raffinose up to 0.50 per cent. Between 0.5 and 1 per cent raffinose, the $C-C'$ ratio increases, tending to make the side of the crystal appear more nearly square. Above 2 per cent raffinose, however, the type of deformation changes. The ratio of growth along the $A-A'$ axis—i. e., in thickness—to growth along the $B-B'$ axis (length) decreases rapidly with increase in raffinose concentration until at 5 per cent no growth occurs in the direction of the $A-A'$ axis.

Growth along the $C-C'$ axis also diminishes to about one-half its value in pure sucrose solutions. At these higher concentrations the crystals become very thin, narrow plates. Column 3 of Table I gives a rough measure of the rate of crystallization of sucrose under the conditions of the experiment. It will be observed that even 0.5 per cent raffinose diminishes the rate about 25 per cent, and, at 2 per cent raffinose and above, the rate is reduced to a half or a third of its value in pure sucrose solutions.

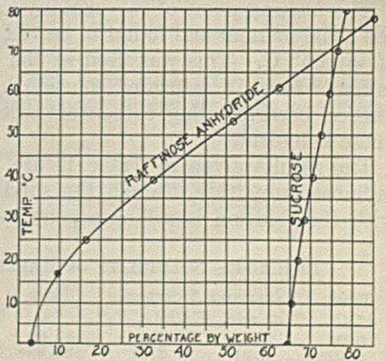

FIGURE 2. SOLUBILITY OF RAFFINOSE ANHYDRIDE IN WATER

Summarizing these results, raffinose diminishes the rate of deposition of sucrose on sucrose crystals on all faces. High concentrations of raffinose eventually prevent deposition of sucrose on the pinacoid faces which intercept the inclined axis and greatly retard deposition of sucrose on the faces parallel to the inclined axis.

Solubility of Raffinose in Water. The solubility of raffinose in water has been determined from 0° to 78° C. At temperatures below 78° C. raffinose crystallizes from water with five molecules of water of crystallization. Above this temperature the hydrate is not stable.

The apparatus used for the determination of the solubility of raffinose consisted of a brass cylinder 2 × 7 inches (5.1 × 17.8 cm.) fitted at the open end with a removable cover plate carrying a bearing 4 inches (10.2 cm.) long, in which a stirrer shaft rotated. When in use the apparatus was submerged in a constant-temperature bath within one inch (2.5 cm.) of the top of the bearing. The constant-temperature bath was the one used by Brown, Sharp, and Dahlberg (*3*) in their work on the solubility of sucrose in beet house sirups.

For the determinations at 0° C., the apparatus was placed in a double-walled Parr colorimeter apparatus and surrounded by finely chipped ice. Temperatures were measured with thermometers tested by the Bureau of Standards. Samples for analysis were drawn with the same sampling device used by Brown, Sharp, and Dahlberg (*3*). It consists of a cover plate similar to the one used on the container, pierced by a thin copper tube on one end of which was soldered a disk-shaped filter of monel metal screen. A tire valve and a stopcock were also threaded into this plate. It was found necessary to cover the monel metal screen filter with duck filter cloth. The operation was simple. Water and pure raffinose hydrate were placed in the container, the cover plate carrying the stirrer was secured tightly, and the entire apparatus was clamped in the bath. The stirrer was turned at a rate of 100 r. p. m. After 16 to 48 hours the apparatus was raised sufficiently to lift the cover plate from the water, and the top was dried carefully and removed. The sampling apparatus, previously dried and heated to the temperature of the bath, was quickly placed in position. Compressed air was admitted through the tire valve, forcing clear solution upwards from the filter into a weighed flask surrounded by cracked ice to minimize evaporation. This operation required but a few seconds. The flask was stoppered, cooled if necessary, and weighed. At the higher temperatures, the sample was diluted with a weighed quantity of water before analysis. Analysis was made by dry substance determinations according to Brown and Sharp's procedure, except that the temperature of the oven was held at 70° to 72° C., or by accurate polarizations, or both. Duplicate dry substance determinations varied no more than 0.02 per cent.

Raffinose determination by dry substance and by polarization agreed very closely. At several temperatures solubility equilibrium was approached from both sides with very satisfactory concordance.

The melting point of the pentahydrate was determined in the usual manner and found to be 78.0 with a probable error of ±0.05° C. This was used as the temperature at which raffinose forms a saturated solution in its water of crystallization corresponding to concentration 84.84 per cent raffinose anhydride.

The results given in Table II are expressed in terms of raffinose anhydride, though the solid phase in equilibrium with the solution is raffinose pentahydrate.

Table II. Solubility of Raffinose in Water

Temp.	Raffinose Anhydride		Temp.	Raffinose Anhydride	
° C.	% on soln.	G./100 g. H_2O	° C.	% on soln.	G./100 g. H_2O
0.00	3.3	3.4	30.00	21.3	27.1
0.02[a]	3.31	3.42	39.38[a]	32.27	47.65
10.00	6.2	6.6	40.00	33.3	49.9
16.38[a]	9.48	10.47	50.00	46.5	86.9
16.90	9.77	10.83	53.20[a]	51.25	105.13
20.00	12.0	13.6	60.00	60.6	153.8
24.80[a]	16.10	19.19	61.60[a]	62.50	166.67
25.05[a]	16.28	19.45	70.00	74.3	289.1
25.50[a]	16.85	20.26	78.0[b]	84.84	559.63

[a] Determined.

[b] Melting point of the pentahydrate.

When plotted, these results lie on a smooth curve (Figure 2), which from 24° to 78° C. is nearly a straight line. The solubility of sucrose according to Herzfeld (*5*) is shown on the same graph for comparison.

These results agree roughly with the approximate ones reported by Browne (*4*) but are very different from the single result obtained by Schecker (*7*) at 24° C. His value of 28.4 per cent raffinose anhydride is nearly 13 per cent too high. The three results at about 25° C. reported in this paper lie exactly on the curve. Two of these points were obtained by approaching saturation equilibrium from an undersaturated condition and the other from a supersaturated condition. In the latter case, a 32 per cent raffinose anhydride solution was brought to equilibrium over raffinose hydrate crystals in 48 hours.

The raffinose used for these determinations was prepared from Johnstown molasses. Direct polarization and dry substance determination indicated that the material contained at most 0.01 or 0.02 per cent sucrose.

Very little is known of the solubility and other properties of anhydrous raffinose, although certain inferences may be drawn from the following series of tests: One gram of raffinose anhydride was weighed into each of six small dishes. These were placed in individual desiccators over sulfuric acid solutions of such strength that the vapor pressures of water in the desiccators were kept at 7.3, 11.8, 14.0, 15.5, 17.6, and 18.8 mm. of mercury at 25° C. These dishes were weighed at frequent intervals for one month. After 3 days the sample kept in an atmosphere containing 7.3 mm. of water vapor had increased in weight 5.02 per cent and was caked. All the others gained from 11.5 to 15.1 per cent and were in solution. Those exposed to 11.8 and 14.0 mm. vapor pressure were like clear glass, and those exposed to 15.5 and more formed viscous solutions. At the end of 2 weeks all had gained weight, but only the ones exposed to 17.6 and 18.8 mm. had gained the theoretical amount to form the pentahydrate. These two had partially crystallized into a mass of needle-shaped crystals. Those exposed to 11.8, 14.0, and 15.5 were clear liquids.

This is a striking example of the difference in solubility of a substance and of its hydrate. At 25° C. the solubility of the pentahydrate is 19.4 grams raffinose anhydride per 100 grams water, whereas the anhydride forms a solution containing about 1000 grams per 100 grams water at this temperature. The solution formed in this manner is too viscous to permit a rapid transition to the pentahydrate, which is the stable form below 78° C. The difficulty encountered in drying raffinose hydrate at temperatures above 80° C. is related to the high solubility of the anhydride. At 80° or above, the hydrate is unstable. The solution of the anhydride evaporates to a glass, from which water is forced with difficulty. Raffinose hydrate is easily and completely dried under moderate vacuum at 70° to 75° C. Its vapor pressure at 25° is 2.3 mm. mercury. The anhydride does not show definite melting point.

The uses of raffinose have been limited to small quantities required for the preparation of certain culture media, and to that employed by various investigators in studying its chemical and physical properties. Heretofore the price has been so high that no one has been interested in developing further uses.

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Received October 23, 1933. Presented before the Division of Sugar Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Hydrogenation of American Coals in Diphenyl

W. L. BEUSCHLEIN, C. C. WRIGHT, AND C. M. WILLIAMS

Department of Chemical Engineering, University of Washington, Seattle

This work shows that the effect of the dispersion agent upon the rate of coal hydrogenation is specific. The commercial treatment of a coal can be expected to be intimately dependent upon the dispersion agent and the process treatment of products. Repeated hydrogenation with anthracene and extraction with benzene of Wilkeson coal is shown to be an effective method for dissolving the coal.

THE hydrogenation of some American coals in a stationary retort using phenol (*2*) and anthracene (*3*) as dispersion media has been reported by this laboratory. This work has been extended to include diphenyl as the dispersion agent, and some of the previous experiments have been repeated using a rotating bomb with stirrer. Some comparative methods for examination of the products resulting from the hydrogen treatment have been included.

EXPERIMENTAL METHOD

The hydrogenation apparatus with the stationary retort has been described (*1*, *2*). For the purpose of stirring the coal charge during the treatment, the retort was placed in a horizontal position upon a set of rollers which were rotated slowly by means of a small motor with appropriate reduction gearing. The inner cylinder used with the stationary retort for holding the coal sample was discarded during rotary operation and replaced by a short length of chain loosely spread along the bomb by a stout copper rod. As the apparatus rotated, the chain rolled and scraped along the bomb wall and insured thorough mixing. The spacer rod was effective in retaining the chain throughout the length of the bomb. Only constant volume experiments were possible as the hydrogen storage cylinders had to be disconnected during rotation of the retort.

TREATMENT WITH DIPHENYL

A 50-gram sample of coal (−60 mesh), together with 20 grams of diphenyl, was placed in the retort. No catalyst other than the natural coal ash was employed. After removal of air by hydrogen flushing, the retort was charged with hydrogen to a pressure of 141 kg. per sq. cm. at room temperature, and then heated at 350° C. for 8 hours. During the experiments, pressures of approximately 317 kg. per sq. cm. were attained, and, upon cooling to room temperature, the final pressure was always lower than the initial. Pressure readings taken during runs were often unreliable owing to clogging of the gage tubing with solid diphenyl. This same trouble often prevented the determination of the volume of gases left in the bomb after an experiment.

Of the twelve coals treated, each product upon removal from the bomb appeared as a gray mass of crystals and tarry matter. Water separated out in amounts varying from 0.1 to 5.0 grams, depending upon the coal treated. The larger quantities were found on treating sub-bituminous coals high in oxygen. The solid and liquid products from the bomb were extracted with benzene in a Soxhlet extractor, and the insoluble residue was subsequently carbonized at 550° C. in a Fischer retort without steam. The benzene-soluble portion and the tar obtained from the carbonization were combined, and the total weight, corrected for diphenyl, is reported as total tar. The results are presented in Table I. Since tars form one of the valuable products when coal is distilled commercially, the low-temperature carbonization of hydrogenated residues was intended to throw some light upon the tar yields of treated and untreated coals.

For comparative purposes, three coals were hydrogenated with anthracene substituted for diphenyl. The analytical

TABLE I. BENZENE EXTRACTION AND DISTILLATION OF HYDROGENATED COALS[a]

Dispersion medium:	DIPHENYL				ANTHRACENE		
	FIXED CARBON	EXTRACTED TAR	DISTILLATION		EXTRACTED TAR	DISTILLATION	
			Tar	Coke		Tar	Coke
	%	%	%	%	%	%	%
COAL,[b] BED, AND STATE							
Fairfax, 5, Wash.	63.3	25.6	1.8	61.5	..	...	..
Wilkeson, 7, Wash.	63.7	24.0	1.8	58.1	19.7	3.6	65.9
Flat Top, Mary Lee, Ala.	59.9	42.6	1.5	41.2	..	...	..
Boone 2, Chilton, W. Va.	57.9	50.1	2.8	44.7	..	...	..
204, Elkhorn, Ky.	59.0	14.2	6.7	62.4	..	...	..
Orient 1, Illinois 6, Ill.	47.7	47.5	2.2	46.6	..	...	..
Occidental, 2, Wash.	46.9	13.8	5.9	51.1	37.2	2.5	33.3
Rolapp, Castle Gate, Utah	49.1	39.0	3.0	41.6	..	...	..
Roslyn 7, Roslyn, Wash.	43.5	46.4	1.5	25.8	..	...	..
New Black Diamond, Jones, Wash.	44.4	12.5	1.7	53.2	17.5	3.6	51.9
Tono, 1, Wash.	39.3	15.6	2.7	49.7	..	...	..
Ford's Prairie, Foron, Wash.	30.8	32.7	2.4	29.5	..	...	..

[a] All results reported on ash- and moisture-free basis.
[b] A complete description of the coals has been reported in a previous paper (*2*).

TABLE II. PHENOL EXTRACTION OF HYDROGENATED COALS[a]

Dispersion medium:	ANTHRACENE			DIPHENYL		PHENOL		
Products:	A	B	C	A	B	A	B	C
	%	%	%	%	%	%	%	%
COAL								
Wilkeson, Wash.	2.1	94.0	18.2	25.5	72.8	1.4	69.3	34.0
Flat Top, Ala.	10.9	72.1	18.7	..	..	...	..	..
Occidental, Wash.	8.1	63.1	21.3	13.5	64.6	2.7	26.4	44.2
New Black Diamond, Wash.	2.9	53.7	11.1	..	..	2.2	32.1	31.2
Ford's Prairie, Wash.	2.9	35.4	23.2	..	..	...	..	..

[a] All results reported on ash- and moisture-free basis.

procedure was the same as for the diphenyl, and the results have been included in Table I, together with those previously reported for anthracene using the stationary retort (*3*).

The results presented in Table I for experiments using diphenyl show little correlation between the yield of tar and the original composition of the coal stated as percentage of carbon, fixed carbon, or ratios of carbon to hydrogen, carbon to net hydrogen, etc. In several instances the conversions to tar are similar to those previously reported for the same coals using anthracene as the dispersion medium in a stationary retort. However, for the three coals investigated, there appears to be no apparent agreement between the conversions obtained with anthracene as the dispersion agent in the rotating retort and those obtained with the same medium in the stationary retort. It was thought that stirring should increase the ease of hydrogen absorption, in particular, if some equilibrium were to exist between soluble products formed and diffusion of them into the dispersion medium.

Effect of Dispersion Media

As a further comparison of dispersion media, two coals were hydrogenated with diphenyl, three with phenol, and five with anthracene. The method of Shatwell and Graham (*4*) for the analysis of the products was followed whereby they were separated into three parts: A, insoluble in phenol; B, soluble in phenol and insoluble in chloroform; and C, soluble in phenol and chloroform. The apparatus and procedure for the hydrogenation were those used in the previous diphenyl experiments except where phenol was the dispersion agent, and then the weight ratio of coal to phenol was 1:1. The results appear in Table II.

Three of the five coals dispersed in anthracene and all of those in phenol were rendered almost completely soluble in phenol, the residues being less than 3 per cent. From the limited data available, these two agents appear to be much more effective than diphenyl. The yield of B product was largest for the high-carbon coals, decreasing with the carbon content; this indicated that those coals most deficient in hydrogen were the least easily converted into the C product which is a liquid tar. Experiments on the conversion of B products to C products might show some valuable properties of various solvents. The tar acids and bases can be indicated by the losses occurring in the washings of the phenol-soluble extracts (B and C products) with dilute sodium hydroxide solution. It was found that, regardless of the dispersion medium, these tar acids and bases in the products were less with high-carbon coals than with those of lower carbon content. The chloroform-soluble fraction corresponds in physical characteristics to the benzene-soluble portion obtained in the coking runs. The amount of tar appears to be about the same, irrespective of rank of coal. It would rather appear from the data that the fractions of the low-rank coal which produce tar acids and bases have been metamorphosed in the higher ranks so that they produce the B products upon hydrogenation.

Repeated Hydrogenation and Extraction

The use of the benzene extraction method upon hydrogenated residues has obvious advantages when tarry products are desired. Wilkeson coal was extracted with benzene and was found to have a negligible solubility. A fresh sample with anthracene was then hydrogenated, and the products were extracted with benzene. A portion of the insoluble material was carbonized, and the remainder was returned to the retort with more anthracene and retreated with hydrogen. This procedure was repeated a third time, the product being extracted and a portion carbonized. The results are described in Table III and show that removal of the benzene-soluble portion and the addition of anthracene allow hydrogenation to proceed. Whereas the single treatment shows a yield of 19.7 per cent tar, two additional treatments increase this to 54 per cent. This indicates that the coal could be rendered essentially benzene-soluble by successive treatments. Apparently, extraction during hydrogenation would be advantageous for effecting solution of the coal.

Table III. Effect of Repeated Benzene Extraction of Hydrogenated Coal[a]

(Wilkeson, Wash., coal dispersed in anthracene)

	Benzene Extraction		Carbonization of Solid Residue		
	Solid residue	Soluble tar	Coke	Tar	Total Tar
	%	%	%	%	%
Raw coal	99.5	...	80.9	...	10.1[b]
1st treatment	80.0	19.7	65.9	3.5	23.2
2nd treatment	59.5	16.3	47.0	1.1	17.4
3rd treatment	35.9	17.9	29.6	2.3	20.2
Final yield	35.9	53.9	29.6	...	...

[a] All results on ash- and moisture-free basis of original coal.
[b] Nitrogen used in place of hydrogen.

Comparison of Treatments

In Table IV are shown the results obtained by treating New Black Diamond coal with hydrogen under various conditions of time, pressure, and dispersion medium. It is evident that initial pressures of 140 kg. per sq. cm. at room temperature are advantageous for converting the coal into phenol-soluble products. That the dispersion medium plays an important part is indicated by the small decrease in phenol solubility obtained when no medium is used as compared with those for anthracene and phenol.

Table IV. Various Treatments of New Black Diamond, Wash., Coal[a]

Dispersion Medium	Initial Pressure of Hydrogen	Time of Hydrogenation at 350° C.	Products				
			Coke %	Total %	Tar A %	Tar B %	Tar C %
	Kg./sq. cm.	Hours					
Anthracene[b]	141[b]	8	73.2	5.7	..	..	..
Anthracene[c]	141	8	38.0	28.8	..	..	..
Anthracene	141	8	51.9	21.1	..	..	..
Diphenyl	141	8	53.2	14.2	..	..	..
None[d]	Extracted only		..	..	88.0	0.9	0.4
Diphenyl	38.7	8	..	..	68.5	8.9	..
Diphenyl	38.7	54	..	..	33.7	..	..
Anthracene	141	8	..	..	2.9	53.7	11.1
None	127	8	..	..	62.7	13.8	6.1
Phenol	38.1	4	..	..	54.0	21.7	7.5
Phenol	38.1	8	..	..	43.3	..	..
Phenol	141	8	..	..	2.2	32.1	31.2
Phenol[d]	141	8	..	..	49.9	13.2	12.8

[a] All results reported on ash- and moisture-free basis.
[b] Hydrogen replaced by nitrogen.
[c] Experiments without stirring reported in a previous paper (*3*).
[d] Experiments reported in a previous paper (*2*).

The effect of the ash in the original coal upon hydrogenation has not been investigated in any of the experiments reported in this paper. In those runs showing less than 3 per cent residue insoluble in phenol, some of the ash passed through the extraction thimble with the hot phenol and appeared in the B products.

Acknowledgment

The authors are indebted to the United States Bureau of Mines for the samples of coal used in these experiments. The investigation was made possible by a Grant-in-Aid of the National Research Council to W. L. Beuschlein.

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Received September 20, 1933. Presented before the Division of Gas and Fuel Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Line Coördinate Charts for Vapor Pressure–Temperature Data

FRANK E. E. GERMANN AND ODON S. KNIGHT, University of Colorado, Boulder, Colo.

The methods are briefly reviewed which have been used to represent vapor pressure–temperature data. It is shown that this may best be done by reducing the data first to straight lines and then by plotting these lines as points on line coördinate charts. The literature on vapor pressures of organic liquids has been critically reviewed. As a result, 183 organic liquids and solids were found whose vapor pressures are well known in the range 500 to 900 mm. of mercury. These, as well as water, have been represented on the charts. The use of these plots makes calculations for corrections in boiling points due to a variation in pressure unnecessary, as charts 9 × 24 inches (22.9 × 61 cm.) permit reading temperatures to 0.25° C. if the pressure is known, or to 2 mm. if the temperature is known.

PROBABLY the first attempt to correlate vapor pressure data was made by Dalton (*5*) in 1801. He attempted to show that the vapor pressure of a liquid increases in geometrical progression as the temperature increases in arithmetic progression, and that all liquids experience an equal lowering of the boiling point if the pressure is diminished the same amount from the same initial pressure. The statement of these rules by Dalton stimulated a great deal of work on vapor pressures, with the result that the first of them was shown to be quite inexact, and only in isolated cases, such as with the fatty acid series of compounds, was the second shown to hold. Kirchhoff (*11*) in 1858, and Rankine (*16*) in 1866 developed what is sometimes known as the Kirchhoff formula, but more often as the Rankine formula:

$$\log P = A + B/T + C \log T$$

where A, B, and C are constants

This formula has been found to apply to a large number of substances from the freezing point to the critical temperature, with a maximum error of 3 per cent. It has been modified by Nernst (*14*) who attempted to put it on a better theoretical basis.

Ramsay and Young (*15*) in 1885, suggested the relation:

$$T_A/T_B = T'_A/T'_B = \text{a constant}$$

where

T_A and T_B = the boiling points, on the absolute scale, of two substances under pressure p

T'_A and T'_B = their boiling points under another pressure, p'

The law holds for closely related substances, but for widely different substances another term must be added, thus:

$$T_A/T_B = T'_A/T'_B + c(T_A - T'_A)$$

The integrated form of the Clausius-Clapeyron equation may be written in the form:

$$\log p = -k/T + C$$

This equation has been modified by Henglein (*9*) and Hildebrand (*10*), so as to be valid over a larger pressure range. The most serious objection to the use of Hildebrand's equation would seem to be the fact that it applies only to liquids which we have thought of as being nonassociated.

Many attempts have been made to correlate vapor pressures and temperatures by graphical methods. Perhaps the oldest well-known method is that known as Dühring's rule (*7*). Mathematically, Dühring's rule is nothing but a graphical representation of the simplified Ramsay and Young law. Since this law is not exact, Dühring's lines are not straight. Herein lies the greatest fault of this useful method. Among the numerous other methods which have been employed are those of Carr and Murphy (*2*), Cox (*3*), Davis (*6*), Calingaert and Davis (*1*), Wilson (*18*), Maxwell (*13*), and Wilson and Bloomquist (*19*).

Cragoe (*4*) makes use of the integrated form of the Clausius-Clapeyron equation. Hass and Newton (*8*) modified Cragoe's formula to secure greater accuracy, but the results are still only approximate. A personal communication from Hass would indicate that boiling points near atmospheric pressure should be obtained with an accuracy of ±1° C. However, the equation must be solved by the method of successive approximations and is accordingly rather time-consuming.

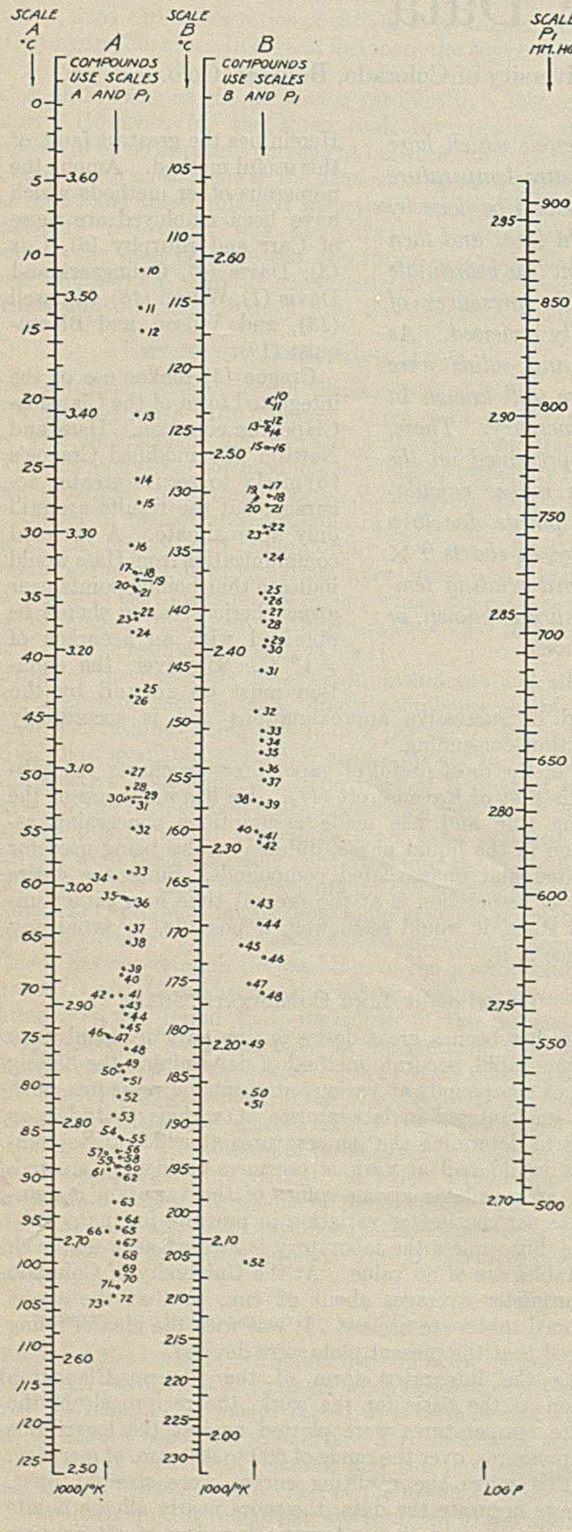
One of the most useful of vapor pressure charts yet published is that of Ravenscroft (*17*). He has made use of the Dühring rule and has made assumptions concerning association in the liquid phase, different scales being used for associated and unassociated compounds. Since the entire matter of association is at the present time in a rather unsettled state, it would seem well, if possible, to avoid any reference to it.

DRAWING OF LINE COÖRDINATE CHART

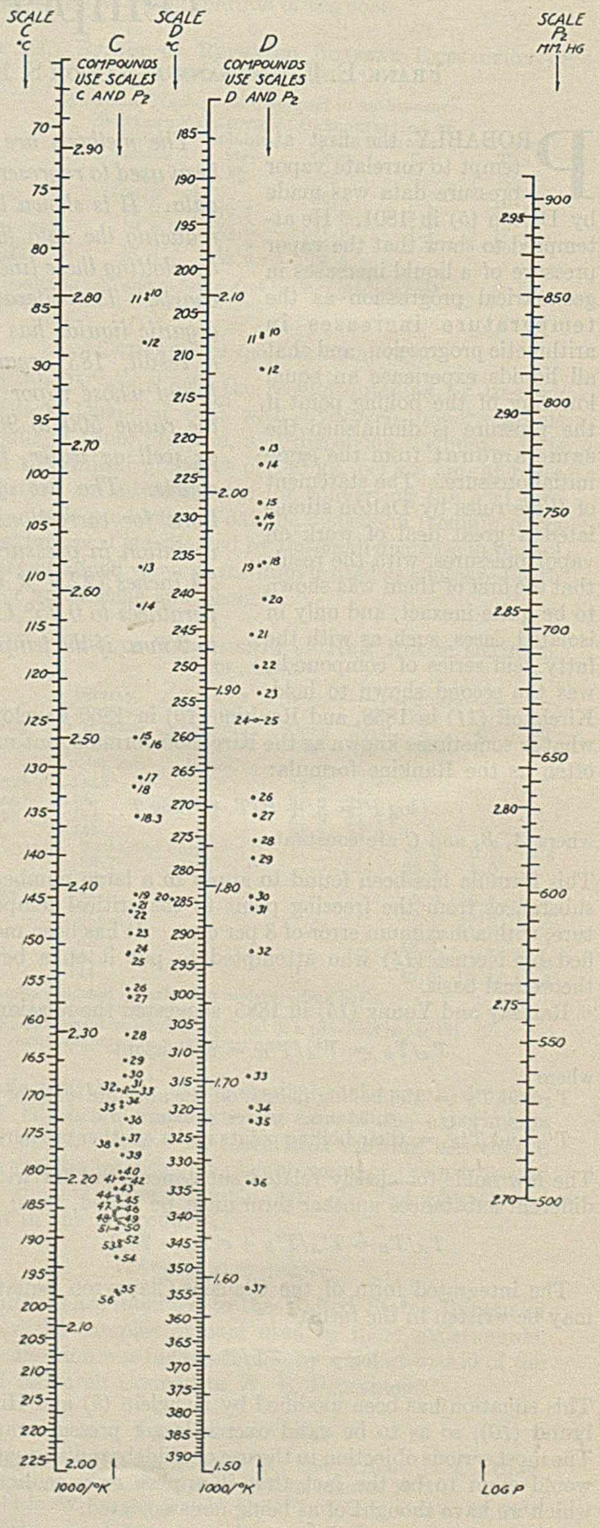
There has been a great desire on the part of chemists to find some rapid, accurate method of determining the boiling points of compounds at various atmospheric pressures, such as are encountered in laboratories at various altitudes, as well as to determine the temperatures at which these compounds would boil at various pressures artificially created. Tables are available giving values of the variation in temperature per centimeter variation in pressure for many substances, but, unless the laboratory is located near sea level, these tables are of no value. At the University of Colorado the barometer averages about 62 cm., so that the above mentioned tables are useless. It was with the idea of filling this need that the present plots were devised.

Using the integrated form of the Clausius-Clapeyron equation as the basis for the work, the reciprocals of the absolute temperatures were plotted against the logarithms of the pressures, over the range of 500 to 900 mm. of mercury. Over this range the resulting curves were straight lines. The more accurate the data, the more nearly all the points fell on the straight line. A critical review of all existing literature on vapor pressures of organic liquids and some solids resulted in the establishing of such straight lines for 183 organic compounds. In cases where various workers had reported vapor pressures on the same compound, the relative merits of the methods used were studied, and weighted

BOILING POINTS OF CHAIN COMPOUNDS



BOILING POINTS OF RING COMPOUNDS



curves were drawn. In all cases, individual variations among the results were greater than the possible error in assuming the lines to be straight. In other words, the straight lines drawn represent improvements over the original data, within the range considered.

These straight lines were then reduced to points on line coördinate charts (9 × 24 inches, or 22.9 × 61 cm.), each point being assigned a number corresponding to a given compound. For convenience the compounds were separated into chain and ring compounds, the only reason for this

Table I. Alphabetical Index to Boiling Point Charts

(A, B, C, and D refer to groups of compounds on the charts; numbers refer to compounds within these groups)

Acenaphthene, D-26
Acetaldehyde, A-13
Acetic acid, A-72
Acetone, A-28
Acetophenone, C-46
n-Amyl alcohol, B-20
n-Amyl *n*-butyrate, B-44
n-Amyl formate, B-13
n-Amyl isobutyrate, B-42
n-Amyl *n*-propionate, B-36
Aniline, C-34
Anthracene, D-35
Anthraquinone, D-37

Benzaldehyde, C-29
Benzene, C-10
Benzoic acid, D-21
Benzonitrile, C-37
Benzophenone, D-32
Benzoyl chloride, C-41
Benzyl alcohol, C-51
Bromobenzene, C-22
α-Bromonaphthalene, D-27
m-Bromotoluene, C-33
o-Bromotoluene, C-30
p-Bromotoluene, C-31
o-Bromo-*p*-xylene, D-10
n-Butyl alcohol, A-73
tert-Butyl alcohol, A-47
sec-Butyl chloroacetate, B-40
n-Butyl formate, A-63
sec-Butyl formate, A-53
n-Butyric acid, B-38

Camphor, C-52
Carbazole, D-36
Carbon disulfide, A-25
Carbon tetrabromide, B-48
Carbon tetrachloride, A-39
m-Chloroaniline, D-15
o-Chloroaniline, C-53
Chlorobenzene, C-15
1,1-Chlorobromoethane, A-44
Chloroform, A-32
α-Chloronaphthalene, D-23
Chloropicrin, A-67
m-Chlorotoluene, C-24
o-Chlorotoluene, C-23
p-Chlorotoluene, C-25
m-Cresol, C-47
o-Cresol, C-38
p-Cresol, C-48
Cyclohexane, C-11
Cymene, C-28

n-Decane, B-35
Dibenzyl ketone, D-33
1,3-Dibromopropane, B-39
2,3-Dibromopropylene, B-26
1,2-Dichloroethane, A-45
Diethylaniline, C-55
Diethyl ether, A-17
Diïsobutyl, A-64
Diïsopropyl, A-31
Dimethylaniline, C-39
Dimethyl-*o*-toluidine, C-35
Dimethyl-*p*-toluidine, C-54
Diphenyl, D-22
Diphenylmethane, D-25
Dipropyl ether, A-50
Durene, C-40

Ethyl acetate, A-40
Ethyl alcohol, A-42
Ethyl aniline, C-50
Ethyl benzene, C-16
Ethyl bromide, A-22
Ethyl *n*-butyrate, B-11
Ethyl chloride, A-12
Ethylchloroacetate, B-28
Ethylene bromide, B-21
Ethylene glycol, B-50
Ethylene oxide, A-11
Ethyl formate, A-27
Ethylidene chloride, A-29
Ethyl iodide, A-37
Ethyl isobutyrate, A-65
Ethyl mercaptan, A-18
Ethyl propionate, A-56
Ethyl sulfide, A-51
Ethyl-*n*-valerate, B-23

Fluorene, D-31
Fluorobenzene, C-12
Formic acid, A-58

Glycol diacetate, B-49

n-Heptane, A-55
n-Heptylic acid, B-52
Hexachloroethane, B-46
Hexamethyl benzene, D-24
n-Hexane, A-36
1-Hexene, A-33
Hydrogen cyanide, A-14

Iodobenzene, C-36
Isoamyl alcohol, B-19
Isoamyl formate, B-14
Isobutyl acetate, A-69
Isobutyl alcohol, A-66
Isobutyl benzene, C-26
Isobutyl-*n*-butyrate, B-34
Isobutyl formate, A-54
Isobutyl isobutyrate, B-30
Isobutyl-*n*-propionate, B-24
Isobutyl-*n*-valerate, B-41
Isobutyric acid, B-32
Isocaproic acid, B-51
Isodurene, C-42
Isopentane, A-15
Isopropyl acetate, A-49
Isopropyl alcohol, A-46
Isopropyl benzene, C-19
Isopropyl chloride, A-19
Isopropyl chloroacetate, B-31
Isopropyl formate, A-35
Isopropyl isobutyrate, B-10
Isovaleric acid, B-43

Mesitylene, C-20
Methyl acetate, A-30
Methyl alcohol, A-34
Methyl aniline, C-40
Methyl benzoate, C-43
Methyl butyrate, A-62
Methyl chloroacetate, B-17
Methylene chloride, A-24
Methyl ethyl ether, A-10
Methyl formate, A-16
Methyl isobutyrate, A-52
Methyl *n*-propionate, A-41
Methyl propyl ether, A-25
Methyl salicylate, D-14
Methyl sulfide, A-20
Methyl *n*-valerate, A-70

Naphthalene, C-56
α-Naphthol, D-29
β-Naphthol, D-30
Nitrobenzene, D-12
Nitromethane, A-59
m-Nitrotoluene, D-16
o-Nitrotoluene, D-13
p-Nitrotoluene, D-19
Nitro-*m*-xylene, D-20

n-Octane, B-16

Pentachloroethane, B-37
Pentamethylbenzene, D-17
n-Pentane, A-21
Phenanthrene, D-34
Phenol, C-32
Phthalicanhydride, D-28
Prehnitene, D-11
n-Propionic acid, B-25
n-Propyl acetate, A-60
n-Propyl alcohol, A-57
n-Propyl benzene, C-21
n-Propyl *n*-butyrate, B-27
n-Propyl chloride, A-26
n-Propyl formate, A-43
n-Propyl isobutyrate, B-22
n-Propyl *n*-propionate, B-12
n-Propyl *n*-valerate, B-33
Pseudocumene, C-27
Pyridine, C-14

Quinoline, D-18

1,1,1,2-Tetrachloroethane, B-18
sym-Tetrachloroethane, B-29
Tetrachloroethylene, A-71
Tetranitromethane, B-15
Toluene, C-13
m-Toluidine, C-49
o-Toluidine, C-44
p-Toluidine, C-45
1,1,1-Trichloroethane, A-38
1,1,2-Trichloroethane, A-68
Trichloroethylene, A-48

Urethane, B-45

n-Valeric acid, B-47

Water, A-61

m-Xylene, C-18
o-Xylene, C-18.3
p-Xylene, C-17

being to scatter the points over a larger area. In order to increase the accuracy of the temperature reading, the chain compounds were separated into compounds A with a temperature scale reading from 0° to 125° C., and compounds B with a temperature scale from 105° to 230° C. Similarly, the ring compounds were separated into compounds C with a temperature scale from 65° to 225° C. and compounds D with a temperature scale from 185° to 390° C. With compounds A, scales A and P_1 are used; with compounds B, scales B and P_1; with compounds C, scales C and P_2; and with compounds D, scales D and P_2.

On the right-hand side of scales A, B, C, and D is the original uniform scale of 1000 times the reciprocal of the absolute temperature, while on the left of scales P_1 and P_2 is the uniform scale of the common logarithm of the pressure in millimeters. These fundamental scales are then made direct-reading in the A, B, C, D, P_1, and P_2 scales. Having thus established nonuniform temperature and pressure scales, the uniform scales are no longer necessary.

If, for example, we wish to know the boiling point of water when the barometer reads 620 mm., we note from Table I that water is listed as A-61. Therefore, place a straightedge at 620 mm. on P_1 scale, and pass it through the center of circle 61 under compounds A. On scale A we read 94.4° C., which is the value given by the International Critical Tables for a pressure of 620.01 mm. mercury. It is safe to state that within the pressure range of 500 to 900 mm. the chart will give boiling points within 0.25° C. and pressures within 2 mm. This accuracy is sufficient for most work in the organic laboratory where temperatures of boiling are used as criteria for the purity of compounds. Where vapor pressures are more accurately known, as in the case of water, more accurate readings are easily possible. In other words, the charts have about the same degree of accuracy as the best vapor pressure data for the compound in question.

Insertion of New Data

New points may be inserted on the chart as the data become available. Thus Lenth (*12*) has just published data on the vapor pressures of *n*-butyl chloride. Plot a curve of the reciprocal of the absolute temperature against the logarithm of the pressure and draw the best straight line through the points. Let us assume that the data of Lenth have been represented by such a line. Then at 66.0° C. the pressure would be 50.5 cm., and at 77.5° C., 76 cm. Lay a straightedge from 66.0° C. on scale A to 505 mm. on scale P and draw a light line. Then lay the straightedge on 77.5° C. on scale A and 760 mm. on scale P and draw another light line. At the point of intersection of the two lines draw a small circle and number it 40.3, indicating that it lies about one-third of the way between 40 and 41. It would be listed in the table as *n*-butyl chloride, A-40.3. If then we wish to know the pressure at 73°, we read the value 649 mm. from the chart. Lenth gives the experimental value of 650 mm. and the calculated value of 649 mm.

The charts should be of value in all laboratories, whether they be at sea level or higher, since all calculations are avoided; it is necessary to know only the barometric pressure. Similar charts are being constructed for inorganic substances, as well as for other pressure ranges.

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Received October 23, 1933.

Heat Content of Gases from 0° to 1900° C.

Guy B. Taylor, E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

CALCULATIONS for processes involving heating or cooling by or with gases ordinarily require a knowledge of the heat content—e. g., how many calories or pound Centigrade units (P. C. U.) are required to heat a given quantity of some gas mixture from t_1° to t_2°. Except for the case of saturated steam, reference books give no tables for heat content but supply instead data or formulas for specific heat. In engineering calculations specific heat values are not useful as such but must be translated into terms of heat content. The tables given here are convenient for heat calculations.

The heat contents for the individual gases were calculated by integrating Bryant's[1] equations for specific heat at constant pressure. The specific heat equations are all given in the form:

$$C_p = A + BT + CT^2 \qquad (1)$$

where A, B, and C are constants

The heat content from this form of equation is:

$$H = \int_{T_1}^{T_2} A\cdot dT + BT\cdot dT + CT^2\cdot dT$$

which upon integration becomes, between the limits $T_1 = 0$, $T_2 = T$:

$$H = AT + B/2T^2 + C/3T^3$$

Tables I amd II give heat contents in calories per gram mole (P. C. U. per pound mole) from 0° C. to the indicated temperature. Differences for each 100° are given for interpolation purposes. The calculations were made by using five-place log tables. The constants are given in Table III. The formulas, and consequently the values above 1500° C., are less reliable than below this temperature.

Table I. Heat Contents of Diatomic Gases

(Calories per gram mole)

Temp.	H_2		O_2		N_2		CO	
° C.	*H*	Δ	*H*	Δ	*H*	Δ	*H*	Δ
0	0		0		0		0	
		693		707		685		688
100	693		707		685		688	
		695		728		701		705
200	1388		1435		1386		1393	
		700		749		716		722
300	2088		2184		2102		2115	
		703		767		729		737
400	2791		2951		2831		2852	
		707		784		744		752
500	3498		3735		3575		3604	
		712		800		756		766
600	4210		4535		4331		4370	
		718		814		769		779
700	4928		5349		5100		5149	
		724		826		779		791
800	5652		6175		5879		5940	
		731		837		791		802
900	6383		7012		6670		6742	
		738		847		801		812
1000	7121		7859		7471		7554	
		745		854		810		821
1100	7866		8713		8281		8375	
		754		861		819		830
1200	8620		9574		9100		9205	
		763		865		826		836
1300	9383		10439		9926		10041	
		772		869		835		844
1400	10155		11308		10761		10885	
		782		870		841		849
1500	10937		12178		11602		11734	
		793		871		846		854
1600	11730		13049		12448		12588	
		804		869		852		857
1700	12534		13918		13300		13445	
		815		867		857		860
1800	13349		14785		14157		14305	
		828		861		860		862
1900	14177		15646		15017		15167	

Table II. Heat Contents of Polyatomic Gases

(In calories per gram mole)

Temp.	CO_2		CH_4		C_2H_2		H_2O	
° C.	*H*	Δ	*H*	Δ	*H*	Δ	*H*	Δ
0	0		0		0		0	
		935		873		1141		791
100	935		873		1141		791	
		1001		1020		1224		822
200	1936		1893		2365		1613	
		1064		1160		1304		852
300	3000		3053		3669		2465	
		1120		1291		1380		880
400	4120		4344		5049		3345	
		1172		1412		1448		908
500	5292		5756		6497		4253	
		1220		1528		1513		936
600	6512		7284		8010		5189	
		1261		1633		1572		963
700	7773		8917		9582		6152	
		1299		1731		1626		989
800	9072		10648		11208		7141	
		1331		1821		1673		1014
900	10403		12469		12881		8155	
		1358		1901		1716		1039
1000	11761		14370		14597		9194	
		1381		1973		1755		1064
1100	13142		16343		16352		10258	
		1397		2037		1786		1086
1200	14539		18380		18138		11344	
		1411		2094		1815		1109
1300	15950		20474		19953		12453	
		1418		2141		1836		1132
1400	17368		22615		21789		13585	
		1420		2178		1852		1153
1500	18788		24793		23641		14738	
		1418		2210		1864		1173
1600	20206		27003		25505		15911	
		1410		2233		1869		1194
1700	21616		29236		27374		17105	
		1399		2246		1870		1213
1800	23015		31482		29244		18318	
		1380		2251		1866		1231
1900	24395		33733		31110		19549	

Table III. Constants Used in Formulas

Gas	*A*	$B\cdot10^6$	$C\cdot10^9$	$B/2\cdot10^6$	$C/3\cdot10^9$
H_2	6.88	66	+ 279	33.0	+ 93.00
O_2	6.26	2746	− 770	1373.0	− 256.67
N_2	6.30	1819	− 345	909.5	− 115.00
CO	6.25	2091	− 459	1045.5	− 153.00
CO_2	6.85	8533	−2475	4266.5	− 825.00
H_2O	6.89	3283	− 343	1641.5	− 114.33
CH_4	3.38	17905	−4188	8952.5	−1396.00
C_2H_2	8.28	10501	−2644	5250.0	− 881.00

Received December 6, 1933. This paper is Contribution 135 from the Experimental Station of E. I. du Pont de Nemours & Company.

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MARKET REPORT—MARCH, 1934

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, MARCH 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals

Acetaldehyde, drums, lc-l., wks.	lb.	.16
Acetaldol, 50-gal. drums	lb.	.27
Acetamide, drums	lb.	.40
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.07
Adipic	lb.	.72
Furoic, tech., drums	lb.	.35
Linoleic	lb.	.16
Naphthenic, drums	lb.	.10
Sebacic, tech.	lb.	.58
Ammonium linoleate, drums	lb.	.12
Ammonium oleate	lb.	.10
Aroclors	lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	.60
Calcium furoate, tech., drums	lb.	.30
Capryl alcohol, tech.	lb.	.85
Pure	lb.	2.50
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Crotonaldehyde, 50-gal. drums, c/l.	lb.	.26
Dichloroethyl ether, 50-gal. drums, c/l.	lb.	.21
Diethylene glycol, drums	lb.	.14
Monobutyl ether, drums	lb.	.26
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.26
Dimethylamine, pure 25 & 40% sol.—100% basis, drums	lb.	1.20
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.15
Ethyl acetoacetate, 110-gal. drums	lb.	.37
Ethyl furoate, 1-lb. tins	lb.	1.00
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorocarbonate, carboys	lb.	.30
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Ethylene chlorhydrin, 40%, 10-gal. cbys.	lb.	.75
Dichloride, 50-gal. drums	lb.	.05½
Glycol, 50-gal. drums	lb.	.25
Monobutyl ether, drums, wks.	lb.	.20
Monoethyl ether, drums, wks.	lb.	.15
Monoethyl ether acetate, drums, wks.	lb.	.16½
Monomethyl ether, drums	lb.	.21
Oxide, cyl.	lb.	.75
Furfuramide (tech.), 100-lb. drums	lb.	.30
Furfuryl acetate, 1-lb. tins	lb.	5.00
Alcohol, tech., 500-lb. drums	lb.	.40
Glyceryl phthallate	lb.	.26
Glycol stearate	lb.	.18
Isopropyl ether, drums	lb.	.07
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs.	lb.	1.15
Methyl acetate, 82%, drums	lb.	.12
99%, tanks	lb.	.15
Cellosolve, *see* Ethylene glycol monomethyl ether		
Methyl hexyl ketone, pure	lb.	1.20
Paraldehyde, 110–55 gal. drums, c/l.	lb.	.16
Phosphorus oxychloride, 175 cyl.	lb.	.20
Potassium abietate	lb.	.06
Sodium abietate	lb.	.06
Sodium alginate	lb.	.50
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.15
Distilled	lb.	.40
Tetrachloroethane, 50-gal. drums	lb.	.08½
Trichloroethylene, 50-gal. drums	lb.	.09½
Triethanolamine, 50-gal. drums	lb.	.35
Trihydroxyethylamine linoleate	lb.	.40
Trihydroxyethylamine stearate	lb.	.35
Vinyl chloride, 16-lb. cyl.	lb.	1.00
Zinc dithiofuroate, 100-lb. drums	lb.	1.00
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

Chemicals Previously Quoted

Acetanilide, U. S. P., powd., bbls.	lb.	.26
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks., c/l.	lb.	.11
Acetphenetidin, bbls.	lb.	1.30
Acid, acetic, 28%, c/l., bbls.	100 lbs.	2.91
56%, c/l., bbls.	100 lbs.	5.50
Glacial, c/l., bbls.	100 lbs.	10.02
Glacial, U. S. P., c/l., carboys	100 lbs.	10.52
Acetylsalicylic, bbls.	lb.	.70
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb.	.40
Boric, bbls.	lb.	.04
Butyric, 100% basis, cbys.	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.04½
Chromic, 99%, drums	lb.	.15½
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.28
Cresylic, pale, drums	gal.	.50
Formic, 90%, cbys., N. Y.	lb.	.11
Gallic, U. S. P., bbls.	lb.	.77
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.07
60%, bbls., wks.	lb.	.15
Hydrofluosilic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.75
Lactic, 22%, dark, bbls.	lb.	.04
48%, light, bbls., wks.	lb.	.11½
Mixed, tanks, wks.	N unit	.07
	S unit	.08
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	nom.
Nitric, c. p., cbys.	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11⅞
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic	lb.	1.45
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls., c/l.	lb.	.09½
Sulfanilic, 250-lb. bbls.	lb.	.18
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.23
Tartaric, U. S. P., cryst., bbls.	lb.	.26½
Tungstic, kegs	lb.	1.40
Valeric, c. p., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	4.15½
Amyl, from pentane, tanks	lb.	.143
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.10½
Denatured, No. 5, comp. denat., c/l., drums	gal.	.34
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	.75
Isopropyl, ref., drums	gal.	.50
Propyl, ref., drums	gal.	.75
Wood, *see* Methanol		
Aldol, 95%, drums, c/l.	lb.	.21
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.33

Alum, ammonia, lump, bbls., wks.	100 lbs.	3.00
Chrome, casks, wks.	100 lbs.	7.00
Potash, lump, bbls., wks.	100 lbs.	3.00
Soda, bbls., wks.	100 lbs.	4.00
Aluminum, metal, N. Y.	100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.04
Aluminum stearate, 100-lb. bbl.	lb.	.17
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.35
Iron-free, bags, wks.	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks.	lb.	.04½
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.15¼
Bromide, bbls.	lb.	.39
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.50
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	4.30
Nitrate, tech., cryst., bbls.	lb.	.08½
Oxalate, kegs	lb.	.24
Persulfate, cases	lb.	.20
Phosphate, dibasic, tech., bbls.	lb.	.08½
Sulfate, bulk, wks.	ton	25.00
Amyl acetate, tech., from pentane, tanks, delivered	lb.	.135
Aniline oil, drums	lb.	.16½
Anthracene, 80–85%, casks, wks.	lb.	.75
Anthraquinone, subl., bbls.	lb.	.45
Antimony, metal	lb.	.07¼
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.08½
Salt, dom., bbls.	lb.	.22
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Argols, red powder, bbls.	lb.	.08
Arsenic, metal, kegs	lb.	.44
Red, kegs, cases	lb.	.14½
White, c/l., kegs	lb.	.04½
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	45.00
Chloride, bbls., wks.	ton	74.00
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05
Nitrate, casks	lb.	.08½
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzidine base, bbls.	lb.	.65
Benzol, tanks, wks.	gal.	.20½
Benzoyl chloride, drums	lb.	.40
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, drums	gal.	.85
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.58
Bismuth, metal, cases	lb.	1.30
Bismuth, nitrate, 25-lb. jars	lb.	1.20
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.40
Blanc fixe, dry, bbls.	ton	70.00
Bleaching powder, drums, wks.	100 lbs.	1.90
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.018
Bordeaux mixture, bbls.	lb.	.10½
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butyl acetate, drums, c/l.	lb.	.11
Cadmium bromide, 50-lb. jars	lb.	1.25
Cadmium, metal, cases	lb.	.55

Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	1.85
Calcium acetate, bags	100 lbs.	3.00
Arsenate, bbls	lb.	.06¾
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	19.50
Cyanide, 100-lb. drums	lb.	.30
Nitrate, bags, 15% N	ton	25.50
Phosphate, monobas., bbls	lb.	.07½
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bags,	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl	lb.	.06½
Camphor, Jap., slabs	lb.	.54
Carbazole, bbls	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.051
Carbon black	lb.	.04†
Carbon dioxide, liq. cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.05¼
Casein, stand. gr., bbls	lb.	.12
Cellulose acetate, bbls	lb.	.80
Cerium oxalate, kegs	lb.	.25
Charcoal, willow, powd., bbls	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq. c/l., cyl.*	lb.	.055
Chlorine, tanks	100 lbs.	1.85
Chlorobenzene, mono-, drums	lb.	.06
Chloroform, tech., drums	lb.	.20
Chromium acetate, 20° soln., bbls	lb.	.05
Coal tar, bbls., wks	bbl.	8.50
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	1.25
Cod liver oil, bbls	bbl.	28.00
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec	100 lbs.	8.00
Copper carbonate, bbls., 52/54%	lb.	.15½
Chloride, bbls	lb.	.17
Cyanide, drums	lb.	.39
Oxide, red, bbls	lb.	.12½
Sulfate, c/l., bbls	100 lbs.	3.75
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.18¼
Cyanamide, bulk, N. Y.	Ammonia unit	1.07½
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls	lb.	2.35
Dibutylphthalate, drums, wks	lb.	.20½
Diethylaniline, drums	lb.	.52
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.29
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, tech., drums	lb.	.17
Dinitrochlorobenzene, bbls	lb.	.14½
Dinitronaphthalene, bbls	lb.	.34
Dinitrophenol, bbls	lb.	.23
Diphenylamine, bbls	lb.	.31
Diphenylguanidine, bbls	lb.	.36
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.75
Ether, conc., drums	lb.	.09
Ethyl acetate, tanks, c/l	lb.	.07½
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene chlorohydrin, anhyd. drums	lb.	.75
Glycol, c/l., wks	lb.	.26
Feldspar, bulk	ton	10.00
Ferric chloride, tech., bbls	lb.	.05
Ferrous chloride, cryst., bbls	lb.	.06
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls	100 lbs.	1.10
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, c. p., drums	lb.	.12½
G salt, bbls	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.37
Hydrogen peroxide, 25 vol., bbls	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls	lb.	.12
Iodine, crude, 200-lb. kgs	kilo	15s. 1d.
Iodine, resubl., jars	lb.	2.25
Iron acetate, liq., 17°, bbls., c/l	lb.	.03
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y	100 lbs.	4.00
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls	lb.	.10
Oxide, litharge, bbls	lb.	.06¾
Peroxide, drums	lb.	.20
Red, bbls	lb.	.07¾
Sulfate, bbls	lb.	.06
White, basic carb., bbls	lb.	.06½
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.,	280 lbs.	1.70
Limestone, ground, bags, wks	ton	4.50
Lithopone, bbls	lb.	.04½
Magnesite, calcined, 500-lb. bbls., wks	ton	65.00
Magnesium, metal, wks	lb.	.30
Magnesium carbonate, bags	lb.	.06½
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls	lb.	.10
Oxide, U. S. P., light, bbls	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.09
Mercury bichloride, cryst., 100 lbs.	lb.	.88
Mercury flasks, 76 lbs	flask	76.00
Meta-nitroaniline, bbls	lb.	.67
Meta-phenylenediamine, bbls	lb.	.82
Meta-tolylenediamine, bbls	lb.	.67
Methanol, pure, synthetic, drums, delivered, c/l	gal.	.37½
Tanks, delivered	gal.	.35½
Methyl acetone, drums	gal.	.54½
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls	lb.	2.50
Naphthalene, flake, bbls	lb.	.06
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.11½
Double, bbls	lb.	.11½
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.09
Oil, castor, No. 1	lb.	.10¼
China wood, bbls	lb.	.07⅞
Coconut, Ceylon, tanks	lb.	.03⅝
Cod, N. F., bbls	gal.	.40
Corn, crude, tanks, mills	lb.	.04¾
Cottonseed, crude, tanks	lb.	.03½
Linseed, bbls	lb.	.097
Menhaden, crude, tanks	gal.	.15
Neat's-foot, pure, bbls	lb.	.13
Oleo, No. 1, bbls	lb.	.06⅛
Olive oil, denat., bbls	gal.	.87
Foots, bbls	lb.	.06⅝
Palm, Lagos, casks	lb.	.03⅞
Peanut, crude, tanks	lb.	.04⅞
Perilla, bbls	lb.	.09
Rapeseed, bbls	gal.	.44
Red, bbls	lb.	.07
Soy bean, crude, tanks	lb.	.065
Sperm, 38°, bbls	lb.	.108
Whale, bbls., natural, winter	lb.	.072
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.05½
Ortho-toluidine, bbls	lb.	.14
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.16
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls	lb.	.45
Para-nitrosodimethylaniline, bbls	lb.	.92
Para-nitrotoluene, bbls	lb.	.35
Para-phenylenediamine, bbls	lb.	1.15
Para-toluidine, bbls	lb.	.56
Paris Green, 250-lb. kegs	lb.	.23
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.52
Phenylethyl alcohol, 1-lb. bot	lb.	3.75
Phosphorus, red, cases	lb.	.45
Phosphorus trichloride, cyl	lb.	.18
Phthalic anhydride, bbls	lb.	.14½
Platinum, metal	oz.	36.00
Potash, caustic, drums	lb.	.07¼
Potassium acetate, kegs	lb.	.27
Bicarbonate, casks	lb.	.07½
Bichromate, casks	lb.	.08⅛
Binoxalate, bbls	lb.	.14
Bromide	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.07
Chlorate, kegs	lb.	.09
Chloride, crystals, bbls	lb.	.04¾
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.10½
Muriate, fert., bulk	ton	35.55
Permanganate, drums	lb.	.18½
Prussiate, red, casks	lb.	.39
Yellow, casks	lb.	.18
Titanium oxalate, bbls	lb.	.32
Pyridine, drums	gal.	1.25
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P	lb.	.14¼
R salt, bbls	lb.	.44
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	13.00
Saltpeter, gran., bbls	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot	oz.	.33⅛
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.23
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.60
Sodium acetate, bbls	lb.	.05
Benzoate, bbls	lb.	.45
Bicarbonate, bbls	100 lbs.	1.85
Bichromate, casks	lb.	.06½
Bisulfite, bbls	lb.	.03
Bromide, bbls., U. S. P	lb.	.35
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls	lb.	.07½
Metallic, drums, 12¼-lb. bricks	lb.	.19
Metasilicate, cryst	100 lbs.	3.25
Metasilicate, gran., bbls	100 lbs.	2.65
Naphthionate, bbls	lb.	.52
Nitrate, crude, 200-lb. bags, N. Y.	100 lbs.	1.315
Nitrite, bbls	lb.	.07¼
Perborate, bbls	lb.	.17
Peroxide, cases	lb.	.20
Phosphate, trisodium, bbls	100 lbs.	2.60
Phosphate, disodium, bags	100 lbs.	2.10
Picramate, kegs	lb.	.67
Prussiate, bbls	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.80
Silicofluoride, bbls	lb.	.05
Stannate, drums	lb.	.35
Sulfate, anhyd., bbls	100 lbs.	2.20
Sulfide, cryst., bbls	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls	lb.	.30
Thiosulfate, reg., cryst., bbls	lb.	.02½
Tungstate, kegs	lb.	.77½
Strontium carbonate, tech., bbls	lb.	.07¼
Nitrate, bbls	lb.	.09½
Sulfur, bulk, mines, wks	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls	lb.	.25
Tin	lb.	.54
Tin tetrachloride, anhydrous, drums, bbls	lb.	.27
Oxide, bbls	lb.	.55
Titanium dioxide, bbls., wks	lb.	.17¼
Toluene, tanks	gal.	.30
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls	lb.	.37
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.15
Whiting, bags	ton	7.00
Xylene, 10°, tanks, wks	gal.	.29
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	4.25
Zinc ammonium chloride, bbls	lb.	.05
Chloride, granulated, drums	lb.	.05⅜
Oxide, Amer., bbls	lb.	.06¾
Stearate, bbls	lb.	.18
Zinc dust, bbls., c/l	lb.	.0625

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3 VITAMIN G (B_2). Differentiation from Vitamin B. Concentration. Quantitative Determination. Physicochemical Properties. Distribution in Foods. Relation to Nutrition.
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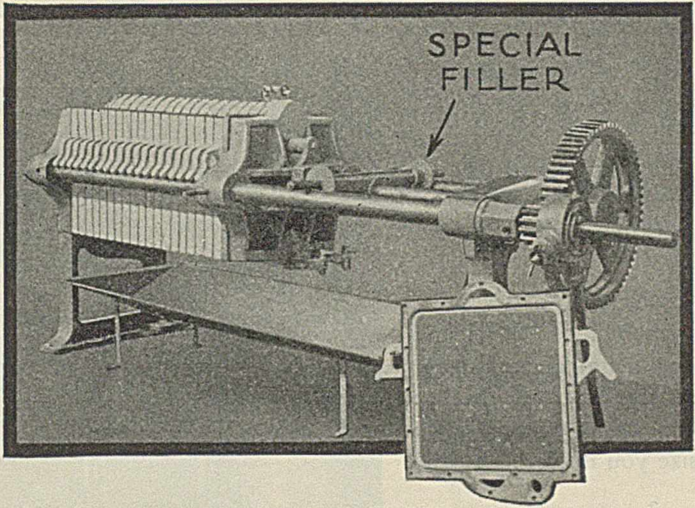

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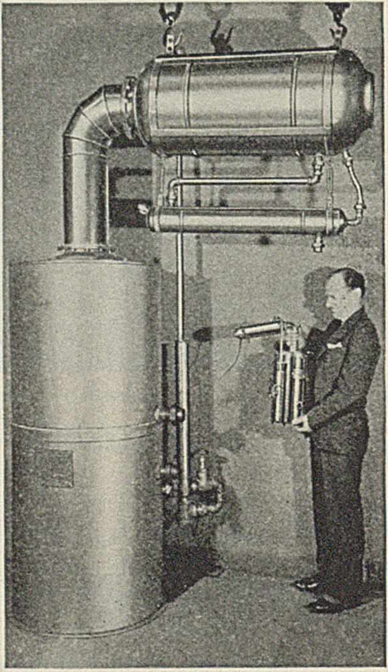

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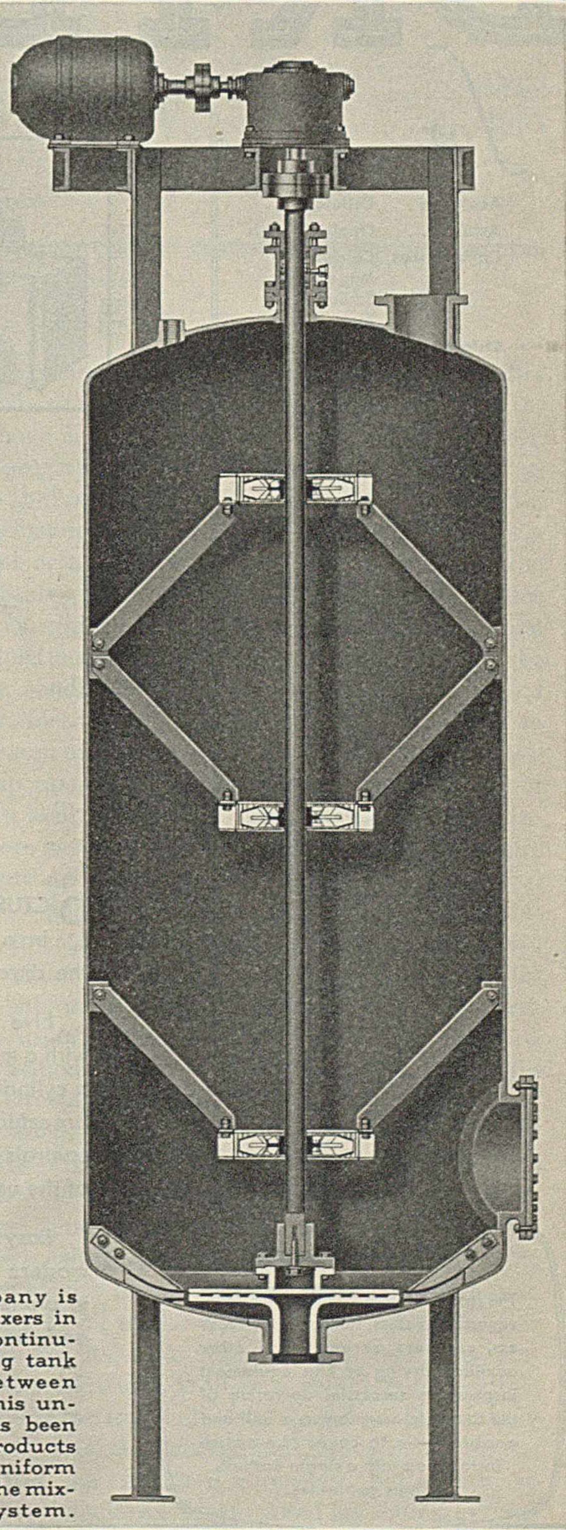

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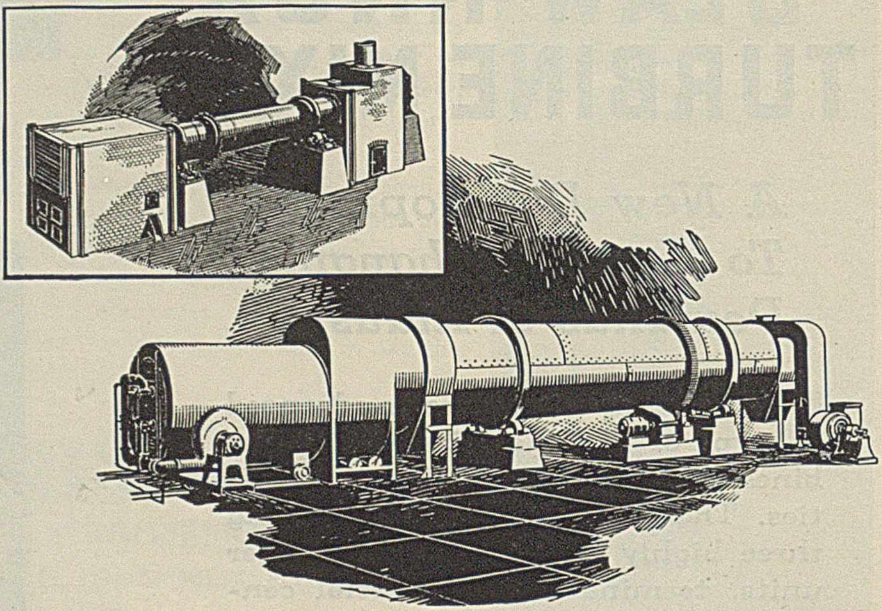

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