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The Editor's Page

AIR-CONDITIONING AND ECONOMIC RECOVERY. At various times during the economic depression, a longing has been expressed for some discovery by science or an invention that might be the basis of a great new industry. Such things have been credited with forcing the business curve upward in the past, and there was reason to believe that, if something good enough could be found, history might repeat itself.

Of the various new things, air-conditioning appears to come nearest meeting such a specification. A few hotels this summer are offering a limited number of air-conditioned rooms on a basis somewhat experimental; business is more attracted to air-conditioned restaurants than to others without such modern improvements; the railways which offer the more quiet, cleaner, and cooler cars take precedence over those which have not seen fit to invest in this new equipment. "Air-cooled" is the headliner in many a theatre. Even the householder is beginning to look at air-conditioning as its cost is constantly lowered.

Now comes a really significant announcement. The Carrier-Brunswick International, Inc., a division of Carrier Engineering Corporation, pioneer in the field of air-conditioning, has a contract to air-condition the famous Robinson mine in the Rand near Johannesburg. The Rand produces about half the world's gold with the amount definitely limited by conditions in the deep mines, some of which already extend to 8000 feet below the surface. Here temperatures from 100° to 120° F., combined with a humidity from 90 to 100 per cent, definitely limit operation, and while there is reason to believe that the richest deposits of gold lie at still greater depths, it has been humanly impossible to work them.

The plan is to force dry, cold air, traveling at a rate of approximately 30 miles an hour, to the lowest parts of the mine. This will cool and dehumidify, as well as thoroughly ventilate, these remote depths where men strive for the precious metal. This first installation of the Robinson mine must be regarded as something of an experiment on which a half million dollars is being risked, but the chances for success are large and the return on the operation promises to be most gratifying. There are doubtless other instances where air-conditioning will allow further production of gold. We are told that in Nevada, for example, some mining operations were abandoned because of working conditions in the mines, even though not so deep as those in the Rand, rather than because of lack of ore.

A great increase in the production of gold, according to the economists, would support amply any possible trade revival, enable the world to return to the gold standard, greatly restore confidence, and cause commodity prices to rise. In fact, it would quickly change the present world economic situation and multiply the number of those who can smile.

We wish all success to this bold engineering feat. It has frequently been said that, of all factors, science is the most likely to help find a way out of the slump, now in its fifth year. It would seem that science may make good this prediction.

* * *

PATENT EXAMINERS. One sign of returning prosperity is the increasing number of resignations in the Patent Office, particularly among the junior examiners. Of the sixty-five divisions, about eight are devoted to chemistry, and another four are known as process divisions. Inquiry discloses that not only are these chemical divisions among the most active, as judged by the number of cases appearing for examination, but also if rated by the loss of their examiners. Places thus vacated may be filled from new appointments or by transfers from the less active divisions. In either case the risk is run of replacing an experienced man with one less capable. Mistakes may result and their cost to industry is beyond estimate.

Why not make the service attractive as a career to even the best examiners? In this connection one would do well to consider the position of the nearly three hundred junior examiners now in Washington. A petition, signed by a group representing approximately all of these men, was printed in the *Journal of the Patent Office Society*

last spring. From this we learn that, in several cases, men after five years' service are receiving slightly less than when they entered the department. This has been due to various deductions because of economy measures, and there has been a lack of promotions which are normally given men for efficient service. When this petition was written there were 123 examiners, base pay $2000, actually receiving $1630 annually; 58, with a base pay of $2100, were getting $1710; another 53 of the $2200 class were getting $1790; 17, with base pay $2300, were getting $1880; and 23, with base pay $2400, were actually receiving but $1960. This situation has improved somewhat with the restoration of part of the pay cuts.

Now these men are trained. More than 90 per cent of them have technical degrees, have had technical and office experience, have studied law, and many have been admitted to the bar. It is not to be expected that capable men will long submit to such conditions, and industry is not slow to take advantage of the situation, offering equal security in position, better remuneration, and greater opportunities for advancement.

But is this the best thing for industry? It seems to us that the men who know and who, through knowing, avoid errors expensive to business should be retained in these important places. The Patent Office should be not merely a training ground, not just a means to an end. It should be attractive as a career, and the steps necessary to make such a career something eagerly sought after should be taken without delay.

* * *

PURE FOOD, DRUGS, AND COSMETICS. Among the bills which failed of enactment in the recent Congress was the one variously known as the Tugwell or the Copeland, designed to strengthen the position of those who, as federal officials, would protect the consuming public in the matter of food, drugs, and cosmetics. The bill went through a number of changes, but now that a new effort will be made, we urge thorough study, and particularly a united front, on the part of those representing the legitimate manufacturing industry. The public desires and deserves more complete protection against the quack, the unscrupulous manufacturer, and the conscienceless dealer. Some abuses cannot be prevented under present laws and a new bill undoubtedly will be introduced in the next session of Congress to better the situation. But the legislation to be enacted should be fair, reasonable, and enforceable with justice.

A number of objectionable features were included in the last draft. Many of these could be easily corrected and still achieve the ends sought. For example, under the bill a drug would be deemed to have been adulterated if it failed to meet the definition, manufacturing formula, and description set forth in an official compendium such as the U. S. Pharmacopeia. The procedures or manufacturing formulas in the Pharmacopeia have been worked out for the guidance of the individual pharmacist who, in making small lots, obviously proceeds in a manner quite different from that employed by the manufacturer. The latter, though he may not follow the official formula, nevertheless produces a standard and approved product. Further, a drug is also considered adulterated if mixed or packed with any substance so as to reduce its quality or strength, and yet it is well known that many vegetable drugs naturally contain active principles in excess of the amount named in the Pharmacopeia and they must be reduced to a recognized standard strength, which has been officially set, if they are to be used satisfactorily by the physician.

The bill in its latest form also contained a number of terms new to legislation and not adequately defined. The word "disease" is an example, and if you will consult the 11th revised edition of Steadman's Medical Dictionary you will find six general definitions and fifty-five special definitions of "disease." Other words not specifically defined were used in the bill which, as can easily be foreseen, would have made a great holiday for the legal profession. The language was also so broad as virtually to require a manufacturer to open his plant to the inspection of a representative of the Department of Agriculture, who might thereby discover the secrets of manufacturing processes and the details of specially devised equipment, with no guarantee whatever that this information would remain confidential. Experience in other fields, as for example, industrial alcohol, has shown that unfortunately inspectors in the past have not been above capitalizing such special information. Again, the Secretary of Agriculture would have it in his power to close down a great plant if there were differences of opinion as to the method of manufacturing or labeling a single product of the plant. He might likewise prohibit interstate commerce in entirely acceptable products if only one item in a long list of manufactures was in dispute.

Of course the effort of special interests left imprints upon the bill, one amendment under adulterated food providing exemption of citrus fruits artificially colored. While it is recognized that wholesome citrus fruits can be colored without harm to the consumer, strictly speaking that is one form of deception. Should a bill intended to right existing evils wink at such practice in one case and bear down hard in another?

The industries concerned have within their ranks many men who see the necessity of bettering conditions and who can bring to the problem a wealth of experience. If officials of equal ability and broad mindedness could work with such a group, an adequate and forcible bill should result. With this enacted into law those who deserve it could be punished, honesty and fair dealing could be rewarded, and the consumer could be fully protected. Is it too much to hope that such a procedure may be followed?

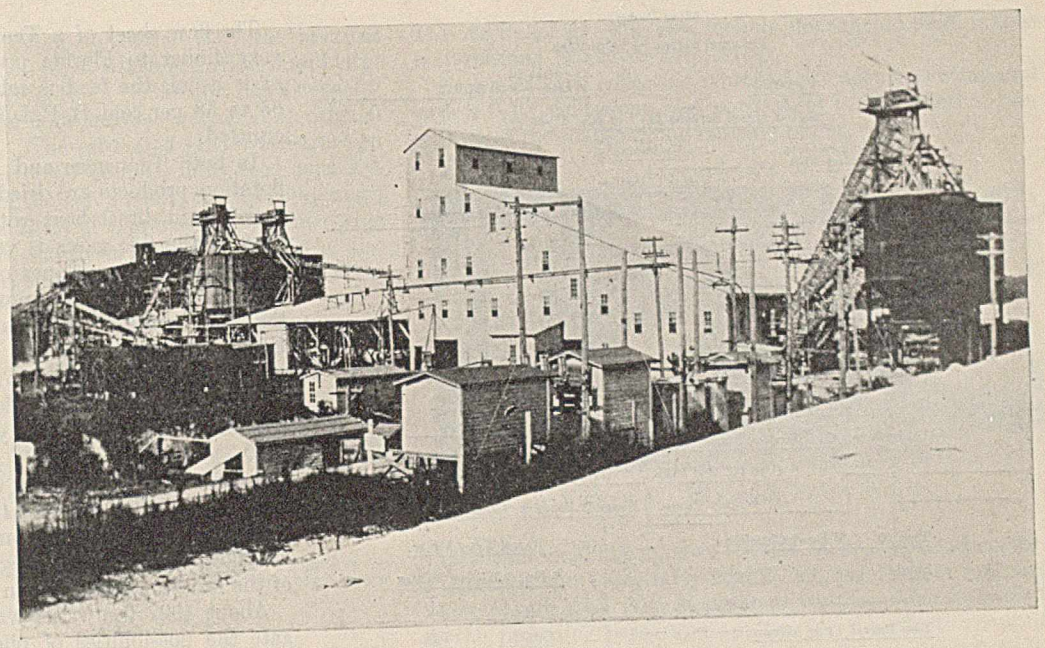

FIGURE 1. PHOSPHATE RECOVERY PLANT NO. 2, MULBERRY, FLA.

Development and Application of Phosphate Flotation

JAMES A. BARR, Phosphate Recovery Corporation, Mulberry, Fla.

SINCE the writer's association with the phosphate industry in the early part of 1910, there have been many changes. The recovery and subsequent treatment of washer fractions and tailing has always been a serious problem. The first real progress along metallurgical lines came with the introduction of flotation.

The early washing plants were somewhat crude affairs and there was very little attempt to save any except the coarser fractions. Some of these washers recovered only the plus quarter-inch phosphate. In Tennessee this was a decided improvement over hand methods where anything that passed a ten-tined potato fork was considered an unavoidable loss. These losses were condoned with the statement that it was cheaper to mine a little more than to spend money on equipment. This does not mean that no research work was carried on or that no serious thought and effort were given to these problems before the application of flotation. Considerable was done on gravity methods, but, because of the closeness of specific gravity of the phosphates and the usual silica gangue, these processes had a very limited application.

Aside from electrostatic separation, flotation offered the most hope. The former was not attractive because of cost and delicate operative conditions, and the latter was seemingly hopeless during these early periods.

In order to visualize the value of flotation in the recovery of fine phosphate particles from our two most important phosphate fields, a brief description of these deposits and the methods of mining and handling the product are given below.

MINING AND WASHING

Florida pebble phosphates occur as an unconsolidated conglomerate or gravel, formed from phosphatic marl during the Pliocene or possibly the late Miocene period. Circulating ground waters probably effected the enrichment. The phosphatic stratum, of 10 to 15 feet average thickness, contains more or less clay and silica sand, overlaid by a sandy clay overburden, averaging 15 to 25 feet in depth.

The overburden is commonly removed by electric drag lines, while the phosphate matrix is usually mined hydraulically and pumped to a washer located in the center of a 160- to 300-acre tract.

Washing consists of dewatering on stationary, sloping flat screens, separation of low-grade oversize in a trommel followed by pugging in log washers to elutriate the clay, and finally screening at an average of 1 to $1^1/_8$ mm. to separate from silica and the remaining clay. Classifiers may be used to reclaim finer fractions, but these are lower in grade as will be discussed later. In any case, the washer tailing will still contain a large percentage of phosphatic grains.

The Tennessee brown-rock deposits are somewhat different both in appearance and character. These were laid down during the Ordovician age and originated from phosphatic limestones from which the free carbonate of lime was subsequently leached by circulating ground waters.

The phosphate occurs as brown to grayish lumps or slabs down to very fine grains, all intimately associated with varying percentages of clay, silica sand, and phosphatic-limonitic or manganiferous minerals of minor percentages. The stratum is underlaid by the unaltered limestone which often intrudes as irregular bowlders in varying states of leaching. The phosphate sometimes, but not often, is exposed at the surface but usually is overlaid by 10 to 25 feet of impure, sandy clay.

Steam or Diesel drag lines are used for removing the overburden and for then mining the phosphate stratum. Some hand-mining is employed, especially where the phosphate runs back under bowlders or into narrow crevices in the limestone, called "cutters."

The phosphate matrix, locally called "muck," is hauled

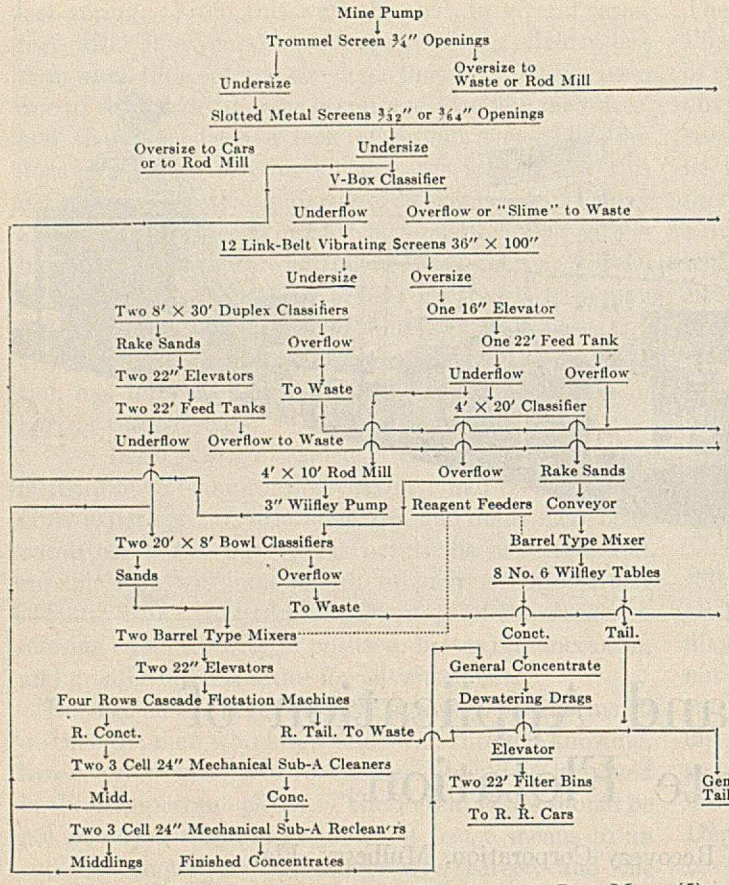

FIGURE 2. FLOW SHEET OF PLANT NO. 2, WITH ROD MILL (5)

to a central washing and drying plant on narrow-gage tramways. Here, as in Florida, the clay is put into suspension with log washers which discharge into a rotary trommel with $^1/_8$ to $^3/_{16}$ inch slots. The oversize, washed free from clay with a violent spray, is hand-picked for removal of mud balls, flint, and limestone nodules. The trommel undersize is deslimed and partially dewatered in hydroseparators with further desliming and dewatering in rake and bowl classifiers. The practice is to save down to 200 mesh, with some recoveries to 350 mesh; the lower limits are a question of economics.

FLORIDA FLOTATION PRACTICE

The washer tailing, when treated by flotation, is deslimed and dewatered in V-boxes and feed bins, and then classified at about 28 mesh. The oversize is ground in rod mills, followed by desliming and dewatering in bowl classifiers. The classifier rake product discharges to rotary mixers where the flotation reagents are added. The +28-mesh fraction may be similarly treated up to this point without grinding and then beneficiated on concentrating tables.

The oiled −28-mesh fraction is fed to roughing flotation cells, discharging a clean tailing to waste and a medium-grade concentrate to the cleaner cells. The cleaning section delivers a high-grade concentrate to dewatering drags and storage tanks with filter panels. Middling is usually returned to the head of the roughers. The froth from the first roughing cell is usually laundered direct to the finished concentrate drag.

The flow sheet of a Tennessee flotation plant is very similar to Florida practice, except that when, as is usual, the feed is relatively high grade (i. e., 65 to 68 per cent B. P. L.),[1] the cleaner section is omitted.

In both Tennessee and Florida the washer and flotation products are dried to about one per cent moisture in direct heat rotary driers. Phosphate dust in the flue gases is very efficiently reclaimed by high-velocity cyclones or settling chambers.

It was not generally known in the United States that the work of Sulman and of Broadbridge and Edser on nonmetallics and phosphates was carried out in England somewhat prior to 1920, for as Gaudin (*3*) remarks, the flotation of a polar nonmetallic mineral was hardly considered possible in 1920.

A little later and before the issue of the Broadbridge and Edser patent (*1*), there was some work done in this country by various engineers working on phosphates but with negative results, after trial of the usual reagents known in sulfide flotation.

About 1922 the writer was instructed to investigate the possibilities of phosphate flotation. Because of the initial plant cost and capacity indicated by sulfide practice, the outlook was not promising when considering a low-priced commodity as phosphate. No progress was made until the writer learned of the Broadbridge and Edser work and made contact with the Minerals Separation N. A. Corporation. The writer set up a laboratory flotation machine in Mt. Pleasant, Tenn., and obtained encouraging results with the first test. Reagent quantities were large but the collector used—oleic acid—was the answer. Early in 1926 the work was transferred to Mulberry, Fla., and carried through to a

[1] Bone phosphate of lime, equivalent to the P_2O_5 content of the phosphate calculated as tricalcium phosphate.

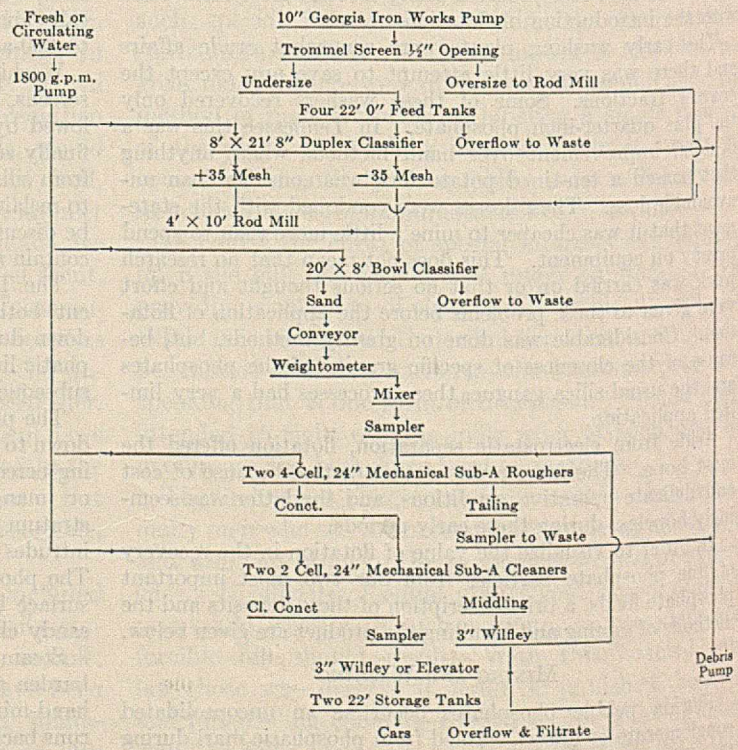

FIGURE 3. PROPOSED NEW FLOW SHEET, 60 LONG TONS OF FEED PER HOUR (5)

successful conclusion as noted by Martin (*5*). He describes in detail the No. 2 flotation plant which is the latest and largest mill in the operation (Figure 1). This unit has a capacity of 100 (long) tons feed per hour and was erected at an original cost of nearly $200,000. The estimated (1933) construction costs are $50.00 per ton (2000 pounds) daily feed capacity. Figure 2 is a flow sheet of the No. 2 plant, and for comparison the much simplified flow sheet of a proposed new unit (being constructed in 1934) is shown in Figure 3. Martin also notes the economics and effects on over-all recoveries of the whole mining and recovery system:

METALLURGICAL DATA ON CONCENTRATOR NO. 2 (*5*)

(Period covered, December, 1931)

Total tons ore treated[a]	52,323.38
Days operated (actual)[b]	22.77
Hours operated per day	24 (3 shifts)
Av. tonnage per 24 hours	2,297.91
Total tons concentrate	12,271.00
Total av. tons concentrate per 24 hours	538.91
Recovery of bone phosphate of lime	82.348
Ratio of concentration	4.2639

[a] All tonnages are long tons of 2240 pounds.
[b] Plant shut down 7 days (3 days Christmas holidays and 4 Sundays due to production curtailment). Balance of lost time due to shutdown for repairs and accidents.

SUMMARY OF DIRECT OPERATING COSTS OF NO. 2 FLOTATION CONCENTRATOR (*5*)

(December, 1931)

	Total for Month	Per Long Ton Feed	Per Short Ton Feed
Operating labor	$1268.19	$0.0242	$0.0217
Power	3131.80	0.0599	0.0534
Supplies (operating)	133.18	0.0025	0.0023
Reagents	1245.03	0.0238	0.0212
Repairs labor	329.74	0.0063	0.0056
Repairs supplies	614.08	0.0117	0.0105
Sampling	129.01	0.0025	0.0022
Assaying	138.95	0.0027	0.0024
Superintendent, office, and local overhead	755.07	0.0144	0.0129
	$7745.05	$0.1480	$0.1322
SEGREGATED INTO LABOR, SUPPLIES, AND POWER			
Total labor	$1726.95	$0.0330	$0.0295
Power	3131.80	0.0599	0.0534
Reagents	1245.03	0.0238	0.0212
Supplies	747.26	0.0143	0.0128
Superintendent, office, and local overhead	894.02	0.0170	0.0153
	$7745.06	$0.1480	$0.1322

Gaudin (*2*) follows xanthate in 1924 with soaps for the flotation of nonmetallics in 1925, under the heading of "Important Steps in the Evolution of Flotation." The general term "nonmetallics" may seem broad, but the similarity of all alkaline earth metals and their reactions toward soaps is a reasonable explanation.

No attempt will be made to go into the theory of flotation in general or, more specifically, that of phosphate flotation. Only the five main steps in the present phosphate flotation practices will be described.

MAIN STEPS IN PROCESS

The starting point in the flotation of phosphates is the selective reaction, in an alkaline pulp, between the soap-forming reagents and an alkaline earth base or in this case the phosphate mineral which is essentially tricalcium phosphate. The soap-forming reagent commonly used is a fatty acid of 12 or more carbon atoms, such as oleic acid. The phosphate particle, thus selectively coated with a relatively insoluble, water-repellent film, attractive to air bubble attachment, all as compared to the gangue mineral, is then amenable to froth flotation by any of the usual machines or to separation by stratification, tabling, etc.

The word "soap-forming" is used rather than the general term "fatty acid," since this group, unless limited by carbon atoms, includes acetic acid, etc., which are not soap-forming. This terminology will also include naphthenic acid, whose soap-forming properties are similar.

In general, the collecting power of a reagent, as compared with a fatty acid alone, will correspond to the relative percentage of the soap-forming radical present.

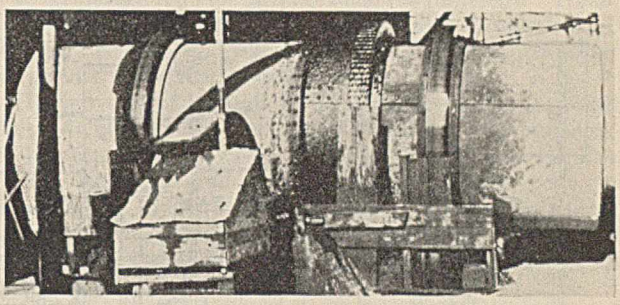

FIGURE 4. MIXER IN PLANT NO. 2

Mention should be made of the difference in action between a glyceride and a free fatty acid. The usual run of fats and vegetable oils gives poor or mediocre results. The statement in the preceding paragraph applies, for the effectiveness of these fats and oils in flotation of phosphates corresponds to the liberation by hydrolysis of the free fatty acid from the glyceride while in the pulp or present at the time of use.

It also follows that, when plating a film of relatively insoluble soap on a phosphate particle, the correct pH is necessary for the best results. In Florida practice this is nominally between 8.5 and 9.2, and the alkalinity is obtained by first adding caustic soda, though other suitable alkalies may be used.

It was early determined, for Florida conditions, that soaps formed *in situ*—i. e., in the pulp—were more effective and required less quantities than when added as soap solutions. It seems reasonable to assume that the reaction between the fatty acid and the alkali is more effective when taking place in immediate contact with the phosphate particle being coated, especially in view of the natural hardness of mill waters. This step is accomplished in practice by adding the reagents separately into the conditioner or mixer (Figure 4).

Another step was the abandonment of the somewhat usual practice of adding reagents to the relatively dilute pulps of the flotation roughers. In phosphate flotation the reagents are separately added to a relatively dense pulp such as is delivered as a rake product from a Dorr classifier, specifically put into the flow sheet for this purpose. With this method of application a material reduction of reagent quantities was possible. The effects of dilutions and mill waters on the reactions in question seems to be a reasonable explanation.

Slimes, colloids, or colloidally acting substances have a pronounced effect on flotation conditions and reagent quantities so that the practical removal is necessary for the best results, especially in Tennessee and Florida. Bowl classifiers are commonly used for this step. Some material is lost in the desliming which is still granular in appearance. As particle sizes decrease, especially in the lower ranges, the selectivity of reagents in all types of flotation decreases. Fortunately this range lies below practical equipment sizes when considering phosphates.

In the search to cheapen reagents, it was found that a hydrocarbon, such as fuel oil, would replace part of the fatty acid or soap-forming reagent required and at the same time increase selectivity; a workable assumption was that the fuel oil would plate over the soap film with an additional nonwettable coating attractive to air bubble attachment.

The steps may be summed up as follows: (1) the practical particle size for froth flotation (28 to 35 mesh maximum);

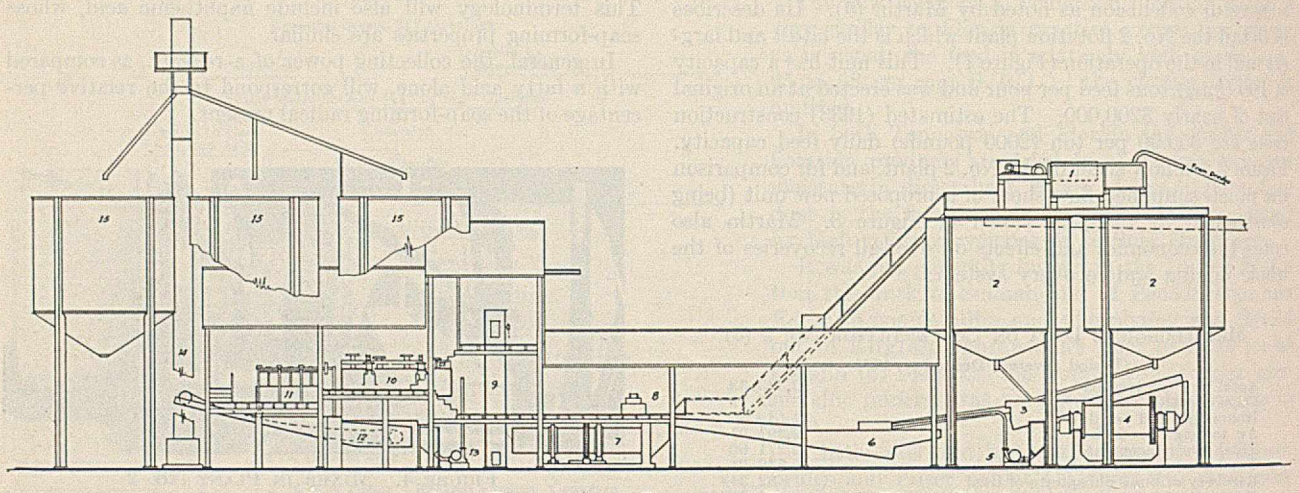

FIGURE 5. SIDE ELEVATION OF PHOSPHATE RECOVERY PLANT NO. 4

1. Four by twelve foot trommel; oversize, approximately 0.5 inch, wasted or shipped direct according to grade.
2. Four 22 × 18 foot steel feed bins, also used to dewater flow from dredge.
3. Six-foot, type F, duplex classifier; overflow, +35 mesh to 6; rake product to 4.
4. Four by ten foot rod mill; discharge to 5.
5. Four-inch centrifugal pump to 3 or 6.
6. Twenty-foot bowl classifier with 8-foot rakes; overflow to waste; rake product to 7.
7. Four by twenty foot rotary mixer; mixes reagents from reagent feeder 8 in a dense pulp; discharge to 9.
8. Four-compartment, cup and disk type reagent feeder with arc type drip trays.
9. Two 14-inch belt and bucket elevators of the centrifugal discharge type; discharge aided by fish-tail water jet; discharge to 10 through automatic samplers.
10. Two rows of 24-inch, four-cell, single-spitz, mechanical subaëration flotation machines; first cell concentrates direct to 12; balance of rougher concentrate to 11; tails to waste.
11. Two rows of 18-inch, three-cell, double-spitz, mechanical subaëration flotation machines; concentrates to 12; mids to 13.
12. Five-foot dewatering drag; overflow to 13, drag to 14.
13. Four-inch centrifugal pump (Wilfley) discharging to 10.
14. Fourteen-inch belt and bucket elevator.
15. Concentrate bins with 8- to 12-inch filter panels in each bin for dewatering; filter panels of 20-mesh bronze screen; bins discharge through hand-operated gates to railroad cars.

(2) desliming; (3) the correct pH of 8.5 to 9.2 obtained with an alkali such as caustic soda; (4) the addition of a soap-forming reagent such as oleic acid; (5) the addition of a hydrocarbon such as fuel oil, and possibly a small amount of frother.

There were many other detailed improvements, some of chemical nature but mostly refinements in operating technic. The mechanical improvements were numerous at the start, requiring some special design and equipment. The trend, as is usual, was toward simplification and capacity increase, with attendant cost reduction.

The above assumptions or theories, as well as many others ascribed to flotation, have not been proved to the satisfaction of all, and are advanced as a reasonable working basis; consequently they are subject to change.

ECONOMICS OF THE PROCESS

Starting with a difficult and, as some said, a hopeless case, the research workers have succeeded in developing a commercial process whose working costs are among the lowest in flotation metallurgy. This is also true of plant construction costs. For instance, a sulfide flotation unit will ordinarily cost from $350 to $750 per ton daily capacity, whereas a phosphate unit will not exceed $60 and will operate, in Florida, for 13 to 16 cents per ton of feed, direct operating costs.

The effects on the economics of phosphates has been one of increasing importance. Heinrichs (4) stresses the benefits of flotation in increasing over-all washer recoveries and lowering costs. One of these (washer site A) is given as being of special interest:

Cubic yards matrix per hour	186
Tons phosphate pebble recovered per hour	19.2
Cubic yards matrix per ton of pebble	9.6

The tailing from the above washer was sent to a flotation plant which recovered 23.7 tons of concentrate per hour. The combined operation then is as follows:

Cubic yards matrix per hour	186
Total tons recovered per hour	42.9
Cubic yards matrix per ton recovered	4.3

Now using 7 cents per ton of matrix as the cost of mining:

9.6 cubic yards times 7 cents (washer only), cents	67.2
4.3 cubic yards times 7 cents (washer plus flotation), cents	30.1
Mining saving, cents	37.1

Then let us suppose, further, that in this case it is necessary to remove 8 cubic yards of overburden per ton of regular washer pebble or 3.59 cubic yards per ton of pebble and concentrate combined. Using a cost of 4 cents per cubic yard for overburden, we then have:

8 cubic yards times 4 cents (per ton washer product), cents	32
3.59 cubic yards times 4 cents (per ton total product), cents	14
Overburden saving per ton recovered, cents	18
Total saving in mining and overburden removal, 37.1 + 18 cents, cents	55.1

In Florida a phosphate washer will recover on an average only 10 to 25 per cent by weight of the matrix, the recovery being the +14-mesh fraction. In some of the so-called coarser deposits flotation will recover an additional amount equal to 40 to 50 per cent of the washer tonnage of equal or better grade. However this class of deposit is not now the most common, especially in the higher grades, so that the following remarks have special significance.

There remain large areas of impressive tonnage totals, where the washer recovery alone is very light—i. e., in one such area 500 to 1500 tons per acre, with 30 cubic yards of overburden and 12 cubic yards of matrix to be handled per

ton of phosphate recovered. With the washer supplemented by flotation, the total tonnage recoverable was increased to 4000 and 8000 tons per acre, thus making a practical mining proposition of an otherwise uneconomic undertaking. The yardage handled is correspondingly reduced to 6 to 7 cubic yards of overburden and 2 to 3 cubic yards of matrix per ton.

One property as prospected yielded 2000 tons per acre of 68 per cent B. P. L. plus 14-mesh washer fraction. Flotation recovered an additional 11,000 tons per acre of 74 per cent B. P. L. The whole matrix if treated by flotation would grade up to 74 per cent B. P. L.

When using a washer alone, there is a tendency to save the finer fractions where the silica grains cannot be effectively separated by screening or classification. This practice either degrades the entire washer output or results in an additional smaller tonnage of lower grade. The resulting tailing, in either case, represents an important loss that is recoverable by flotation at the higher grade.

For example, with a washer screening at 1 mm., the product may often run 72 per cent B. P. L., where with a coarser screen the grade may be raised to 74 or even 76 per cent. The same is true with other grades. Flotation allows the use of the larger screen openings while maintaining the maximum grade with a larger over-all recovery.

There are several possible combinations of flotation with the present washing systems in the Florida field. One involves the use of a semi-portable, low-head washer of the conventional flow sheet, followed by a thickener handling all the washer tailing. This rejects slimes and diminishes the volume which may be economically pumped to a central flotation plant. In this scheme the flotation unit may be placed in the middle of a 1000- to 1200-acre tract of phosphate territory which can be mined out with four moves of the washer. The total tonnage thus recovered by one float plant may range from 5 to 6 million tons or more. The total amortization of the flotation unit plus the cost of the washer moves is thus a fraction of a cent per ton of total output.

It will be seen from the above that Florida phosphate operations now involve the same closeness of mechanical and metallurgical control that has contributed so largely to the success and low costs of the sulfides and metallics in general.

In Tennessee the problems are somewhat different. There the washing practice is to save all the granular phosphate economically possible, and there is ordinarily no current washer tailing that is recoverable by flotation as in Florida.

The province of flotation in Tennessee is mainly to raise the grade of the washer output or fractions. For instance, the grade may be 68 to 70 per cent B. P. L., whereas the demand is for higher grades. Flotation will raise the grade on an average to 77 per cent B. P. L. or better, with a tailing that may be wasted or regulated to about 65 per cent B. P. L. which is used locally for the manufacture of phosphoric acid, or dried and ground for direct application to the soil.

The effect of flotation is to enable the Tennessee miner to exploit the lower grades as this now becomes necessary with the depletion of the higher grade reserves. For example, one washer operation had a remaining life of 5 years if confined to areas producing 72 per cent B. P. L. or better. By adding flotation and mining the lower grades, the life of the operation is being extended to 15 years.

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Oiling Earth Roads

Application of Surface Chemistry

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Factors affecting the qualities of oiled dirt roads are examined theoretically and experimentally, and new surface treatment methods for oiling jobs tried out on the experimental roads are described. In all cases it has been found that the addition of moisture and of surface-active substances, such as soaps, are able to improve the final road. However, it is necessary to consider the general properties, such as the clay content, organic matter, etc., of the soil to be treated.

A new method of making and applying road oil emulsions has been worked out, which promises to be of use in future road construction.

Modern surface chemistry has shown the great influence of the amount and character of surfaces and interfaces upon the mechanical and chemical stability of dispersed systems. Since most of our road courses represent systems with relatively large surfaces and interfaces, it seems promising to analyze road courses from the standpoint of surface chemistry. This has been done to a certain degree in types of courses ranging from sheet asphalt and asphaltic concrete to gravel and dirt surfaces. An attempt is made in this paper to apply surface chemical considerations to the successful oiling of low-cost dirt and gravel roads.

Each surface or interface represents a certain amount of free energy which is proportional to the amount of surface and a function of its physico-chemical character, expressed by the surface tension. In the case of liquid-liquid or liquid-gas interfaces the surface (or interfacial) tension, or the surface energy per unit surface, which is numerically the same, can easily be determined by experiment. The knowledge of surface and interfacial energies involved in any such system would make possible the calculation of the mechanical stability of the system as a function of its cohesional and adhesional forces. The surface energy data also permit the formation of conclusions as to the chemical or thermodynamical stability of the system—in the present case the resistance of the road towards weather influences.

Unfortunately, it is as yet impossible to obtain reliable data on the surface tension of solids against either air or liquids. Even if the necessary data could be obtained, the aforementioned calculations would have a practical value only in the case of higher type pavements, where purity and uni-

formity of the components of the pavement can be guaranteed. Such a guaranty is impossible in the case of low-cost oiled dirt and gravel roads. In these types of roads the earth phase with its large internal and external surface is subjected to all the different climatic influences which cause marked changes in the surface behavior. Although there is hope that

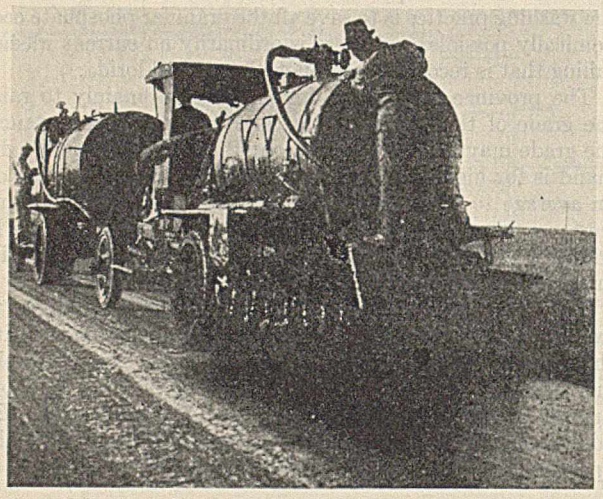

FIGURE 1. EMULSION-LIKE APPLICATION OF OIL AND SOAP SOLUTION

surface chemistry will finally lead to a quantitative evaluation of the stability factors in higher type asphaltic pavements, in the case of low-cost oiled roads it can provide only general principles to guide in experimental attempts to improve construction methods and final quality of this type of road.

According to the second principle of thermodynamics, the free energy in any system tends to decrease. Free surface energy can decrease by reduction of the amount of surface and by accumulation of substances in the surface, either combined or not with orientation. Consequently, in any system those interfaces will be most stable which possess the least amount of free energy, or, since affinity is measured by the decrease in free energy, those phases will tend to come in contact with each other that show the highest affinity toward each other.

The affinity of different road-building materials for water and for oil and asphalt is shown in Table I, from a paper of Nicholson (*1*).

Apparently there is not much promise of obtaining either an asphalt or an oiled dirt road that is absolutely stable against the influence of weather. Discouraging as this outlook is for an asphalt road, it is even worse for oil-dirt surfaces, since we are better able to prevent the entrance of water in an amount sufficient to endanger a well-constructed asphalt pavement. Is it then at all possible to have stable, oiled dirt roads? In drawing conclusions from Table I, however, a consideration of the composite nature of the different phases in the system was neglected. Both the soil and the oil contain an appreciable amount of various substances, dissolved and dispersed, some of which have the same general character and show the same behavior as soap molecules. This dual character is expressed by the following formula:

FIGURE 2. PRETREATED SECTIONS B AND C, IN BACKGROUND AND FOREGROUND, RESPECTIVELY

Marked difference in surface appearance is apparent.

$$\underset{\text{Inorganic character, affinity to water}}{NaOOC} \vdots \underset{\text{Organic character, affinity to oil}}{CH_2—CH_2—CH_2————CH_3}$$

On a dirt road, in the optimum condition for oiling (*2*), the soil particles are surrounded by water films. When the oil has been added, the soaplike molecules and micellae will be positively adsorbed at the water-oil interface and will orient themselves in such a way that the hydrophilic head is stretched toward the water and the inert hydrocarbon tail dissolved in the oil. By evaporation the water film gradually decreases in thickness, and finally the oil is linked directly with the soil particle by means of the oriented surface-active molecules and micellae in the oil-phase boundary. This oriented structure brings about the greatest resistance against water that can be attained with the materials employed.

TABLE I. AFFINITY OF MATERIALS FOR WATER AND FOR OIL AND ASPHALT

SUBSTANCES SHOWING GREATER AFFINITY TOWARD WATER THAN TOWARD ASPHALT	SUBSTANCES SHOWING GREATER AFFINITY TOWARD ASPHALT THAN TOWARD WATER
Silica (impure)	Pure limestone dust
Iron oxide	Hydrated lime
Aluminum oxide	Limestone rock asphalt powder
Gypsum or calcium sulfate	Calcined coal-mine waste, such as Haydite
Barytes	
Lithopone	
Impure limestone	
Light-calcined magnesia	
Certain kinds of slag	
Infusorial earth	
Common clay	

LABORATORY EXPERIMENTS

On the basis of these facts and considerations, the problem was investigated as to whether the amount of surface-active substances in road oil and soil is sufficient for the attainment of the above-described microstructure—the soil and oil only requiring the activating effect of water—or whether the introduction of more surface-active substances would improve the qualities of an oil-dirt road. For this purpose a large number of laboratory experiments was undertaken and in addition two experimental roads were built. The laboratory experiments were mostly concerned with the effect of soap on the resistance of a soil-oil system against the slaking action of water, and with the effect of soap on the cohesional properties of such a system.

For the investigation of the effect of oil and of oil plus soap upon the resistance of a soil system to the slaking action of water, and also for the tensile strength measurements, bricks of an ∞ shape were made with the mold used for preparing mortar test specimens for tensile strength determinations. The test samples were made by molding to the desired shape and drying:

(*a*) Moist field soil
(*b*) Dried pulverized soil with added water
(*c*) Moist field soil with oil
(*d*) Dried pulverized soil with oil
(*e*) Dried pulverized soil with oil and water
(*f*) Dried pulverized soil with oil and soap solution
(*g*) The moist field soil with oil and soap solution

All the samples were dried at room temperature to the same moisture content, then either suspended in water for the slaking experiment or tested for tensile strength in the mortar testing machine.

Besides the variations indicated by *a* to *g*, with many systems the amount of oil was also varied over an interval from 1 to 50 per cent of the dry soil. Soap was added in amounts from 2 to 10 per cent of the amount of applied oil. The addition of water to the soil was regulated to keep the soil mass a little over the lower plastic limit while working. The oil corresponded to Specifications 2 and 3 for Road Oil of the Missouri State Highway Commission, adopted July 7, 1933:

The oil for use in this work shall be nonvolatile asphaltic oil, shall be homogeneous, and shall conform to the following requirements:

The oil shall not foam when heated to 210° F.

Designation	No. 2[a]	No. 3[b]
Sp. gr. (60° F./60° F.) not less than	0.950	0.960
Furol viscosity at 122° F.	150–250	300–500
Flash point, ° F., not less than	194	194
Total bitumen sol. in CS_2, not less than	99.0	99.0
% volatilization (5 hr. at 325° F. 50 grams), not more than	12	10
% residue of 100, penetration, not less than	60	70
Ductility of residue at 77° F., in. (cm.), not less than	19.69 (50)	19.69 (50)
Temp. of application, ° F.	135–175	150–200

[a] No. 2 oil is for use on earth roads, first application for bituminous mat, and bituminous mat construction by the road-mix method prior to May 15 or after October 1.

[b] No. 3 oil is for bituminous mat construction by the road-mix method between May 15 and October 1, and by the plant-mix method prior to May 15 or after October 1.

As soaps, sodium-Ivory soap and potassium soap prepared from the same fatty acids as contained in the sodium soap were used.

Many hundreds of these test samples were made from a large number of different soils, ranging from light sandy soils to Wabash gumbo, with variations of organic matter as well as of the other constituents. The results of these tests which necessarily were qualitative in character are summarized as follows:

(1) There was not much difference between the slaking resistance and tensile strength of soil systems prepared according to methods *a* and *b* as long as the soils had a relatively low

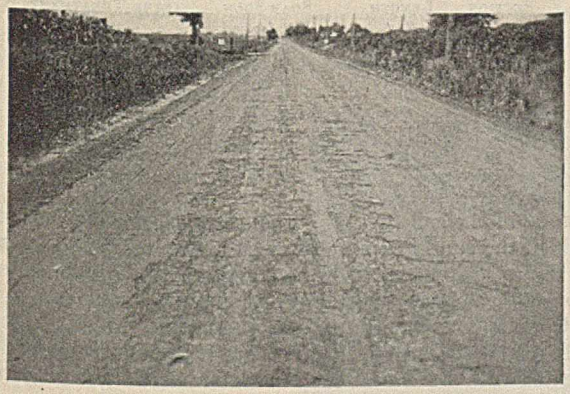

FIGURE 3. SECTION OILED WITHOUT PRETREATMENT

structural capacity. However, if the structural capacity was high, particularly owing to high content of organic matter, then in case of treatment *a* the breaking, in both tests, followed the structure of the secondary soil particles. The tensile strength was lowered and the samples decomposed under water into large units which showed appreciable resistance against further slaking. On the other hand, samples prepared according to method *b* disintegrated more slowly but to smaller units and showed greater tensile strength.

(2) With the same amount of oil, the tensile strength and the water resistance were lowest when the samples had been prepared from oil and dry soil only, somewhat higher when water had been added to the mix, and highest when soap solution was used. In the cases of moist field soils the structural influence was likely to decrease the protecting properties of the oil.

(3) In all cases in which the soils had a relatively low content of organic matter, soap showed beneficial effects. Sodium soap proved to be better with low colloid content of the soil, potassium soap with high colloid content of the soil.

In some cases where an oil-treated soil slaked down in less than a day's time, the sample of the same soil treated with soap in addition to the oil resisted the water for over a year. This high protective effect, in some cases, was obtained with the use of as little oil as 3 per cent of the weight of the dry soil along with 0.3 per cent soap.

(4) With increasing organic matter the soap influence became erratic. This was first attributed to the effect of sodium on the hydrophilic properties of the soil-exchange complex. However, since potassium soap had the same effect although the potassium ion usually decreases the hydrophilic properties of the exchange complex appreciably, the reason for this behavior undoubtedly must be sought in the dispersing and dissolving effect of alkali ions on the organic matter in the soil. Coagulation of this organic colloidal material with calcium chloride and subsequent treatment of the soil with oil and soap solution resulted in nonshrinking, water-resistant systems. A small addition of copper sulfate to these systems proved especially beneficial.

(5) Soap in all cases made the mixing of the soil and the oil easier, and provided a better and more even distribution of the oil throughout the soil system. To indicate the character of the experimental results obtained, data for four typical soils are given in Tables II to VI.

TABLE II. RESULTS ON FOUR REPRESENTATIVE TEST SOILS

Soil	1[a]	2[b]	3[c]	4[d]
Passing sieve No.	40	..	40	10
Low liquid limit	26.1	..	34.7	62.3
Lower plastic limit	22.0	..	25.5	27.3
Plastic index	4.1	..	9.2	35.0
Vol. change at field moisture equivalent	3.9	..	6.8	54.8
Shrinkage limit	20.9	..	23.0	10.8
Shrinkage ratio	1.7	..	1.6	2.0
Sand (diam. > 0.001969 in.)	67.0	60	29.0	5.0
Silt (diam. 0.001969–0.0001969 in.)	25.0	23	54.0	35.0
Clay (diam. 0.0001969–0.00003937 in.)	5.0	6	7.0	..
Colloids (diam. < 0.00003937 in.)	3.0	11	10.0	60.0
Field moisture equivalent	23.2	..	27.2	37.7
Vacuum moisture equivalent	17.8	..	23.4	42.2

[a] Very sandy soil with very low plastic index and very low volume change.
[b] Sandy soil with practically no volume change.
[c] Silty soil of low plastic index and low volume change.
[d] Clay soil of very high plastic index, extremely high volume change, and high content of organic matter.

TABLE III. DATA OBTAINED WITH SOILS 1, 2, AND 3[a]

Source of Specimens	Period for Disintegration in Water			Tensile Strength of Dried Specimen		
Soil:	1	2	3	1	2	3
				Lb. per sq. in.		
Moist field soil	1 min.	30 min.	30 min. (larger aggregates)	52	55	100
Dry soil and water	1 min.	30 min.	40 min. (small aggregates)	50	55	160
Moist field soil and oil	3 days	4 days	1 day (to large pieces)	41	40	40
Dry soil and oil	30 min.	20 min.	30 min.	..	..	...
Dry soil, oil, and water	3 days	4 days	4 days	40	40	80
Dry soil, oil, and soap soln.	More than 50 days	More than 50 days	More than 50 days	47	45	130
Moist field soil, oil, and soap soln.	More than 50 days	More than 50 days	More than 50 days	48	45	120

[a] The amount of oil and soap used was 5 and 0.5 per cent, respectively, per weight of dry soil. The data presented are for sodium soap, those for potassium soap are somewhat lower for tensile strength in case of soils 1 and 2, but identical with the sodium values for soil 3. In all cases the values obtained with potassium soap fall in the error range of the data obtained with sodium soap, which is about ±10 per cent. Soils 1 and 2 showed no volume change in the water-containing systems, soil 3 showed low shrinkage. Structural influence played a role with soil 3.

TABLE IV. INFLUENCE OF AMOUNT OF OIL ON TENSILE STRENGTH OF SPECIMENS PREPARED FROM SOIL 3 WITH WATER AND OIL AND WITH SOAP SOLUTION AND OIL

	Tensile Strength			
	After drying soil without soap		After drying soil with 0.5% soap	
Oil	Dried + H_2O	Moist field	Dried + H_2O	Moist field
%	Pounds per square inch			
3	98	..	..	..
5	80	40	130	120
10	63	..	85	..
20	15	..	28	..

TABLE V. EXPERIMENTS WITH CLAY SOIL 4[a]

Source of Specimens	Shrinkage in Drying	Behavior of Dried Specimens under Water	
		5% oil	10% oil
Moist field soil	Very high, breaks in shrinking because of structure	Disintegrates to larger units in 30 min., no further disintegration	
Dry soil and water	Very high, but no breaking	Disintegrates to fine particles in 60 min.	
Moist field soil and oil	High, breaks in shrinking because of structure	Disintegrates to large units in 60 min., no further disintegration	Disintegrates to large units in 100 min.
Dry soil and oil	None	Disintegrates after 15 min.	Disintegrates after 20 min.
Dry soil, oil, and water	High, no breaking	Breaks form in 60 min., no complete disintegration after 10 days	
Dry soil, oil, and soap soln.	Medium, no breaking	Slight breaks after 2 days, slow breaking to large units	
Moist field soil, oil, and soap soln.	Medium, some breaking	Breaks in 1 day to large units, no further decomposition.	

[a] Data obtained with potassium soap; use of sodium soap reduces water resistance for about 10 per cent; soil possesses high content of organic matter and high structural capacity.

TABLE VI. EFFECT OF CALCIUM CHLORIDE AND COPPER SULFATE ON SOIL–OIL SOAP SYSTEM

(Clay soil 4 with high content of organic matter; preparation method *f*; 10 per cent oil, 1 per cent potassium soap per weight of dry soil)

$CaCl_2$ %	$CuSO_4$ %	Shrinkage in Drying	Behavior of Dried Specimens under Water
0	0	Medium	Slight breaks develop after 2 days, slow breaking to large units
2	0	None	Slight breaks develop after 4 days with very slow breaking after 7 days
2	0.3	None	No breaks after 40-day submersion in water

ROAD EXPERIMENTS

For the further investigation of the stated problem, two experimental roads were built, one in May, 1932, the other in October, 1933.

FIRST ROAD EXPERIMENT. The road was part of a detour north of Cairo, Mo. The kind of soil along the road is as follows:

Section	A	B	D	G
Sand (0.03937–0.001969 in.), %	18	9	16	14
Silt (0.001969–0.0001969 in.), %	58	48	52	62
Clay (0.0001969–0.00003937 in.), %	9	20	19	14
Colloids (smaller than 0.00003937 in.), %	15	23	13	10

In consideration of the method used in making this mechanical analysis and the general character of the material as shown by the above figures, practical uniformity of the soil character can readily be assumed. The road surface before treatment was dry and crusted, and possessed many shrinkage cracks, especially in the middle part. An appreciable amount of loose material was on the shoulders. The road surface appeared uniform through the different sections. Special mention should be made of the rather high crown of this road which caused the accumulation of the oil along the road shoulders.

The materials used to treat the road were (1) sodium soap, 88 per cent content, yellow, neutral, from Swift and Company, Chicago, (2) road oil No. 2, Missouri State Highway Commission Specification, and (3) water (hard) from the city supply at Moberly, Mo.

The road was divided into sections A to H. A to D were pretreated with soap solution and oiled after drying, D to H were treated "emulsion-like." An untreated section was left between D and E. The method for the emulsion-like application (Figure 1) is as follows: Two distributing trucks, one filled with the road oil and the other with an aqueous solution of the emulsifying agent (in this case soap solution) were coupled together. Both liquids were spread through separate spray bars, attached to the rear distributor and directed to spray on the same spot of the road surface, thereby forming the desired emulsion at that point. The special advantage of this method is the possibility of controlling and varying the character of the emulsions to fit the requirement of particular soils or soil conditions without being concerned with the stability of the emulsion under conditions of storage or transportation. The emulsion was used as a primer; after its penetration into the soil, a second (oil) coat was applied.

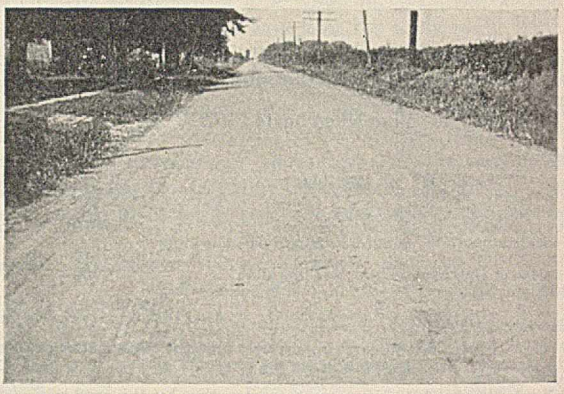

FIGURE 4. EMULSION-LIKE TREATED SECTION H

The following table shows the length of the different sections, the amount of applied material, and the final quality of the road surface:

Section	Length	Soap Soln.	Quality of Surface after Treatment
	Feet	Gal./sq. yd.	
A	1300	0.365	Good
B	825	0.420	Good
C	295	0.880	Poor
D	735	0.460	Good
E	800	0.420	Good
F	650	0.390	Good
G	725	0.310	Very good
H	425	0.590	Very good
Intersection		0.000	Fair

A total of one gallon of oil per square yard was applied about half in the emulsion-like priming (or first coat) and the rest in the final application. The condition of the different sections after 2 months is shown in Figures 2, 3, and 4.

CONCLUSIONS FROM FIRST EXPERIMENTAL ROAD. (1) the road sections which were pretreated or emulsion-like treated with 4 per cent soap in water solution ranging from 0.31 to 0.59 gallon per square yard showed surfaces superior to those of sections treated with oil alone. The emulsion-like treated sections were in the best condition.

(2) Section C which had been pretreated with 0.88 gallon of aqueous soap solution per square yard appeared worse than any of the untreated sections. The detrimental effect of the treatment was apparently due to the large amount of applied water, which penetrated deep enough into the soil to cause the original surface cracks to develop as the soil dried out. Consequently, the oil following these cracks left the surface without having an opportunity of mixing with the surface soil. Also, the changing of the surface properties of the soil colloids through the exchange of calcium and hydrogen ions for sodium ions undoubtedly had an enormous detrimental influence. This influence does not seem to be significant in the case of the emulsion-like treatment.

(3) Surface dust, one of the greatest obstacles to a good oiling job, improved the quality of the oil mat in all soap treatments.

CONCLUSIONS FROM SECOND EXPERIMENTAL ROAD. To avoid the eventual bad influences of the sodium ion on the properties of the soil colloids, potassium soap was used in the second oiling job, which was done in October, 1933, near Urich, Mo. Besides the general results which corresponded to those obtained on the first road, and of the many laboratory test samples, the following observations seem to deserve special mention:

(1) In spite of the cool weather at that time the oil-soap emulsion was so well absorbed by the soil that after 3 hours the distributors could travel over the road without picking up any material or rutting the road surface; on the other hand, the straight oil applications congealed and were not absorbed for several days.

(2) Besides this time-saving element, it seems to be advisable, especially in acid soils, to apply the second oil coat as soon as possible after the emulsion-like treatment because intervening rain and traffic may injure the treated surface, especially since some of the soap in the system may have kept its emulsifying properties. This danger can be practically eliminated by determining the amount of the soap to be used, based upon data covering exchange capacity and lime content of the soil. But even if there is an excess of soap, the immediate application of the second coat protects the system.

ACKNOWLEDGMENT

The author expresses his sincere appreciation to the officials of the Missouri State Highway Department for making this study possible, and to the members of the Department of Soils of the University of Missouri for their suggestions and criticisms during the progress of the investigation.

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Improved Casein Manufacture

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SKIMMED milk is the most important by-product of the dairy industry, and casein is the most important material manufactured from it. The process of casein recovery appears to be simplicity itself, but its lack of apparent complications is the stumbling block of most operators. Both acid additions and natural fermentation of skimmed milk are used commercially to coagulate the casein. (For detailed descriptions of the various methods of casein manufacture heretofore used, see literature citations *4*, *5*, *6*.)

It is so easy to allow milk to stand and sour or to add to it just enough acid to cause precipitation that the complexity of the material involved (a protein colloid) and the variations possible in the quality of the product (commercial casein) are often overlooked. The pronounced variations in the product of these simple operations simply carried out have caused almost endless trouble to the largest consumers of casein —the paper manufacturers —who use approximately 80 per cent of the total amount consumed annually in the United States, principally to glaze papers for the fine printing demanded by modern advertising. The next largest amount probably goes into glues. There are many other uses such as cold water paints, leather dressings and finishings, pastes, shoe polish, casein plastics, special food products, medicines, oil cloth, linoleum, soaps, etc.

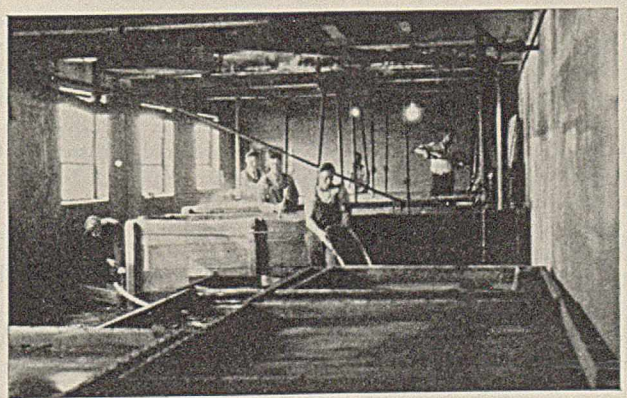


FIGURE 1. OLDER BATCH PROCESS OF ACIDIFICATION OF MILK FOR CASEIN MANUFACTURE
Much hand labor is required.

Casein, like many other products, is much less simple than its name indicates. As it occurs in milk it is made up of a variety of proteinous bodies in intimate mixture. The necessity for absolute uniformity in a material so widely used in such quantities is paramount. Therefore, the acidification of milk either by fermentation or the addition of acids must be conducted under rigidly exact conditions to attain that essential end. Most important of these is the control of acidity at precisely the proper point to secure exact precipitation. This point, most accurately measured by pH determinations, has been shown by experience to be practically unattainable by batch methods. A second essential is to conduct the precipitation in such a way as to minimize ash. A recently developed continuous process involving several unique features (*3*) permits proper control of all the elements in the precipitation and subsequent handling of the casein, and is producing a product which users have found sufficiently superior to the average market commodity to justify a premium price.

To understand the significance of the new, it will be valuable to review briefly the older processes and to summarize the important characteristics of casein itself from a physico-chemical point of view.

OLD PROCESSES

Milk normally is slightly acid (pH about 6.6) and is, from the point of view of casein production, a colloidal suspension of proteins and albumins in an aqueous solution of lactose and certain mineral salts. The simplest method of recovering the casein consists in fermenting the lactose to lactic acid by microörganisms naturally present. For this purpose the skimmed milk is run into large, relatively shallow, open vats and held at a temperature favoring fermentation (about 100° F. or 37° C.). When the acid intensity reaches a pH value of approximately 4.6, sufficient lactic acid will have developed to cause the formation of a desirable curd. This is

broken up, usually by hand-operated rakes or by heating, and allowed to settle. The whey is drawn off immediately and the curd washed two or three times with water. It is then pressed in hydraulic or hand presses to expel as much moisture as possible. The cakes of pressed curd are milled, spread on drying trays, and dried in tunnel driers. The final step in the process is the grinding of the dried casein to a fine powder.

This method is largely used in the Argentine and produces, strange as it may seem, a superior grade of casein. Its principal disadvantages are inherent in the fermentation process itself which consumes time and which yields a curd occluding various impurities held within the clots themselves. These impurities are difficult to remove economically or efficiently. Batch operation is also disadvantageous from an efficiency point of view.

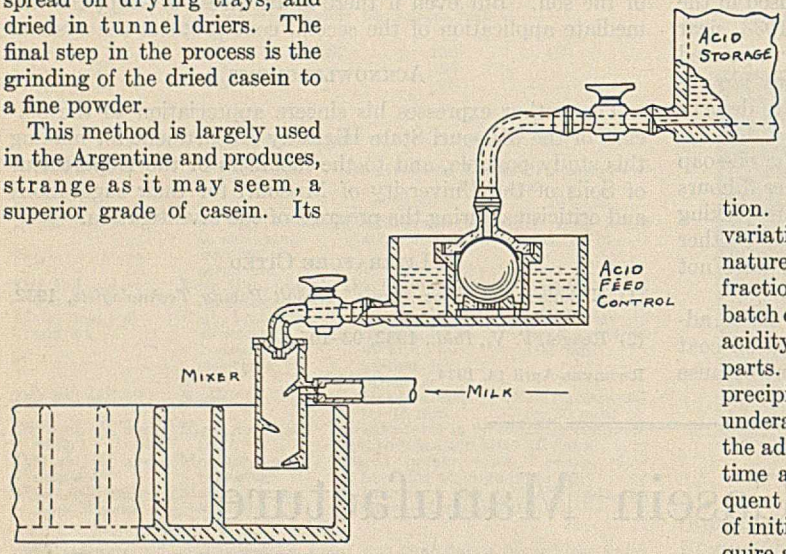


Figure 2. Acid Feed Regulator and Milk Acidifier

The second method is less tedious and more easily adapted to modern production methods. It consists of adding a diluted mineral acid (usually sulfuric but sometimes hydrochloric) to the skimmed milk in large shallow vats, mixing the whole carefully, precipitating the curd, and proceeding as described above. As practiced, all the operations in the process are carried out by hand as in the cruder fermentation process, and it possesses very much the same drawbacks as fermentation, with the exception of the time consumed. It has this further disadvantage which prevents complete uniformity of the product. In adding a relatively small amount of acid to a large volume of milk, there are always parts of the mix which are at one time or another more acid than others. Not only are there such points of higher acidity, but these are never exactly the same in extent or intensity in any two batches. Consequently, despite great care on the part of each operator, there will be precipitated in each batch of his product some casein containing "foreign" proteins in varying amounts. This lack of uniformity of output and the large amount of hand labor involved in the process has always placed the product of this method of acidification at a disadvantage on the market. Nevertheless, this process is largely used in the United States and accounts to a great extent for the low opinion users ordinarily hold of domestic casein.

Regardless of the particular process used, all batch methods present certain serious difficulties. However, many improvements have been made in the various batch methods in recent years. The most important among these is the so-called grain-curd process developed by the Bureau of Dairy Industry of the U. S. Department of Agriculture. If a batch method is to be used, the grain-curd process should be the one selected.

Sulfuric acid, although frequently used, is inferior to hydrochloric because of the lower solubility of its calcium salt and the consequent difficulty in producing a low ash precipitate.

Physico-Chemical Properties of Casein

Casein, in addition to being one of the purest, belongs to the most complex group of proteins, the phospho-proteins. It contains carbon, oxygen, nitrogen, hydrogen, phosphorus, and sulfur. In milk it exists as a colloidal suspension combined in different proportions with small amounts of calcium. The several other constituents of milk further complicate the situation. In coagulating such a mixture, it is obvious that variations in acidity produce variations in the exact nature of the mixture precipitated. Thus, even a small fraction of one per cent of acid cannot be added to the batch of milk carefully enough to prevent momentary overacidity in part of the mixture and underacidity in other parts. Under these circumstances the overacid portion will precipitate every proteinous compound present and the underacid part will be incompletely coagulated. Because the added acid is not only neutralized but is at the same time absorbed and adsorbed by the precipitate, subsequent thorough mixing will not entirely correct the fault of initial inhomogeneity. Complete precipitation will require an overdose of acid, and the final product will contain a mixture of proteins which cannot be duplicated accurately except by chance in the making of later batches.

The precipitated curd, holding within itself more or less acid, is washed and later pressed to remove as much moisture as possible. The washing operation, like the precipitation, is liable to leave unequal acidity in the pressed curd. During the pressing operation, as well as in the subsequent drying of the mass, this residual acid hydrolyzes the casein to a greater or less extent depending on its concentration at various points in the mass. The heating required during the drying operation emphasizes rather than minimizes these differences in acid concentration so that the finished casein from the final grinding retains the characteristics produced in it during these steps in its manufacture.

Obviously this simple series of steps cannot be made to yield a material of rigidly uniform properties as required by the paper industry which must produce, practically by the square mile, paper whose printing characteristics are perfectly uniform. To overcome these disadvantages, the process has been reduced to a continuous operation in which each step is accomplished by an unerring machine. The accomplishment of this end has involved chemical engineering skill and ingenuity of a very high order.

New Process

The major credit for the development and improvement of this new continuous process should be given to F. L. Chappell of Hobart, N. Y., dean of America's casein manufacturers.

Since control of acidity is the prime factor in the success of the process, the acid-mixing chamber is the heart of the plant. Even though the unit itself is small, its proper functioning is fundamental to the entire operation (Figure 2). The small stoneware cylinder contains baffles to secure practically instantaneous mixing of the ribbon-like streams of milk and acid which meet within it. In this way the actual acidification of any particular small volume of milk occurs in a small fraction of a second, and the baffle arrangement secures completely uniform mixing of the two streams. No part of the milk stream is even for an instant in contact with more acid than is required to bring its pH to the desired point.

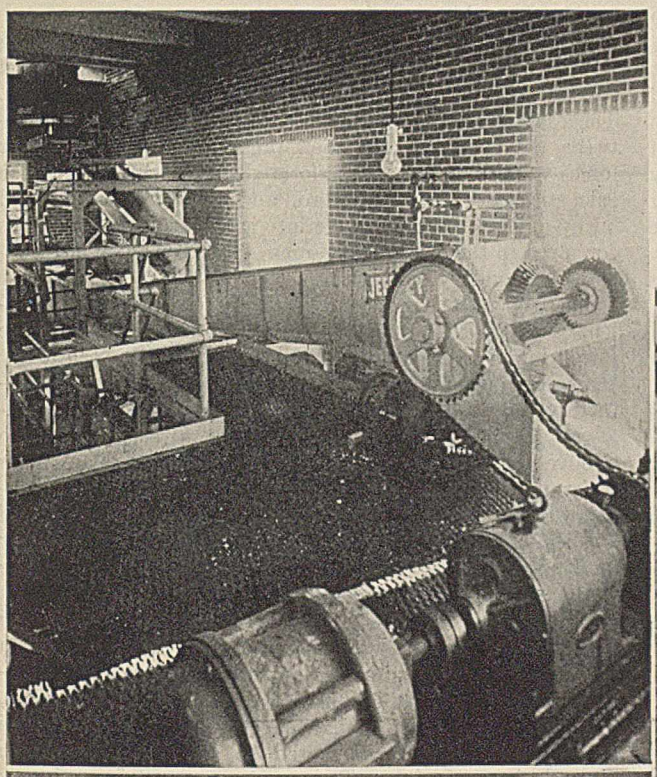
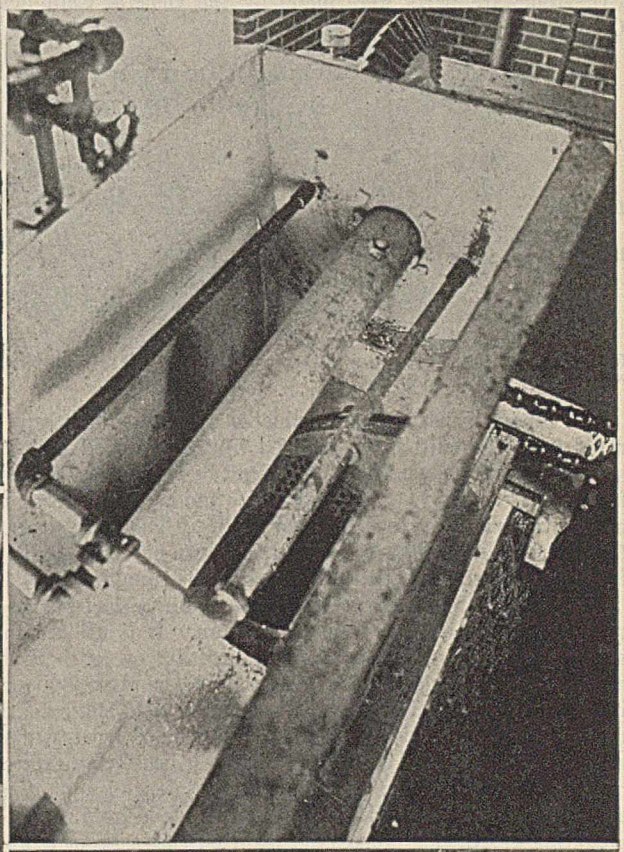


FIGURE 3. (LEFT). SCREW CONVEYOR FOR SEPARATING WHEY FROM CURD

FIGURE 4. (BELOW). DISINTEGRATOR FOR BREAKING UP CURD (FROM WHEY SEPARATOR) BEFORE WASHING



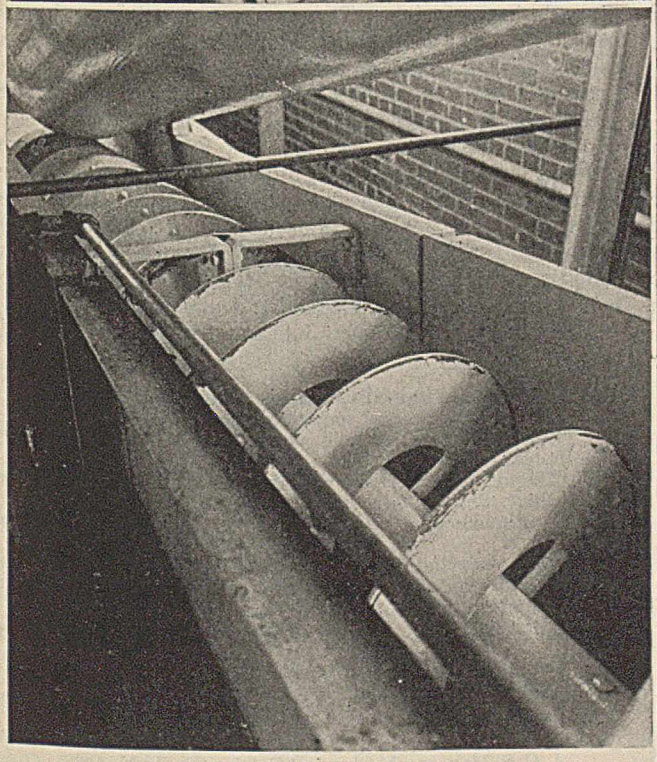


FIGURE 5. (ABOVE). INCLINED SCREW CONVEYOR FOR CONTINUOUS WASHING OF CASEIN CURD

The curd moves upward against a descending stream of water.

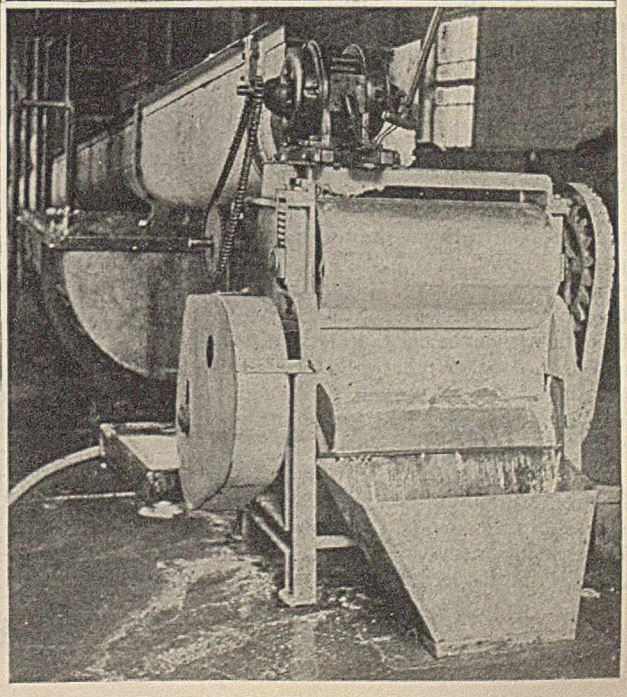


FIGURE 6. (RIGHT). CONTINUOUS CASEIN-DEWATERING PRESS

The upper chromium-plated roll presses the curd against the lower perforated roll to remove moisture before drying.

Hydrochloric acid (specific gravity 1.20) diluted with four times its volume of water and skimmed milk preheated to 110° F. (43.5° C.) meet in the mixer.

Complete precipitation of the casein requires a somewhat longer time than the mere mixing operation, so the acidified skimmed milk, after leaving the mixing chamber, runs through a subsequent series of baffles which continue the agitation of the mixture for a few seconds until the curd has partially separated from the whey. This subsequent mixing chamber is an open stoneware tray provided with baffles to force the mixture to travel back and forth on its way to the washers. (All stoneware parts were made by the General Ceramics Company.)

TABLE I. ANALYSES OF CASEIN FROM DIFFERENT SOURCES

SOURCE	ASH	ACID[a]	pH	SOLUBILITY IN BORAX
	%	*Cc.*		*% of borax*
Argentina	2.02	8.2	4.26	16
Sulfuric	1.60	7.8	3.46	18
	3.35	7.2	4.70	12
	4.75	13.0	4.55	18
Lactic	2.77	19.6	3.80	22
	2.47	11.	4.22	16
	2.48	10.4	4.22	18
Hydrochloric:				
Batch process	2.76	10.6	3.68	22.5
Grain-curd process	2.78	8.90	4.5	15
New process	1.08	0.2	4.80	8
	1.60	1.6	4.67	12

[a] Amount of 0.1 *N* sodium hydroxide required to neutralize 50 cc. of the filtrate secured from a mixture of 10 grams of casein and 100 cc. of distilled water.

The whey, which contains valuable constituents, is separated from the curd in an inclined trough provided with a screw conveyor shown in Figure 3 (built by the Jeffrey Manufacturing Company). The curd settles and is carried upward out of the whey by the conveyor flights. The clear whey, from which the curd has separated, is drawn off continuously from near the surface at the lower end of the trough.

This whey from the precipitation contains lactose, inorganic salts, and some residual albumin. It is utilized in several ways. It may be evaporated direct to powder to yield a valuable feed for poultry and stock; it may be worked up for its lactose content; it may be fermented to yield lactic acid; or, as has been recently proposed, its albuminous constituents may be separated and used. Since there is usually an excess of whey, the particular use to which it is put depends upon the existing demand for products that can be made from it.

During the settling process the warm curd has a strong tendency to cohere into large clots. After these are drained to free them substantially from whey in the latter part of their upward progress, they are dropped into a disintegrator or beater. This disintegrator (Figure 4) consists of a perforated metal cylinder in which revolves a shaft provided with arms that break the clots into small pieces under streams of cold water.

The disintegrated curd is washed through the perforated metal screen into an upward-inclined washing trough, and pushed against gravity and a stream of cold wash water by a second screw conveyor (Figure 5). This washer is similar to the whey separator except that large quantities of water wash the whey from the curd. The curd is delivered at the upper end of the washer practically free from water-soluble impurities. This slow, thorough, continuous washing yields casein in relatively small pieces containing very little excess acid or ash.

The discharge from the washer delivers curd to a continuous automatic press of unique design which presses adherent water out of the mass and leaves it with about a 50 per cent moisture content. Moisture is removed continuously in this recently developed pressing operation, and in addition the large, hard-pressed cake resulting from batch pressing is avoided.

The press (Figure 6) consists of a hopper with an oscillating wall feeding casein between two rollers, one of which is solid and chromium plated and the other is perforated bronze. The oscillating side of the feed hopper forces the curd between the two rolls, and their pressure against each other forces water through the perforated roll to the drain. The cake sticks to the perforated roll and is continuously scraped off by a wooden scraper knife into a hopper from which it is conveyed to the drier. (The press was built by Ireland Machine & Foundry Company.)

These operations provide a relatively porous mass of flocculent casein which is low in acid and ash and in excellent shape for drying in any convenient way. Practice has been to dry the casein on trays in a tunnel drier, but other more satisfactory and quicker methods have been developed. The disadvantages of the tray drier are obvious. Casein, pressed to remove moisture, is in more or less coherent pieces and tends to form a skin on the surface when heated which holds moisture within the piece. Since it is also difficult to remove acid and ash uniformly from the casein produced by the older methods, hydrolysis takes place with the consequent damage to the product as its temperature is raised.

Improved driers (*1*) evaporate the residual moisture from finely divided casein by picking up the particles in a stream of dehydrated heated air. Because these particles are relatively small and quickly dried by the action of the air current, hydrolysis and other similar effects are minimized. The most successful driers are based on an adaptation of the spray-drying principle. The casein from the continuous press, in a fairly fine state of subdivision, is picked up by a rapidly moving stream of hot dry air and carried through a series of flues. These flues have sections of large diameter placed at intervals during their course where the velocity of the air stream is so reduced that heavier particles are dropped out and removed for further disintegration before return to the system. The finer particles are carried on by the air stream. The final dried dust (5 to 7 per cent moisture) is removed from the moist air by a turboclone blower which supplies suction to the system. It is then ground to the requisite fineness to meet the market demands.

The principal advantages inherent in the new method are:

1. Uniform and immediate mixing of milk and acid.
2. Uniform and prompt separation of curd from whey.
3. Use of hydrochloric acid which yields easily soluble salts with inorganic ash constituents.
4. Thorough and uniform washing of soluble impurities from the casein.
5. Continuous pressing which prevents the formation of large aggregates.
6. Prompt drying of small pieces of curd to prevent surface skinning that would hold moisture and acid in the particles and promote hydrolysis.
7. A finished casein superior to that made by other methods.

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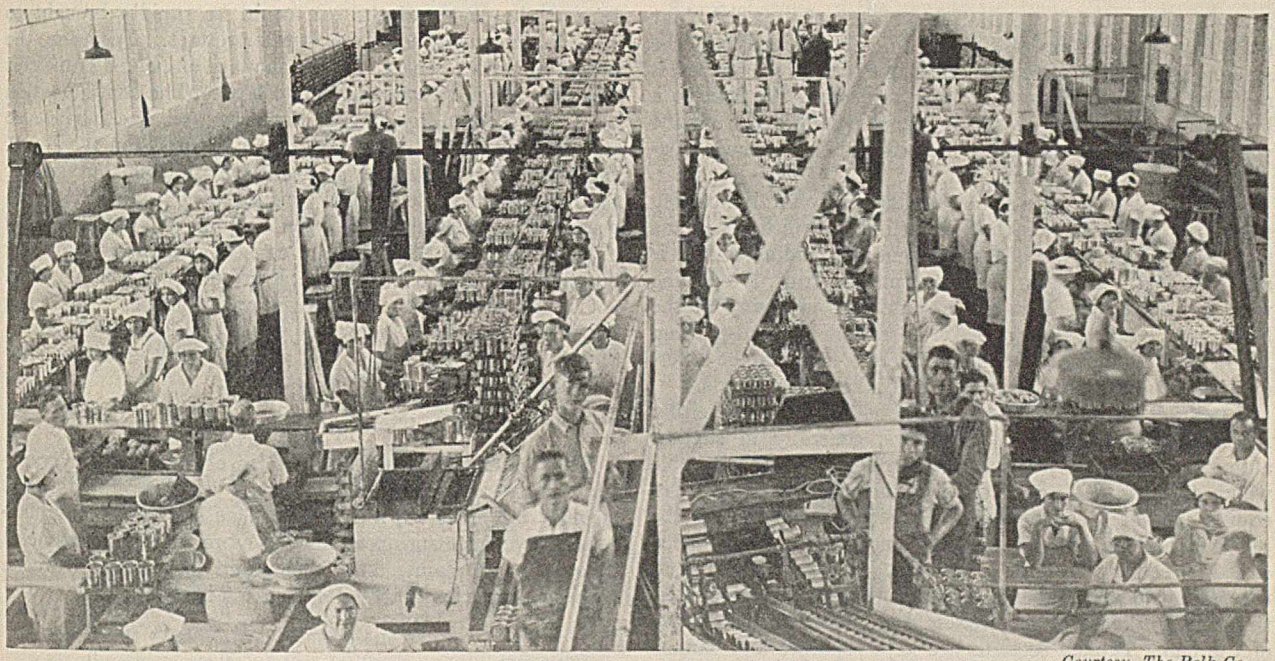

Courtesy, The Polk Co.

FILLING ROOM OF GRAPEFRUIT CANNERY

The Canning of Grapefruit and Grapefruit Juice

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APPROXIMATELY 90 per cent of the canned grapefruit produced in the United States proper (excluding Porto Rico) is packed in Florida. Porto Rico, where the canning of this product was first started, ranks next to Florida in point of production. Small quantities are also canned in Texas and Arizona. Grapefruit was first canned commercially in Florida in 1919 or 1920. The output in that state has increased from 10,000 cases of 24 No. 2 cans each in the 1921–22 season to an average of over 1,700,000 cases for the last four canning seasons. In addition, a considerable quantity is canned in the form of grapefruit juice. During these four years the canning industry in Florida has used an average of around 15 per cent of the total production.

CANNING OF GRAPEFRUIT

The largest market for canned grapefruit is in the United States, although increasing quantities are being exported; the largest foreign market is the British Isles with Canada ranking next. Practically no grapefruit is canned outside of the United States and its possessions so that the theoretical foreign market is large although actually somewhat limited because grapefruit, either fresh or canned, is practically unknown in most foreign countries.

The canning of this product in Florida generally starts in December, the time varying somewhat depending on the date of maturity of the fruit, and continues through April and sometimes later.

The two classes of grapefruit most commonly used for canning are tree-ripened and packing-house fruit. The former consists of fruit which has matured before being picked; the latter of fruit which has been picked for shipment as fresh fruit but which the packing houses, on account of market conditions, overripeness for shipping, blemishes on the skin, or irregularity in shape, have not been able to use. A small portion of the canned product is also produced from orchard "drops."

Grapefruit for canning purposes must conform with the United States standards; the juice must contain not less than seven parts of soluble solids to each part of acid calculated as citric. Well-matured grapefruit produces a product of better flavor than the less mature fruit, the percentage of naringin (the bitter principle of the fruit) is less, the sections do not break so easily, and the addition of less sugar is necessary to secure the desired sweetness.

PREPARATION OF FRUIT. In order to obtain uniformity in the sizes of the sections of fruit in each can, the fruit is graded for size previous to canning. The sizes generally used for packing in No. 2 cans are 54, 64, and 70 (referring to the number of fruit per shipping box), sections of fruit of different sizes being packed separately. For smaller sizes of cans, the smaller sizes of grapefruit may be used.

After grading to size, the fruit may be handled in one of two different ways, depending on whether it is to be hand-peeled or lye-peeled. In the latter case the fruit is carried mechanically through water at a temperature near boiling, remaining in the water only long enough to loosen the outside yellow peel, which, after scoring, is readily peeled off by hand. The fruit with the adhering white membrane is then placed in small woven-wire baskets, which are conveyed through a boiling, weak (1.5 to 2 per cent) lye solution, and is subjected to the action of the solution for 10 to 15 seconds. The trays of fruit are then exposed to copious sprays of water which thoroughly remove the lye and also the loosened white membrane which is only partially dissolved. The sections of

fruit are then carefully separated by means of a special blunt knife from the membrane between the sections and from the seeds. In the hand-peeling method, the outside yellow peel is removed with a knife without first subjecting the fruit to a hot water treatment. By means of a sharp knife, the outside white membrane is carefully removed and the sections separated as in the previous method.

The yield is generally somewhat higher by the lye-peeling method owing to the fact that, in peeling the white membrane from the fruit by means of a knife, some of the adjacent flesh is also removed. However, with overmature fruit, lye-peeling may give lower yields and it is sometimes necessary at the latter part of the canning season to change to hand-peeling. As far as the quality is concerned, there is no apparent difference between the product obtained by the two methods.

Canning Operation. The sections prepared by either method are collected in thin layers, generally in shallow aluminum trays, which are transferred to the filling table where the sections are filled into the cans by hand. No equipment has been devised which will satisfactorily fill the product mechanically. Careful placing of the sections in the cans is necessary in order to secure a fancy canned product, the sections generally being placed so that, as far as possible, the convex surface of the section is in contact with the side of the can. Broken sections are kept separate and canned as such or, in some instances, manufactured into grapefruit juice. The total filled-in weight of fruit per No. 2 can is approximately 17 ounces.

Sufficient sirup or dry sugar and water is then added to fill the interstices between the sections, or sometimes sirup is added before the fruit is filled into the can. The amount of dry sugar added either as such or in the form of sirup varies from 1.6 to 2.0 ounces per No. 2 can or enough to give a Brix hydrometer reading of 16 to 18 in the "cut-out" sirup after equilibrium has been reached between the fruit and the added sirup.

The cans, after being filled, may be handled by either of the two following methods; both have for their purpose the securing of a partial vacuum in the closed can:

(1) The exhaust method in which the cans unclosed, or in some instances with covers loosely crimped on the cans, are passed on a mechanical conveyor through a water bath maintained by means of temperature controllers at approximately 180° F., the total time in the bath being 25 to 30 minutes for No. 2 cans, and the covers are then double-seamed on the cans.

(2) The more recently developed vacuum-closing method in which the unheated cans are closed by means of a vacuum closing machine under a vacuum of 22 to 25 inches.

In either case the closed cans pass directly from the closing machine on to a conveyor which carries them through the sterilizing bath. It has been found advisable on account of the effect on the flavor and texture to sterilize grapefruit at lower temperature (180° to 190° F.) than other canned fruits which are generally sterilized in boiling water. Since, in the exhaust method, the contents of the cans have been subjected to heat treatment before entering the sterilizing bath, the sterilization treatment need not be so severe as in the vacuum closure method.

In the former method, the cans are conveyed through a water bath held at approximately 180° F., requiring for No. 2 cans 25 to 30 minutes to pass through the bath. Where the vacuum closing method is used, the time necessary in the bath which is usually held at 190° F. is approximately 30 minutes or approximately 40 minutes at 180° F.

In either case it has been found that the heat treatment should be sufficient to give a minimum temperature of 165° F. at the center of the can. Attainment of this temperature is not in itself sufficient to sterilize the product, as the time factor also must be considered. That is, if the temperature at the center of the can could be rapidly brought to 165° F., this might not give a sterile product. Yeasts are the organisms which generally cause spoilage of canned grapefruit and they are not very resistant to heat. The contamination with yeast organisms during handling and packing is also generally quite low. For cans larger in size than the No. 2, the time for sterilization is necessarily longer, but similar temperatures are used. The cans are cooled immediately in water after processing, and the cooling is continued until only enough heat is left in the cans to evaporate the water remaining on the surface, which, if present, will cause rusting.

Canned grapefruit becomes somewhat firmer after being left in the cans for a short time so that, as a rule, shipments of the product are not made until at least 2 weeks after canning.

Type of Can Used

Plain (unenameled inside) cans are always used for grapefruit. Experiments have been made with several different enamels but none, so far, has been as satisfactory as plain cans. Hydrogen springers develop more rapidly in enameled cans than in plain. The percentage loss from hydrogen springers at various dates after packing is as follows:

	9 Months	12 Months	18 Months
Plain cans	0	0	0
Enameled cans	6	17	32

The above data cover one experiment with cans made of the same quality of tin plate and packed under the same conditions. These cans were stored at lower temperatures than prevail in Florida, and greater losses would naturally occur at higher storage temperatures. In addition to losses from hydrogen springers, the fruit in enameled cans becomes yellower than in plain cans. Canned grapefruit when stored at ordinary temperatures gradually becomes slightly yellow. When packed in plain cans, the reducing action of tin has a bleaching effect which retards color changes. In the enameled can, the color change, therefore, is more rapid. In addition, grapefruit packed in enameled cans has a slightly different and less agreeable flavor than that in plain cans; this difference in flavor is apparently connected with changes which are retarded or prevented by direct contact with tin. The change in color of grapefruit in plain cans, together with the toughening which accompanies it, is retarded by low storage temperatures. When stored for 3 years at 33° F., the color, flavor, and texture were not appreciably different from those observed directly after canning. Canned grapefruit from the same lot held at room temperature storage for the same length of time showed such decided changes that it could not be considered merchantable. Storage at low temperature for extended periods of time, however, is too expensive to be profitable. In one lot of canned grapefruit held at 33° F., there was an abundant crystallization of naringin. Such crystals have been noted by Fellers (*3*) under commercial conditions.

The development of hydrogen springers, although not so common as with some other canned fruits, is one of the difficulties encountered by grapefruit canners. As has been shown by Kohman (*6*), Bohart (*1*), and others, the storage temperature of the canned product, the vacuum obtained in the cans when packed, and the amount of head space in the cans are factors affecting the rate of development of hydrogen springers. The lower the storage temperature, the greater (within the limits of commercial practice) the head space in the can; and the higher the partial vacuum, the less the difficulty with hydrogen springers.

A comparison of heat exhaust with vacuum closing in their relation to the development of hydrogen springers at various dates after packing is given (in percentage loss):

	12 Months	18 Months	24 Months
Hot-water exhaust of 28 min. at 184° F.	2	35	42
Hot-water exhaust of 53 min. at 184° F.	0	5	9
Closed under 23-in. vacuum	0	9	17

The vitamin content of canned grapefruit as affected by the various methods used in commercial canning—that is, lye-peeling *vs.* hand-peeling and heat exhaust *vs.* mechanical exhaust (vacuum closing)—has been investigated by Eddy, Gurin, and Kohman (*2*). They found no apparent variation in vitamin content due to the various methods of canning or no particular difference between the vitamin content of canned grapefruit and raw grapefruit.

There is a large amount of waste in the canning of grapefruit. According to Street (*8*), about 1 pound of fruit for canning is obtained from each 3 pounds of fresh product purchased. This waste consists of the outside yellow peel, the interior white membrane, and the seeds.

The Florida Agricultural Experiment Station (*5*) has shown that the dried waste has some value as a stock food. Some waste is mixed with calcium cyanamide and peat for use as fertilizer, the acid of the waste assisting in the change of the cyanamide to urea. It may be utilized also as a source of pectin, but owing to the cheapness of other raw products as a source of this material, grapefruit waste has not been used on a commercial scale for this purpose. Some yellow peel is used in the manufacture of candied grapefruit peel. No particular use has been found for the volatile oil of the peel. Certain medicinal properties, for which there is no definite proof, have been ascribed to naringin, the glucoside of the fruit which occurs abundantly in the waste. Possible utilization of the waste is complicated by the fact that the volume at any one cannery is relatively not great, and it would be expensive to collect it from several widely distributed canneries.

Grapefruit juice has a decided corrosive effect on metals. Aluminum trays have been used for years for handling grapefruit sections and have given satisfactory results. Monel metal is employed particularly for equipment for grapefruit juice. Chrome-nickel steel is also coming into use for trays and for equipment with which grapefruit sections or grapefruit juice may come in contact.

The quality of canned grapefruit depends on the character of the raw product used and the care used in packing it. In the standards established for canned grapefruit by the Bureau of Agricultural Economics of the United States Department of Agriculture, sixty-five points of the total possible score depend to a large extent on the character (flavor, texture, etc.) of the raw product used and thirty-five on the packing operations.

Canning of Grapefruit Juice

Grapefruit juice consists of the juice of the fruit together with some suspended pulp. Because the unsweetened juice is too sour for the average consumer, most of the commercial product is slightly sweetened by the addition of dry sugar or of sugar sirup. In the latter case the government food authorities have ruled that the sirup added must contain at least 65 per cent of sugar in order that dilution with excessive quantities of water may be avoided.

The manufacture of grapefruit juice affords an outlet for good-quality fruit of small size and of fruit such as is used for canned grapefruit which does not command a ready market as whole fruit.

The juice may be extracted by reaming or burring the cut halves, or by pressing the cut halves individually; in some instances it may be prepared from broken sections of fruit produced during the preparation for canning. In extracting the juice, it is desirable to use methods which will reduce to a minimum the amount of volatile oil removed from the peel. The presence of such oil in the juice causes undesirable flavor changes in the canned product. The burring equipment used has revolving corrugated cones of the same type as that used at soda fountains. With the other type of extraction equipment, each half of the fruit is carried mechanically on to a stationary cone and the juice extracted by pressure alone.

After the juice has been extracted from the split halves of the fruit, it is passed through a fine-mesh screen of some kind to remove seeds and large pieces of pulp. The equipment most commonly used for this purpose consists of a thin metal cylinder or cone made of monel metal or stainless steel, and having small perforations. This cylinder has a revolving beater inside. The extracted juice is fed into this equipment which not only removes seeds and coarse fiber but also breaks up the pulp into fine particles so that there is less tendency for it to separate in the can. When broken sections of fruit are used, the juice is extracted by passing them through a cylindrical screen of the same type referred to above.

The juice is collected in suitable tanks where dry sugar or sugar sirup of 65° Brix is added in sufficient quantity to give a Brix reading of 14 to 16. From this point, the juice may be handled in any one of the following ways:

(1) It may be heated in the tank to a temperature of 160° to 180° F. and filled into cans, and the cans closed and pasteurized.
(2) The juice may be filled into the cans cold, and the cans passed through a hot-water exhaust box, closed, and pasteurized.
(3) The juice may be filled into the cans cold, and the cans closed on a vacuum closing machine and then pasteurized.
(4) The cold juice may be subjected to flash-pasteurization by some such equipment as that referred to by Mottern and von Loesecke (*7*).

The latter method is not being used commercially to any extent although it subjects the juice to less heat treatment than any other method. Excess head space in the cans results in abnormal corrosion of the container and objectionable changes in the flavor of the product. For this reason the cans are filled as full as possible with juice at the time of closing. The heat treatment used after closing the cans naturally depends on the previous treatment used but should, in any case, be sufficient to bring the center of the can to a temperature of at least 170° F. Whatever heat treatment is used, it should be followed by prompt and thorough cooling of the cans after the heat treatment is completed.

There is no definite information available in the literature as to the effect on flavor and vitamin content of various methods of canning grapefruit juice with respect to their efficiency in removing air from the product and from the head space of the can. Fellers (*4*) reports that vitamin C was well preserved in canned juice which had been prepared according to method 2 given above. However, the vitamin C content of the original juice was not known.

There are no government or trade standards for canned grapefruit juice and there is no agreement as to what method of preparation and canning gives the best product. It is generally considered, however, that the prompt canning of the juice after extraction is essential to secure a satisfactory product.

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Prospects of a Petroleum Chemical Industry

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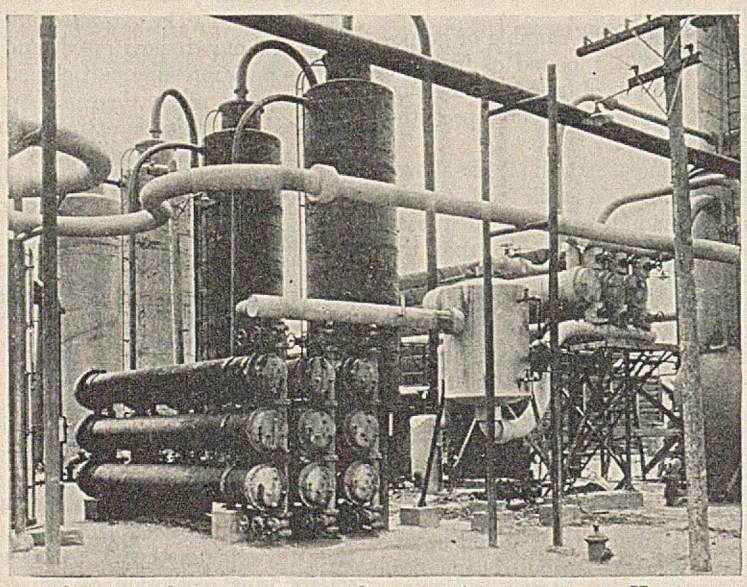
Expanding knowledge of the chemistry of petroleum and efforts to utilize this almost unlimited natural resource more completely have made available a large number of new chemicals and products. The prospects of an even more extensive chemical industry from this source are discussed.

THE purpose of this paper is not to enumerate all the chemical possibilities through the conversion of petroleum material, since the number of these proposals is legion. However, it is clear that the real developments involving various chemical engineering problems have fallen to the gases from petroleum, rather than to the liquid and high-boiling constituents. One reason for this is that the gases afford a means of extracting concentrates or even pure hydrocarbons such as methane, ethane, propane, butane, ethylene, propylene, butylene, etc. For making useful products, such concentrates are better adapted than difficultly separable mixtures of higher hydrocarbons of undetermined constitution.



GASOLINE STRIPPING PLANT, SHOWING ABSORBERS AND HEAT EXCHANGERS

Crude petroleum consists essentially of a mixture of hydrocarbons of varying degrees of molecular complexity. In addition there are present smaller proportions of compounds of oxygen, nitrogen, and sulfur, together with mechanically held gas, water, or clay and other inorganic substances, either in solution or colloidal suspension. The hydrocarbons may range from the simplest to those having molecular weights greater than 1000, and include not only paraffins and cycloparaffins (naphthenes) but also aromatics and polynuclear aromatics and cycloparaffins. The occurrence of unsaturated hydrocarbons, prior to distillation, has been the subject of much controversy. If such hydrocarbons are present in crude petroleum, the proportion must be exceedingly small.

It has been calculated that a hydrocarbon represented by the comparatively low number of 20 carbon atoms has 366,319 possible isomers (or 3,395,964, if stereoisomers are included) (*75*). The difficulties involved in separating such a complex mixture as petroleum are evidently very great. Although many individual hydrocarbons have been isolated by laborious fractional distillation and crystallization methods from petroleum fractions, particularly natural-gas gasoline and both straight-run and cracked gasolines, the gaseous hydrocarbons are the only compounds readily separated. Also, some of the gaseous hydrocarbons are often more reactive than their higher boiling analogs. At the present time, therefore, these gaseous fractions are the more promising crude materials for chemical conversion.

The first real chemical industry founded on petroleum was probably the production of alcohols by reaction of the olefins of cracking gas with sulfuric acid.

CRACKING GAS

Industrial cracking processes are, for the most part, concerned with the conversion of high-boiling distillates into low-boiling liquids of the gasoline type. The utilization of the large quantity of lower hydrocarbon by-products (cracking gas) from this procedure is already exerting a tremendous influence on the development of industrial organic syntheses. It has been estimated that the volume of this gas is of the order of 250 billion cubic feet annually (*51*).

The composition of cracking gas is dependent chiefly upon the temperature of cracking. The so-called liquid-phase operations [employing temperatures below 500° C. (932° F.) and pressures up to 1000 pounds per square inch] yield a gas containing a fairly large proportion of paraffin hydrocarbons together with a relatively small content of olefins. Of the latter, propylene is apparently the predominating unsaturated hydrocarbon. Vapor-phase processes (operating at higher temperatures and at lower or atmospheric pressures) give a cracking gas having a large proportion of ethylene in addition to propylene and other olefins. Diolefins, particularly butadiene, are also present in appreciable quantities (one per cent or more).

Prior to its utilization, cracking gas may be subjected to compression and absorption operations, thereby dividing it into at least two main fractions: (*a*) gaseous olefins, consisting of ethylene, propylene, and butylenes, and (*b*) liquid olefins, consisting of amylenes, hexylenes, and higher olefins. Further separation of these two main fractions is, of course, possible.

Gaseous and low-boiling hydrocarbons may also be obtained from cracked distillates. Cracked naphtha—e. g., containing fixed gases soluble at the temperature and pressure of the condensing equipment on the cracking coils—is fed to a tower which is called a "debutanizer." About 30 per cent of the most volatile components are taken overhead in this tower, and substantially all are condensed. This volatile overhead cut is then fed to a second tower which is called a "stabilizer." Here a sharp fractionation is made between propane and lighter hydrocarbons, and butane and less volatile hydrocarbons (*120*).

The analysis of the overhead gas and residue (bottoms)

from pressure cracking stills varies with variations in cracking conditions but, by way of illustration, is approximately as follows:

Overhead from Debutanizer	% by vol.	Bottoms from Stabilizer	% by weight
Methane and fixed gas	3	Isobutane	4
Ethylene	4	Isobutene	4
Ethane	21	1-Butene	3
Propylene	16	*n*-Butane	13
Propane	49	2-Butene	6
Isobutane	2	*n*-Pentane	20
		Amylenes	13
		n-Hexane	15
		Hexenes	9
		Heptane and higher	13

With modern pressure-fractionating equipment, the separation of liquefied petroleum gases into propane, *n*-butane, and isobutane is a relatively simple procedure which is being conducted in many plants. The resulting butane is employed as a carbureting agent, and propane, in addition, is used in refrigerating equipment. Liquefied isobutane or propane are extracting agents for the refining of resins and gums (*80*, *103*) or oils and asphalts (*3*, *93*, *122*).

Alcohols

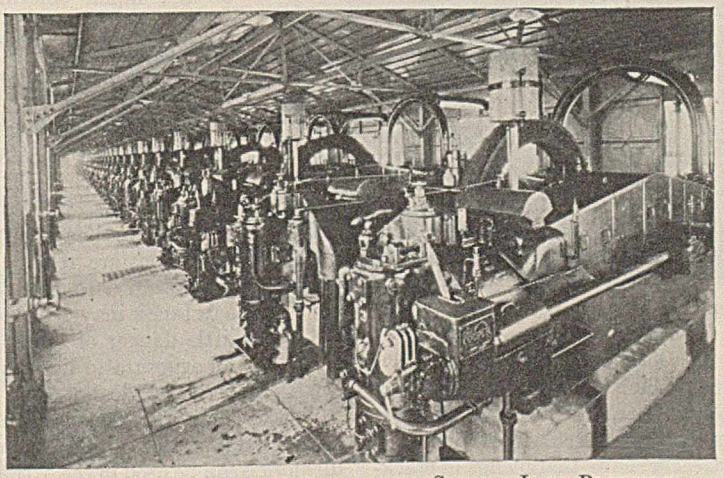
The conversion of olefins to alcohols is accomplished by absorption in sulfuric acid. The alkyl sulfuric acids which are formed as intermediates are then hydrolyzed to alcohols. Except with ethylene, secondary and tertiary alcohols are thus obtained. The reactions for ethylene and propylene may be represented by:

$$H_2C{=}CH_2 \xrightarrow{+H_2SO_4} CH_3CH_2SO_4H \xrightarrow{+H_2O} CH_3CH_2OH + H_2SO_4$$

$$CH_3CH{=}CH_2 \xrightarrow{+H_2SO_4} \begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!CHSO_4H \xrightarrow{+H_2O} \begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!CHOH + H_2SO_4$$

The products from ethylene and propylene are exclusively ethyl and isopropyl alcohols, respectively. With butylenes and higher olefins, either secondary or tertiary alcohols, or a mixture, are obtained, as well as a certain proportion of polymers.

Possibly the most important factors connected with this method of manufacturing alcohols are the temperature and concentration of the acid, both of which determine to a large degree the proportion of olefin converted to alcohol or to polymers. With ethylene, temperatures as high as 60° to 80° C. (140° to 176° F.) may be employed (*34*, *128*, *159*); for other olefins (propylene and higher) the temperature is generally kept at 20° to 30° C. (68° to 86° F.) or lower (*55*). Ethylene is absorbed in 96 to 100 per cent acid, propylene in 90 to 94 per cent acid, higher straight-chain olefins (e. g., 1- and 2-butene and 1- and 2-pentene) in 80 to 90 per cent acid, and isoölefins (isobutene and isopentene) in 60 to 70 per cent acid (*19*, *155*). Reaction between the olefin and acid, especially with gaseous olefins, is increased and facilitated by increased pressures and agitation in the presence of a liquid (e. g., a high-boiling petroleum fraction) which is a solvent for the olefin but which is immiscible with the acid. Many different catalysts have been proposed which not only aid absorption of the olefin by the acid but also reduce losses from polymerization.



Compressing Gas to 35 Pounds per Square Inch Pressure before Stripping

Alcohols which are produced on a commercial scale by the sulfuric acid process are ethyl, isopropyl, *sec*- and *tert*-butyl, *sec*-amyl, and *sec*-hexyl.

The use of the two lower alcohols, ethyl and isopropyl, as solvents and in pharmaceutical preparations is too well known to require further comment. Unique uses for higher secondary and tertiary alcohols are in the purification of paraffin slack wax (*150*), in paint-removing compositions (*13*), and as fuels for internal combustion engines (*163*). Alcohols also serve as the basic materials from which esters and ketones may be obtained.

It looks highly promising to bring about reaction between, say, ethylene and water to combine them directly as alcohol. However, this work, which has been carried on intensively in England, particularly by the Imperial Chemical Industries, and further by the Bataafsche Petroleum Maatschappij, has not appeared to indicate a promising yield. The success of the operation, if it has any future, is now held to reside in the discovery of an effective catalyst.

In experiments on direct hydration of this nature, mixtures of olefins and steam are led over catalysts at temperatures varying from 100° to 600° C. (212° to 1112° F.), generally about 100° to 350° C. (212° to 662° F.). The ratio of steam to hydrocarbons is usually low, though in some instances a ratio as high as 50:1 is used (*111*). This ratio governs, at least to some extent, the type of product obtained, alcohols being formed primarily when the ratio is high and ethers when the proportions of olefins and steam approach one another. Pressures from 1 to about 350 atmospheres have been advocated. The catalysts employed include metals and their alloys (*148*), metallic oxides (*141*) and phosphates (*4*, *78A*, *147*), nonvolatile mineral acids (*97*)—e.g., sulfuric or phosphoric acid—and volatile organic acids, such as acetic (*46*).

Esters

The reactions of alcohols with acids, acid anhydrides, or acid chlorides are familiar methods for preparing esters. The direct combination of olefins and acids is of more interest. Direct esterification of ethylene or propylene by organic acids is apparently difficult to effect but can be accomplished by first absorbing the olefin in sulfuric acid and then treating the solution with either the organic acid or a salt of the acid (*54*, *173*). Higher olefins are much more amenable to this treatment. Butyl acetate, for example, is obtained on passing butylene, at temperatures of 50° C. (122° F.) or higher and under pressures of 100 to 180 pounds per square inch, countercurrent to a stream of glacial acetic acid containing some sulfuric acid (*67*). Amylene may be esterified in a similar manner (*17*). Esters so obtained may serve as solvents for

various gums and resins and in the preparation of lacquers (*50, 124*).

Ketones

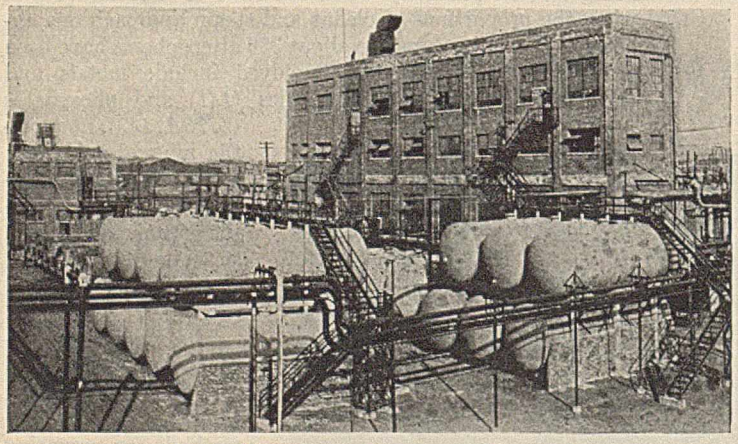
Dehydrogenation or oxidation of secondary alcohols yields ketones. The general reaction may be written:

$$\begin{matrix} R' \\ R \end{matrix}\!\!>\!CHOH \longrightarrow \begin{matrix} R' \\ R \end{matrix}\!\!>\!CO + H_2$$

Of this class of compounds, acetone is probably the most important industrially. It is a well-known solvent for cellulose esters, for many gums and resins, for some fats and waxes, and for acetylene, particularly for the prevention of explosions during the storage of that gas. This ketone is employed also in the manufacture of smokeless powder, celluloid, and certain kinds of artificial silks, as well as in the scouring of wool. Mixed with toluene or benzene, acetone yields a solvent which has been used as a dewaxing medium for lubricating oils.

Although acetone (and other ketones) has been produced largely by fermentation processes, isopropyl alcohol offers a convenient source. Dehydration of this alcohol is effected at temperatures of 250° to 430° C. in the presence of copper (*140*), metallic sulfides (*82*), or various salts of zinc, nickel, cobalt, aluminum, calcium, or magnesium (*83*). Catalysts for the vapor-phase oxidation of isopropyl alcohol include copper (*81*), brass (*172*), silver (*117*), and zinc oxide (*123*). Other metallic oxides, such as manganese dioxide and barium peroxide, have been suggested also (*167*).

Methyl ethyl ketone, made by oxidation of *sec*-butyl alcohol derived from butylene, finds application in the cellulose lacquer industry. It possesses a boiling point somewhat higher than that of acetone and because of its lower vapor pressure is less likely to cause "blushing" in lacquers. Provided this solvent could be made in quantity and sufficiently cheaply, methyl ethyl ketone would replace acetone for many purposes.



Alcohol-Plant Receiving Tanks for Crude Alcohols (Foreground)

The foregoing discussion clearly shows that olefins in cracking gas can be made to unite (directly or indirectly) with water to yield alcohols, from which two main classes of derivatives are obtained, esters and ketones. Reverting again to cracking gas, the olefins present can react with chlorine to give olefin dichlorides or with hypochlorous acid to form chlorohydrins. These latter compounds in turn are converted into two other classes of derivatives—glycols and olefin oxides.

Chlorohydrins

Although known since about 1859, ethylene chlorohydrin did not become an important compound until the World War when it was used in the manufacture of mustard gas.

One method of preparing ethylene chlorohydrin consists in passing ethylene into an aqueous solution of a hypochlorite from which hypochlorous acid is set free by the addition of a weak acid (*59, 166*)—e. g., sodium hypochlorite and sodium bicarbonate or carbon dioxide. Passage of ethylene and chlorine into water or an aqueous solution of a base—e. g., sodium carbonate, either in the absence or presence of an immiscible liquid which serves as a solvent for the chlorohydrin—is another method (*14, 70*). In such operations the temperature is kept low (about 10° to 12° C., or 50° to 53.6° F.), and the chlorohydrin concentration is maintained at about 6 to 10 per cent. Reaction in the vapor phase between chlorine, ethylene, and steam, employing catalysts such as manganese dioxide, chromates, or ferric oxide, has been proposed (*116*).

The chlorohydrins of propylene and butylene have been prepared similarly. With butylene and higher olefins a considerable proportion of dichlorides is formed simultaneously which materially reduces the yields.

Chlorohydrins have been suggested as solvents for the extraction of aromatics, phenols, and sulfur and nitrogen compounds from brown-coal-tar distillates (*152*), for the preparation of wetting agents (*92*) (by condensation with amines), in the making of synthetic resins by esterification with rosin (*57*) or by interaction with phenol alcohols (*28*), and in the manufacture of lacquers and plastics (*132*).

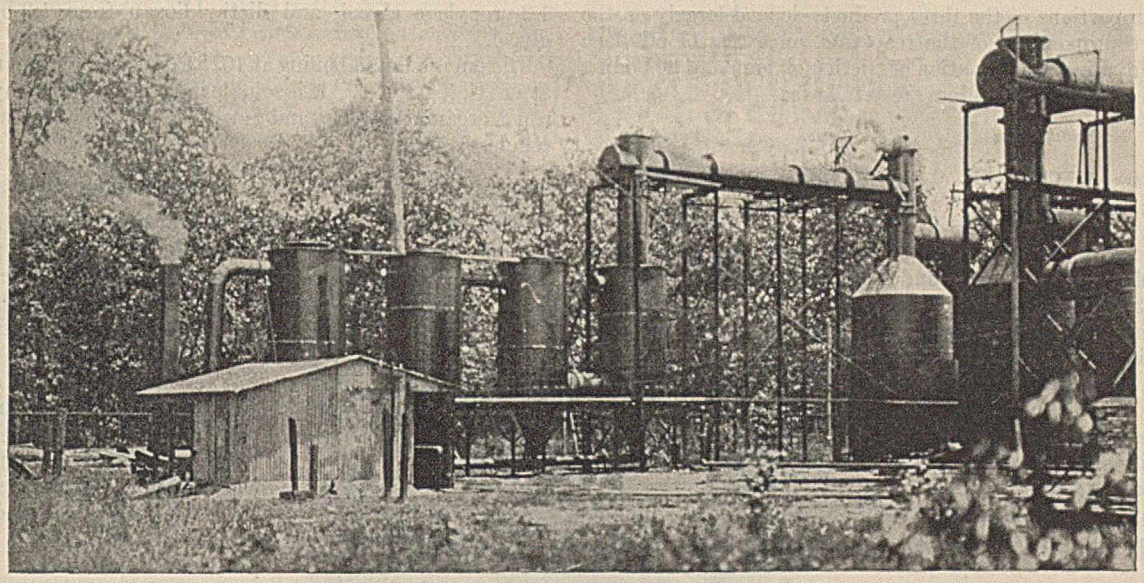
Ethylene Dichloride

Ethylene dichloride is made by the direct addition of chlorine to ethylene or to the ethylene fraction of cracking gas. With dry gases and at ordinary temperatures, reaction is rather slow. It is much faster when carried out in the liquid phase, in the presence of catalysts or of solvents, or at high temperatures. Under the last named conditions it is difficult to limit the reaction, since substitution products are also formed. Ethylene dichloride has been suggested as a solvent for this reaction (*113, 160*). Another method is to mix liquid chlorine with ethylene at 0° C. (32° F.) (*30*). The dihalide is also prepared by allowing a mixture of chlorine and ethylene to flow through a reaction tower countercurrent to a stream of water.

Ethylene dichloride is a colorless liquid (d_4^{20} 1.2569), boiling at 83.5° C. (182.3° F.) and freezing at −36° C. (−32.8° F.), slightly soluble in water, more so in alcohol and ether, and miscible with oils and fats. It burns with difficulty and the flames are readily extinguished. Because of resistance to hydrolysis and oxidation, this substance may be used at its boiling point with little danger of corrosion. Slow hydrolysis on exposure to light is retarded by addition of a small proportion of alcohol (*61*).

This dihalide is employed as a fumigant, as a solvent, and in the manufacture of ethylene glycol. As a solvent ethylene dichloride can be used in the extraction of oils, fats, and resins, and, mixed with methyl or ethyl alcohol, will dissolve cellulose nitrate or acetate. Another application is in the dewaxing of lubricating oil fractions (*104*) since paraffin wax is only slightly soluble in this solvent at temperatures below 25° C. (77° F.). Either alone or mixed with carbon tetrachloride it is a good cleansing agent (*133*). On a volumetric basis ethylene dichloride is a cheaper solvent than carbon tetrachloride and superior in stability towards water and steam.

An interesting product derived from ethylene chloride is that designated by the term "Thiokol" (*125, 126*). The latter is made by the interaction of the dihalide with poly-



PLANT FOR MAKING CARBON BLACK BY LEWIS WET PROCESS

sulfides of alkali or alkaline earth metals. Thiokol resembles soft rubber in properties but is characterized by a high sulfur content and insolubility in practically all organic liquids. It can be incorporated with crude rubber and the mixture vulcanized. The resulting products are also insoluble in organic liquids, particularly petroleum distillates, and are used, for example, in materials such as hose for handling gasoline.

GLYCOLS

Hydrolysis of ethylene dichloride (*18*) or of ethylene chlorohydrin (*15*, *31*, *48*) with solutions of alkalies leads to the formation of ethylene glycol. Direct oxidation of ethylene to glycol in the presence of water has also been employed. For example, ethylene and oxygen are introduced into water containing iodine (or compounds which readily liberate iodine, such as potassium triiodide or ferric iodide) and a manganese or iron oxidation catalyst (*146*). Or ethylene is allowed to react with air and water at 150° to 300° C. (302° to 572° F.) under pressure in the presence of metallic catalysts (*148*).

Ethylene glycol is a colorless, odorless liquid which possesses a sweet taste, boils at 197.5° C. (387.5° F.), and has a density of 1.115 at 20° C. (68° F.). It is miscible in all proportions with water, alcohol, and many other solvents.

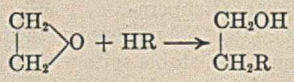
Possibly the most common uses of glycol are as a solvent and an antifreeze for automobile radiators. In addition, it is employed in the manufacture of cosmetics, in the preservation of anatomical and biological specimens, in the treatment of skins and furs, and as an aid in the finishing and dyeing of fabrics. Derivatives of ethylene glycol, however, have found diverse industrial applications (*32*). Thus, the monoethers (e. g., the monoethyl ether or Cellosolve) are widely used in lacquers (*35*). The nitrates form the basis for low-freezing dynamites (*137*). Esters of glycols and polybasic acids (e. g., phthalic) are of resinous nature and are useful in lacquers (*23*, *56*, *100*).

Higher boiling materials, the so-called polyglycols, are formed as by-products during the making of glycols. These substances can be made also by dehydration of ethylene glycol or by the action of water on ethylene oxide. The lowest polyglycol, diethylene glycol, has proved to be an almost ideal lubricant for wool spinning (*2*). Various derivatives of polyglycols, such as the monoethyl ether of diethylene glycol or Carbitol, have found varied applications (*37*).

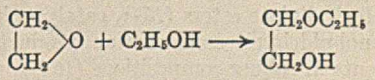
OLEFIN OXIDES

Compounds of the olefin oxide type, although classed as neutral substances, are capable of taking part in an astonishing number of reactions, and interest is centered chiefly in their derivatives rather than in the oxides themselves. Thus far only ethylene oxide appears to be utilized commercially, although higher olefin oxides are known. These oxides are made by heating either chlorohydrins with solid or anhydrous alkalies or concentrated solutions of chlorohydrins with alkalies (*16*, *166*). Ethylene oxide is said to be obtained on conducting ethylene, steam, air, and hydrogen over metallic catalysts at 150° to 400° C. (302° to 752° F.) (*149*).

Ethylene oxide (and alkalene oxides generally) reacts with organic substances containing an easily replaceable hydrogen atom—e. g., alcohols, acids, phenols, and amines—and also with water. These reactions may be represented as:



Glycol monoethers are made by the reaction of ethylene oxide, or other aliphatic oxide, with an alcohol (*89*, *174*):



Catalysts for the above reaction include sulfuric acid (*62*), the sulfates of nickel, zinc, or chromium (*69*), hydrosilicates of aluminum (*91*), and dialkyl sulfates (*9*, *36*). When an excess of the olefin oxide is employed, it is possible to make polyolefin glycol ethers. For example, introduction of ethylene oxide into anhydrous ethyl alcohol containing a small amount of sodium (as a catalyst) leads to the formation of the ethyl ether of tetraethylene glycol and higher polyglycols (*105*). The monoalkyl ethers of ethylene glycol are solvents for cellulose nitrate, resins, gums, and oils. They are miscible with organic solvents, and the lower ethers are soluble in water. The methyl ether is a solvent for cellulose acetate, and is especially adapted to the preparation of lacquers (*38*).

ETHANOLAMINES

Ethylene oxide reacts with aqueous ammonia to yield a mixture of three basic substances, mono-, di-, and triethanolamines, which can be separated by distillation (*86*, *101*, *135*).

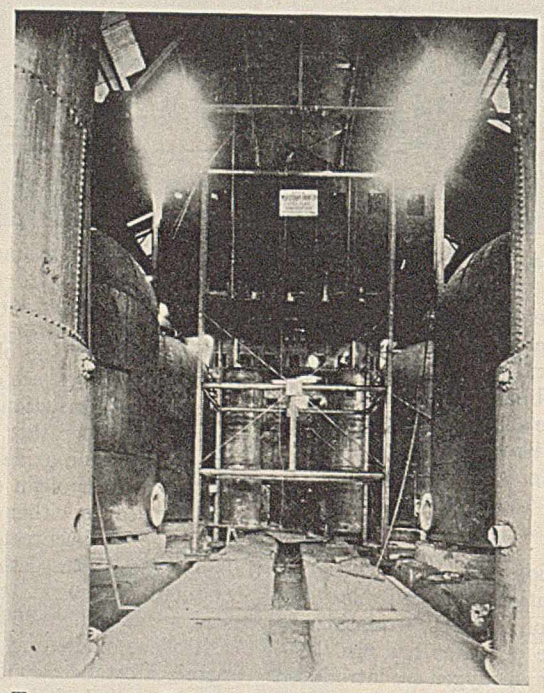
The proportions of the three products depend largely on the relative proportions of the reactants, an excess of ethylene oxide favoring the formation of triethanolamine. The boiling points of the ethanolamines are as follows:

Ethanolamines	Temp. ° C. (° F.)	Pressure Mm. (in.)
Mono-, $NH_2CH_2CH_2OH$	171 (339.8)	757 (29.8)
Di-, $NH(CH_2CH_2OH)_2$	217 (422.6)	150 (5.9)
Tri-, $N(CH_2CH_2OH)_3$	277 (530.6)	150 (5.9)

These substances are miscible in all proportions with water, alcohol, acetone, glycerol, and ethylene chlorohydrin, but not with ether and some aldehydes.

Monoethanolamine is a colorless, slightly viscous, hygroscopic liquid, with a faint ammoniacal odor. Diethanolamine is a colorless, odorless liquid, with viscosity characteristics similar to those of glycerol. The dinitrate of monoethanolamine (*118*) and the trinitrate of diethanolamine (*119*) have been proposed as explosives. Pure triethanolamine is a white crystalline solid at room temperature. The commercial product is a clear, viscous, hygroscopic liquid, with a density of 1.124 at 20° C. (68° F.) soluble in most organic liquids containing oxygen, but only slightly soluble in hydrocarbons.

In the Girbotol process of the Girdler Corporation aqueous solutions of a mixture of the ethanolamines, particularly the di- and triethanolamines, are employed for the removal of carbon dioxide and hydrogen sulfide from gases (*12*). The resulting carbonates and acid sulfides readily decompose at temperatures above 50° C. (122° F.) with regeneration of the solvent. The ethanolamines form stable salts with sulfur dioxide and therefore are unsatisfactory for the removal of that gas.



Thermatomic Plant, Showing Water Coolers and Box for Bag Filters

Other uses have been suggested for these amines—e. g., as extraction agents in the refining of mineral oils (*44*, *138*), plasticizers for cellulose esters (*151*), catalysts in the formation of phenol-aldehyde condensation products (*24*), preservative agents in rubber compositions (*162*), and stabilizers for tetraälkyl leads (*22*).

Ethanolamines combine readily with fatty acids to yield soaps (*161*) whose consistency depends primarily upon the acid employed. The oleate resembles petroleum jelly, whereas the stearate is a hard, waxlike solid. These compounds are soluble in water, benzene, toluene, and turpentine, but only slightly so in lubricating and petroleum oils. In contrast with the usual sodium or potassium soaps, those of the ethanolamine type are characterized by low alkalinity. The oleate may be used for promoting oil-in-water emulsions.

Dioxan

Diethylene dioxide, or dioxan, $O{-}CH_2CH_2{-}O{-}CH_2CH_2$, although structurally related to ethylene oxide, should more properly be considered as a derivative of ethylene glycol. It is made industrially by heating ethylene glycol with dehydrating agents, such as sulfuric acid (*60*) or anhydrous ferric sulfate (*1A*). Similarly, dimethyldioxan is obtained from 1,2-propylene glycol, and diethyldioxan from 1,2-butylene glycol.

Dioxan is a liquid boiling at 102° C. (215.6° F.) and melting at 11° C. (51.8° F.). It is soluble in water and in many of the usual organic solvents, and is a solvent for resins, fats, and cellulose esters.

Production of Unsaturated Hydrocarbons

The action of heat on saturated hydrocarbons results in the formation of unsaturated compounds and also in many instances leads to a rearrangement within the molecule. Perhaps the largest source of unsaturated hydrocarbons is cracking gas, the composition of which has already been discussed. Butadiene is a component of vapor-phase cracking gas. Acetylene is formed from hydrocarbons at temperatures considerably above those employed in cracking. These two unsaturated compounds are of particular interest.

Acetylene

Acetylene is one of the thermal decomposition products of hydrocarbons at 800° C. (1472° F.) or above. Below this temperature it is not formed, or only in small proportions (methane, for example, requires heating to 1000–1200° C. or 1832–2192° F.). Acetylene is made by the thermal decomposition of practically all hydrocarbons in the electric arc. Generally, better yields are obtained from low-boiling or gaseous petroleum hydrocarbons than from higher boiling distillates. Short periods of heating, reduced pressure, and addition of hydrogen or steam to the gaseous hydrocarbons minimize their decomposition to carbon and hydrogen.

One important reaction of acetylene is its hydration to acetaldehyde, which may be subsequently oxidized to acetic acid. Hydration can be conducted in either the liquid or gaseous phase. In liquid-phase operations, a stream of acetylene is passed through dilute sulfuric acid (about 6 per cent) to which has been added mercuric oxide, the mercury salt thus formed serving as a catalyst. Reaction proceeds with the evolution of heat, and vaporized acetaldehyde is carried along in the gas stream from which it is recovered by cooling. Oxidation of the aldehyde readily yields acetic acid. A number of by-products (*6*) are formed in minute proportions in the hydration of acetylene. One of these, diacetyl, is used for flavoring butter substitutes.

A difficulty encountered in vapor-phase operations is the ease with which acetaldehyde is converted to other substances, such as crotonaldehyde or esters. This is overcome by the addition of a gaseous oxidizing agent—e. g., by conducting acetylene, steam, and oxygen at 100° to 200° C. (212° to 392° F.) over a catalyst consisting of a mercuric salt (*96*).

Acetylene is being produced at a refinery in this country by arcing hydrocarbon gases and is used subsequently for making acetic acid. Thus petroleum has definitely become a source of another hydrocarbon, acetylene.

Other important derivatives of acetylene are vinyl esters

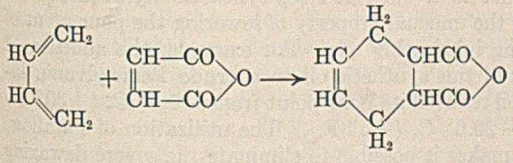
and acetylene polymers. Vinyl esters are obtained from acetylene and acids by direct addition in the presence of a mercury catalyst. Vinyl esters can be transformed by various methods into light-colored resins (Vinylite) which at present are finding rather wide utilization in coatings and plastics, particularly in phonograph records (*39, 52, 53*).

Of the various polymers of acetylene, one is the result of the action of heat on the hydrocarbon in contact with certain metals. This is known as cuprene and is an insoluble, brown, amorphous solid (*76*). Liquid polymers are made by absorption of acetylene in solutions of cuprous salts. Mono- and divinylacetylene are thus formed. Divinylacetylene slowly thickens to a viscous liquid which, after application as a film, hardens farther to an insoluble coating (*121*). Monovinylacetylene, when combined with hydrochloric acid, yields the liquid called "chloroprene" (*26*). The latter can be changed readily into an elastic solid which resembles natural rubber more closely than does any other synthetic material. Acetylene rubber of this type is known as DuPrene.

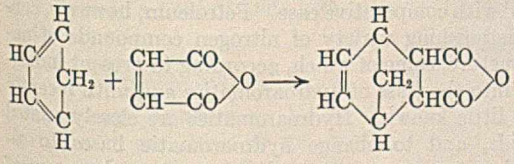
Butadiene

Butadiene is a gaseous product of the pyrolysis of hydrocarbons at temperatures just below those at which transformation of straight-chain hydrocarbons to aromatics takes place. To illustrate, the maximum yield of butadiene from ethylene is obtained at 750° C. (1382° F.) (*175*) and from propane, propylene, and butane (*66*) at about 727° to 728° C. (1340.6° to 1342.4° F.). Cyclohexane is converted largely to butadiene at 654° C. (1209.2° F.).

An interesting reaction of butadiene, and other conjugated diolefins, is that with maleic anhydride to yield cyclic acid anhydrides (*1, 43, 59A*). This may be represented as:



Such products are often readily formed by allowing the diolefin and maleic anhydride to react in the presence of benzene. Not only aliphatic but also cyclic diolefins—e. g., cyclopentadiene—combine with maleic anhydride:



By this reaction it was shown that butadiene, piperylene, isoprene, and cyclopentadiene were present in the low-boiling fractions of a gasoline cracked at a high temperature (*8*).

Butadiene and similar diolefins have been considered for some time as a source of artificial rubber (*25, 170*). When heated with various substances which act as catalysts, butadiene polymerizes and forms a solid mass possessing some of the properties of rubber. Considerable work has been done recently on this reaction, but the development is hampered by economic considerations. However, a resin has been produced from the diolefins of vapor-phase-cracked distillates by polymerization with aluminum chloride (*157, 158*). This petroleum resin produces varnishes which dry very rapidly. Another related material is a dark colored liquid product consisting of a mixture of polymerized olefins and diolefins, known as Puresinol (*95*). This is a by-product in the refining of highly cracked gasoline distillates and is proposed as a substitute for linseed and other drying oils. Its specific gravity is 0.956, Saybolt viscosity at 100° F. (37.8° C.) is 200 seconds, and iodine number is 175. Brittleness of the dried film would appear to limit its uses.

Aromatics

Certain crudes, particularly Borneo petroleum, contain aromatic hydrocarbons to some extent. Aromatics are also formed in cracking processes. However, in the production of Hydrosolvents by hydrogenation it has been found that aromatic compounds are produced in large proportions.

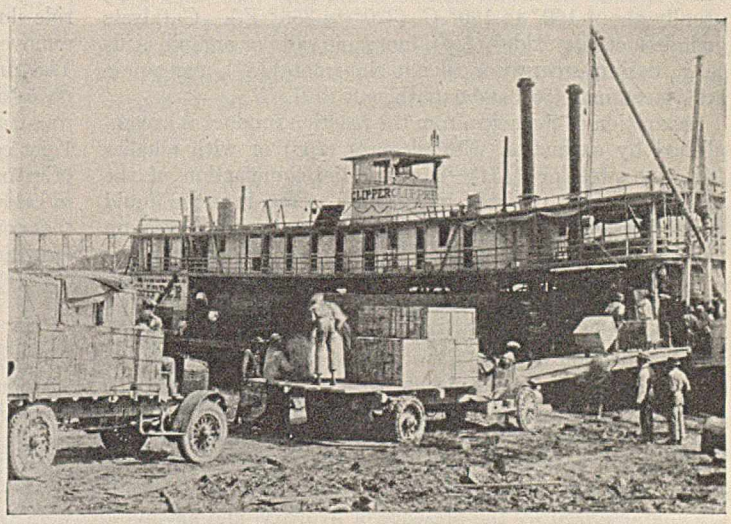
If an overhead cut is made of a Hydrosolvent, the following results roughly express the proportion of aromatic hydrocarbons:

° F.	(° C.)	%
200–275	(93.3–135)	10
275–365	(135–185)	35
365–419	(185–215)	38
419–460	(215–237.8)	8–10

Distillate under 200° F. (93.3° C.) end point is added to gasoline.

The increase in aromatic content with boiling point is of significance in the coating industry, since a coating in which such a liquid is present as the thinning agent becomes richer in more powerful solvents as evaporation increases. This tends to permit the binder in the composition to orient satisfactorily, giving an unusually hard and glossy surface.

In the crude Hydrosolvent cut there is probably about 1 per cent benzene, 4 per cent toluene, 18 per cent xylenes, and



Loading Carbon Black on Ouchito River Packet Boat

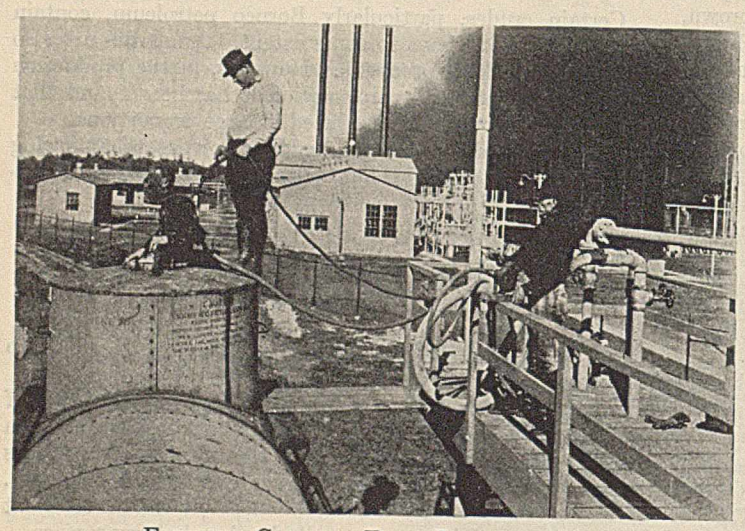
25 per cent of the trimethylbenzene type of hydrocarbons, including mesitylene and isomers, such as methylethylbenzene, propylbenzene, etc. There are also indications of the presence of hydrogenated naphthalenes, particularly tetralin and decalin. There may be also some octalin. Although some naphthalene may be in the distillates, it is likely to be negligible in amount.

The hydrocarbons from coal tar are characterized by the insignificant proportions of trimethylbenzene hydrocarbons, and the high yield of these through hydrogenation of petroleum appears to fill a gap not supplied by coal tar. In other words, the hydrocarbons of coal tar are benzene, toluene, and xylene, and then rather suddenly there is a jump to naphthalene, anthracene, and other polycyclic hydrocarbons. Hydrogenation, therefore, should serve as a means to place the

petroleum industry in the coal-tar field, especially for products in which coal tar is lacking.

Oxidation Products

The oxidation of petroleum hydrocarbons of high molecular weight, such as paraffin wax, is a method for the preparation of acids of high molecular weight. Air, oxygen, ozone, oxides of nitrogen, and nitric acid can be used as the oxidizing agents, though air is most generally employed. Reaction is carried out at temperatures above the melting point of the wax, usually about 160° to 180° C. (320° to 356° F.). Catalysts include metallic oxides (*143*), inorganic salts of organic acids (e. g., barium stearate or calcium cinnamate) (*87*), manganese acetylacetonate (*85*), and naphthenate (*90*).



Entering Gasoline Tank Car with Mask

Separation of the acids from the reaction product is accomplished by extraction with alcohols (*108*) or with alkalies (*64*), by sweating (*131*)—i. e., partial liquefaction of the product by heat followed by pressing to separate the liquid and solid portions—and by distillation under reduced pressure (*106*).

These acids are designated "wax acids," as this term indicates wax as their source rather than fats. Furthermore, some investigators have intimated that these acids contain a large proportion of substances having an uneven number of carbon atoms per molecule as contrasted with fatty acids which contain an even number of carbon atoms. Wax acids can be employed in the manufacture of synthetic fats by esterification with glycol or glycerol (*63*, *77*) and for making soaps. The latter is the more important use. Crude wax acids are characterized by the presence of hydroxyl and aldehydic groups. The removal of these groups, which interfere in certain applications, is a problem to which considerable attention is being given. Instead of wax acids, higher alcohols can be obtained by employing the proper catalyst. Sulfation of these wax alcohols forms soaps of the hard-water type, a procedure which appears cheaper than making detergents from the alcohols of vegetable-oil hydrogenation.

In addition to acids of high molecular weight, water-soluble acids of low molecular weight are also obtained by oxidation, as well as intermediates such as aldehydes, ketones, esters, acid anhydrides, and hydroxy acids. In preparing alcohols, the wax is oxidized for a shorter time than that employed for making acids. Catalysts which are particularly useful in this reaction are acetic acid or weak inorganic acids such as boric (*107*). The alcohols are separated from nonoxidized wax and other substances by distillation under reduced pressure with steam.

Oxidized kerosene fractions are used for the production of an alcohol denaturant known as Aldehol (*10*).

Chlorination Products

Although a vast amount of work has been conducted on the chlorination of petroleum hydrocarbons, only brief mention can be made of some of the products obtained.

Chlorination of methane, for example, yields methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4). Methyl chloride, because of its low boiling point, has been used as a refrigerant. The remaining three substances can serve as solvents, chloroform to a limited extent as an anesthetic, and carbon tetrachloride as a fire extinguisher. Carbon tetrachloride and antimony trifluoride react to give dichlorodifluoromethane, a substance particularly applicable as a refrigerant because of its low toxicity.

Chlorination of natural-gas gasoline gives a mixture of amyl chlorides which can be hydrolyzed to amyl alcohols (*29*) (marketed under the name of Pentasol) and the latter esterified with acetic acid (Pentacetate).

The production of Paraflow is an outstanding development in the utilization of chlorinated petroleum hydrocarbons. Paraffin wax is chlorinated until its chlorine content is about 10 to 12 per cent and is then reacted with benzene, naphthalene, or anthracene in an inert solvent (e. g., kerosene) at 60° to 71° C. (140° to 160° F.), with aluminum chloride as a catalyst. After reaction is completed, the aluminum chloride sludge is withdrawn, and the solvent and excess wax are removed by distillation, the latter under reduced pressure. The product is a chlorine-free, synthetic hydrocarbon oil possessing the unusual property of lowering the pour point of wax-bearing lubricating oils. For example, the addition of 1 per cent of this synthetic oil to a crude Pennsylvania lubricating oil reduced its pour point from −1.1° C. (+30° F.) to below −20.6° C. (−5° F.). The utilization of Paraflow, therefore, makes it possible to eliminate the severe dewaxing operations required in the refining of many lubricating oils (*40*, *41*).

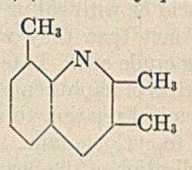
Nitrogen Compounds from Petroleum

In coal oil and shale oil there are present aromatic compounds of nitrogen whose identification has been accomplished with comparative ease. Petroleum, however, contains an astonishing variety of nitrogen compounds of unknown structure, some of which, according to present indications, fall into the class of hydroaromatics and until recently were very little known. Hydroaromatics are closely related to alkaloids, and to change hydroaromatic bases to alkaloids it is necessary only to make the proper placement of oxygen. A brief mention is therefore made of these nitrogen compounds as opening up a new field of scientific interest and practical value, some of them already having been found useful in insecticides (*165*) and as pickling inhibitors (*94*).

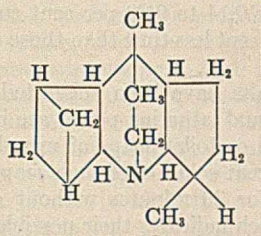
The nitrogen content of crude petroleum is rather low, about 0.1 per cent or less, though some California oils have shown as high as 0.82 per cent on analysis (*129*). Apparently the nitrogen compounds in crude oils are nonbasic and are not extractable with acids. Distillates from such crudes, however, contain nitrogen bases, thus indicating a decomposition of rather complex nitrogenous substances during distillation (*130*).

To illustrate the types of compounds which have been isolated, only two need be mentioned. Both of these were found in the sulfur dioxide extract obtained in the refining of

kerosene. From the fraction boiling at 276° to 277° C. (528.8° to 530.6° F.) 2,3,8-trimethylquinoline was obtained:



A hydroaromatic base, $C_{16}H_{25}N$, from the same fraction is of interest in that it represents a compound of the cyclopentane type. The structure assigned to this substance is:



This has been named decahydro-3,8-dimethyl-5,7-methano-4,8-ethanopyrindacine.

So far there is no explanation for the presence of hydroaromatics in petroleum and their absence from coal, shale, and bone distillates. Furthermore, none of the bases isolated from petroleum has been obtained from other natural sources.

Sulfur Compounds from Petroleum

The sulfur content of crude oils from different localities varies widely, ranging from less than 0.2 per cent to as high as 4 to 5 per cent (*58*, *71*, *102*). Fractions of high-sulfur content are the basis of Alcotate, an alcohol denaturant (*79*, *126A*). Practically all of the simpler types of sulfur compounds have been identified in such oils; these include mercaptans, thioethers, thiophenes, thiophanes, organic sulfides and disulfides, compounds containing both sulfur and oxygen, and also hydrogen sulfide, elemental sulfur, and carbon disulfide (*11*, *27*, *110*, *136*, *145*). From the refiner's viewpoint these sulfur-containing substances are impurities which, because of their corrosive properties or their odors, must be removed particularly from gasoline and kerosene fractions. To the chemist, the isolation and utilization of these sulfur compounds opens a field of wide possibilities.

Hydrogen Sulfide

Hydrogen sulfide may be extracted from petroleum or its distillates, or from the gases from the distillation or cracking of crudes or distillates of high sulfur content, by solutions of alkalies—e. g., sodium hydroxide, sodium carbonate and bicarbonate, or ethanolamines. Aqueous suspensions of brucite (*68*) have been suggested for the same purpose. Hydrogen sulfide may be liberated, except in the case of sodium hydroxide, by heating the solutions or suspensions.

The uses of gaseous hydrogen sulfide, other than in the laboratory, appear to be rather limited. It reacts at high temperatures with olefins or acetylene in the presence of catalysts to yield mercaptans, thioethers, thiophene and its derivatives, and carbon disulfide (*109*, *154*). When hydrogen sulfide is mixed with methane, ethane, or propane, and the mixture is heated to 1200° C., both benzene and carbon disulfide are obtained (*169*). The salts of hydrogen sulfide, particularly the sodium salt, have been used as aids in dyeing, as reducing agents, depilatories, and denitrating agents, and in the manufacture of sulfur dyes and lithopone.

The preferential oxidation of hydrogen sulfide to sulfur, either by metallic oxides or by sulfur dioxide, are well-known processes and suggest the possibility of high-sulfur petroleum oils as potential sources of sulfur.

Mercaptans

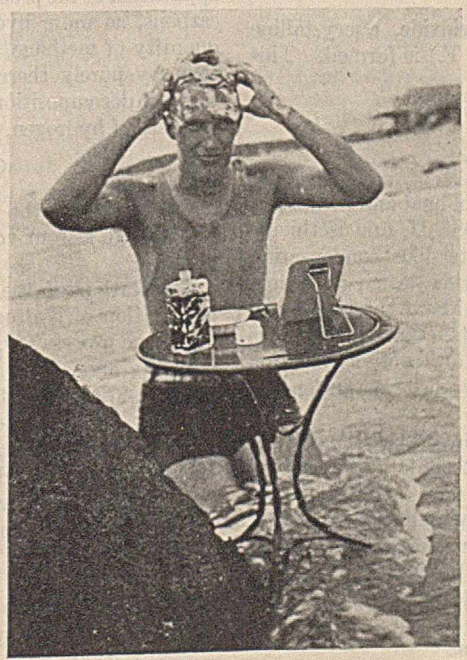
Aqueous solutions of sodium hydroxide and alcoholic solutions of sodium plumbite (*168*) or of sodium or potassium hydroxide (*164*) have been employed for the extraction of mercaptans from petroleum distillates. As an industrial method the use of aqueous sodium hydroxide is probably to be preferred, and mercaptans may be thus liberated by steam distillation (*7*, *112*).

Mercaptans have been suggested as pickling inhibitors (*21*) and as intermediates in the preparation of dyes. Heated with phosphorus tri- or pentasulfide, mercaptans yield liquids which may be employed in ore-flotation processes (*42*). The well-known soporific, sulfonal, is the sulfone of the mercaptole obtained from acetone and ethyl mercaptan. Because of their penetrating odor, volatility, and insolubility in water, the lower boiling mercaptans, especially ethyl mercaptan, have been used for detecting leaks in gas mains (*45*, *73*, *127*, *142*, *156*). A product designated Cal-Odorant, apparently a mixture of hydrocarbons and sulfur compounds, is marketed for odorizing natural gas (*78*). Butyl mercaptan is said to be a stabilizer for chlorinated hydrocarbons—e. g., carbon tetrachloride or tetrachloroethylene (*153*).

Thioethers

Possible methods for the recovery of thioethers include the formation of addition compounds with salts—e. g., mercuric iodide or chloride, titanium tetrachloride, or platinic chloride—and their extraction from acid sludge. Passage of mercaptans over metallic catalysts (sulfides of cadmium or zinc, and aluminum chloride) at 320° to 350° C. (608° to 662° F.) results in the formation of thioethers (*139*, *171*).

Thioethers are solvents for rubber and for resins such as abietic acid, paracoumarone, petroleum resin, and cresol–sulfur chloride resins. Ethyl alcohol and ethyl sulfide, or methyl alcohol and propyl sulfide are solvents for cellulose nitrate. Ethyl sulfoxide, an oxidation product of ethyl sulfide, has been suggested as a plasticizer for pyroxylin.



A Shampoo in the Ocean with New Sulfate Detergent Lathering Freely in the Hardest Waters

Sulfonates

In the refining of mineral oils, particularly in the production of white pharmaceutical petrolatum (vaseline oils), with sulfuric acid, a certain amount of sulfonation

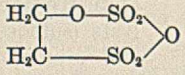
occurs (*49*). Most lubricating oils contain reactive hydrocarbons which are partly removed from the oil by agitation with sulfuric acid. The sludges from such refining operations contain free acids, polymerized bodies, asphaltic materials, and oxidized substances together with various sulfonated products. The disposal of this acid sludge has long been a problem to the refiner. The acid is usually separated by the addition of water and reconcentrated for further treatment of distillates. The residual material is largely used as a fuel (*98*).

Numerous methods have been devised for the removal of the sulfonic acids from sludges and acid-treated oils. In general, separation is effected by some selective action such as that of solvents or adsorbents or by salting-out the acids in the form of their alkali or alkaline earth salts. As is evident, the sulfonic acids vary with the character of the sludge, the type of the original oil, and the refining treatment; hence the methods used for their recovery are generally adapted to a particular material.

Mineral-oil sulfonic acids, varieties of which are known as Kontakt, mahogany acids, and green acids, have found commercial interest. They have been used as detergents, reagents for hydrolyzing fats to glycerol and acids, and textile reagents—i. e., wetting, penetrating, cleansing, or lubricating agents in textile treatment. On some types of dispersions, mineral-oil sulfonic acids act as stabilizers, but on others they exert a coagulating effect. In the petroleum industry the acids recovered from sludges have been used to prevent emulsification in subsequent refining operations. Various sulfonated mineral-oil fractions have been employed also in insecticide compositions. These applications have been so extensively investigated that to single out one as an illustration would be unfair to several hundred others.

The sulfonated minerals oils can be considered to consist largely of sulfonated paraffin and cycloparaffin (naphthene) hydrocarbons and to be derived from petroleum distillates. Aromatic sulfonic acids, though they may be formed also in small quantities in petroleum refining, are largely derived from coal tar. The petroleum sulfonic acids can thus be looked upon as by-products, whereas another series of compounds derived from olefins resulting from pyrolysis of petroleum distillates, for example, can be considered to be principal products.

When ethylene reacts with sulfur trioxide, a crystalline compound which melts at 80° C. (176° F.) is formed. This substance is carbyl sulfate:



It dissolves in water with the liberation of heat and the formation of ethionic acid, $HO_3S—C_2H_4—OSO_3H$, and isethionic acid, $HO_3S—C_2H_4—OH$. Salts of ester-like condensation products of ethionic acid and fatty acids—e. g., oleic acid (*33*), have appeared as Igepons (*47*) and have received much attention as wetting and cleansing agents, especially in textile treatment. Olefins resulting from the destructive oxidation of paraffin wax and naphthenic acids have also been sulfonated to give similar products (*5*).

Although petroleum sulfonic acids have been known and investigated for a long period, great technical interest was not manifested until recently with the development of products of superior detergent quality. The sulfation of olefins, resulting from the cracking of petroleum, has opened a wide field for the petroleum industry, and further developments quite as remarkable are already foreshadowed.

Naphthenic Acids

Other by-products from the refining of petroleum distillates are naphthenic acids, which are extracted from distillates by the alkali wash required in refining operations. The acids are obtained in the free state by acidifying the alkali with sulfuric acid or with sulfur dioxide. Their name is indicative of the fact that they were first observed in naphthene-containing crude oils. Later investigations of the structures and properties of naphthenic acids have shown also that they bear a chemical relation to the naphthene hydrocarbons, particularly to cyclopentane.

An interesting application of the heavy metal salts of these acids, the cobalt, lead, and manganese salts especially, is as paint and varnish driers (*88*). Solutions of such salts in hydrocarbons are known as Soligen driers. Linseed oil varnishes, containing 0.14 to 0.29 per cent cobalt naphthenate, dry in 1 to 10 per cent less time than those containing a resinate drier.

The sodium salts have been suggested as soaps. Their detergent action and lathering power are inferior to those of sodium palmitate or toilet soaps of mixed fatty acids however. A 40 per cent solution of such soaps can be cooled to 0° C. (32° F.) for 30 minutes without effecting complete solidification, which indicates their possible use in the preparation of neutral soft and liquid soaps. Much larger quantities of sodium chloride are required to salt-out sodium naphthenates than coconut oil soaps from aqueous solutions (*99*, *114*).

Hydrogen

According to well-known processes, hydrocarbons and steam react at high temperatures in the presence of catalysts to give hydrogen and oxides of carbon. With methane this may be represented by:

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$
$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

and for higher hydrocarbons by:

$$C_nH_{2n+2} + nH_2O \longrightarrow nCO + (2n + 1)H_2$$

These reactions are reversible, the equilibrium depending upon the temperatures and pressures employed. From an industrial point of view the chief interest in them lies in their application to the production of hydrogen from gaseous hydrocarbons, as more hydrogen can be obtained from a given quantity of methane, or other hydrocarbons, in this manner than by purely thermal decomposition. For example, the thermal decomposition of one volume of methane yields two volumes of hydrogen,

$$CH_4 \longrightarrow C + 2H_2$$

but according to the preceding reaction it is possible to obtain as high as four volumes of hydrogen from one volume of methane.

Application of the above reactions is illustrated in the preparation of hydrogen from cracking gas and steam by a two-stage process (*20*, *74*, *115*, *134*).

In the first stage, reaction between the gases takes place at about 870° C. (1600° F.). The resulting mixture of hydrogen and carbon monoxide is further mixed with steam and conducted over a catalyst at about 455° C. (850° F.). By this second step an additional supply of hydrogen is obtained by the conversion of carbon monoxide into carbon dioxide according to the well-known water gas reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

At the end of these two stages the gaseous mixture contains about 79 per cent hydrogen, 20 per cent carbon dioxide, and 1 per cent of other gases. Carbon dioxide is removed by compressing the gases to a pressure of 240 pounds per square inch, followed by washing with water and then with aqueous tri-

ethanolamine. The final product contains more than 97 per cent hydrogen and can be used in the hydrogenation of oils.

The hydrocarbon gases should be free of hydrogen sulfide, or other sulfur compounds, which poison the catalysts. The latter often consist of oxides of nickel, cobalt, iron, or aluminum, to which may be added activators, such as the oxides of chromium, vanadium, or magnesium (*65*, *72*, *84*, *144*).

Natural Gas

Natural gas, which may be regarded as gaseous petroleum, consists primarily of methane, together with some ethane and propane, small quantities of butane, pentane, and other paraffins up to octane, and smaller proportions of carbon dioxide, hydrogen sulfide, and (in exceptional instances) helium. Natural gases are roughly divided into two classes, "wet" and "dry" gases, the former containing a large proportion of easily liquefiable hydrocarbons. Removal of these higher paraffins from natural gas by (*a*) compression, (*b*) absorption in oil, or (*c*) adsorption—e. g., with charcoal—yields natural-gas gasoline. Before blending this product with other motor fuels, it is subjected to stabilization or distillation under pressure, by which propane and some butanes are obtained. Natural gas is utilized primarily for the large-scale production of carbon black.

It is evident from the preceding discussion that a chemical industry dependent upon petroleum as a raw material is becoming well established. With the large number of possibilities offered by such a multitude of already available substances, future developments may be even more surprising. The chemistry of petroleum derivatives has indicated new sources of hitherto unavailable industrial chemicals and products.

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GAS FROM BROWN COAL BRIQUETS USED AS MOTOR FUEL IN GERMANY. Successful tests involving the generation of gas from brown coal briquets are claimed to have been accomplished in Germany. Considerable attention has been paid in the Reich to the possibility of propelling motor vehicles with gases from charcoal, wood, and brown coal briquets. Charcoal and wood, especially the latter, have been used in Germany for this purpose for several years. The various systems of apparatus, however, which can only be applied to heavy trucks and buses, do not seem to meet all requirements, and are not expected to gain much more ground since the Diesel engine has entered this field.

The use of brown coal briquets has been considered by the Rhenish brown coal industry and tests have been carried out by the Institute for Coal Research. While the possibility of using charred briquets found no more consideration, in view of the difficulty in supplying sufficient quantities, attention was directed chiefly to inventing a system permitting the extraction of gas from ordinary brown coal briquets.

All requirements are said to have been fulfilled by the construction of an apparatus having a fire zone which is fed from two sides. This is effected by a main air nozzle and a subsidiary nozzle, which later is placed on the walls of the fire zone. By working as an injector, the main nozzle is claimed to suck the char vapors and mix them with air, whereby the accumulation of slag is prevented. Successful tests are reported to have been made with this apparatus on a 1.5-ton truck.

Hydration of Portland Cement Compounds

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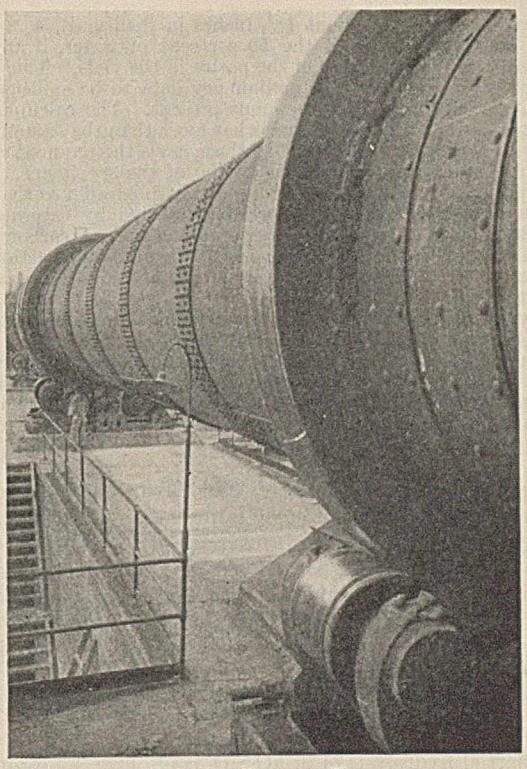
This paper presents the results of an investigation on the reactions which take place when the compounds of cement, individually and collectively, are gaged with water in proportions similar to those used with cements in concrete. There have been studied the chemical nature of the reactions of hydrolysis and hydration, the rate of the reactions, the nature of the reaction products, the physical structure of the hardened specimens, and the compressive strengths and other physical characteristics of the materials. A general theory has been developed which permits an understanding of the chemical and physical mechanism of the hardening process. The effects of the aluminates on the silicates is indicated both in the absence and in the presence of a retarder.



Rotary Cement Kiln

WHEN Portland cement is gaged with a sufficient amount of water to form a plastic paste, it stiffens in the course of a few hours. This phenomenon is spoken of as the initial set (*2*). Subsequently it becomes hard, and more or less rapidly acquires marked resistance to rupture by either compressive or tensile stresses. A certain arbitrarily defined degree of hardness, sufficient to bear a given light weight without indentation, is spoken of as the final set (*2*).

The hydrolytic reactions of the cement compounds in an excess of water have been reported (*14*). In that investigation the products of the reactions were determined when a condition of equilibrium had been attained. The reactions that take place when a cement paste sets and becomes hard may, however, attain a condition of arrested progress, or apparent equilibrium, long before true equilibrium is reached. During the setting and hardening, several forces compete for the available water—the physical forces of adsorption and capillarity, and the chemical forces of hydrolysis and hydration. Furthermore, the reaction products of one compound with water may greatly influence the nature or rate of the reactions of the other compounds with water, or the reaction products may themselves interact with other compounds in the system.

The chemical reactions which determine the setting and hardening of Portland cement can be more completely understood through the examination of the behavior of the compounds of the cement, individually and collectively, when gaged with water in proportions similar to those used with cements in concrete. That has been the objective in this investigation. Seven compounds that may occur in Portland cement have been investigated, individually, with and without gypsum, and in various combinations. The chemical nature of the reactions of hydrolysis and hydration, the rate of the reactions, the nature of the reaction products, the compressive strength and other physical characteristics of the materials have been studied.

The literature on the reactions of set has been reviewed by one of the authors in a previous publication (*5*).

Materials Investigated

The cement compounds used in this investigation were those which comprise the major constituents of a well-burned Portland cement clinker and, in addition, 5–3 calcium aluminate, dicalcium ferrite, and gamma dicalcium silicate. In the tables, abbreviations are used for the compounds as follows:

Cement Compounds	Compounds Not Normally Found in Portland Cement
C_3S for $3CaO \cdot SiO_2$	γC_2S for $\gamma 2CaO \cdot SiO_2$
βC_2S for $\beta 2CaO \cdot SiO_2$	C_5A_3 for $5CaO \cdot 3Al_2O_3$
C_3A for $3CaO \cdot Al_2O_3$	C_2F for $2CaO \cdot Fe_2O_3$
C_4AF for $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	

The materials used and the methods of preparation of the calcium silicates, calcium aluminates, and dicalcium ferrite were the same as those described in a previous report (*14*). The compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ was prepared by heating a mixture of calcium carbonate, alumina, and ferric oxide in the correct proportion to 1350° to 1400° C. (2462° to 2552° F.) for 3 hours.

All materials were ground to pass completely through the No. 100 sieve and approximately 90 per cent through the No. 200 sieve.

Experimental Procedure

The compounds and mixtures of compounds were each mixed rapidly with water. An amount of water equal to 50 per cent of the weight of the cementing material (except as otherwise noted) was measured out, and as much of this was mixed with the material as was required to give a plastic paste. The paste was then

placed to a depth of about $1^1/_2$ inches in shell vials, $4 \times {}^{15}/_{16}$ inch, and the balance of the 50 per cent of water, if any remained, was placed on top of the pastes in the vials. This total water was considered from preliminary data to be sufficient to hydrate completely the compounds present. The calcium aluminates, however, required somewhat more than that amount of water to give a plastic paste. In those cases the required water was used, but none was placed on top of the specimens. The charged vials were stoppered and sealed with paraffin so that the reactions with water could proceed unaffected by external influence, such as evaporation of water at the surface, carbonation by reaction with the carbon dioxide of the air, or extraction by storage water. All specimens were stored at room temperature until tested.

The reactions were investigated by chemical methods to determine the rate of hydration and hydrolysis, and the composition of the end products; by microscopic examinations to determine the progress of the reactions and to identify the reaction products; by x-ray examinations to assist further in the identification of the products; and by physical tests to determine the cementing properties of the various compositions.

Since the terms "hydrolysis" and "hydration" are sometimes used interchangeably, it is desirable to define each. By hydrolysis is meant such reactions of a compound (salt type) with water that a part or all of the compound becomes decomposed, either completely into the corresponding acid and base, or incompletely to form an acid or basic salt or a derivative of the same. Thus the complete hydrolysis of $3CaO \cdot SiO_2$ would give:

$$3CaO \cdot SiO_2 + XH_2O = 3Ca(OH)_2 + SiO_2 \cdot XH_2O$$

The partial hydrolysis of $3CaO \cdot SiO_2$ could give, for example, $2CaO \cdot SiO_2 \cdot XH_2O$, $3CaO \cdot 2SiO_2 \cdot XH_2O$, or $CaO \cdot SiO_2 \cdot XH_2O$ in addition to calcium hydroxide. In this paper the "degree of hydrolysis" refers to the percentage of complete hydrolysis as indicated in the above equation.

By hydration is meant the direct addition of the elements of water as:

$$CaO + H_2O = Ca(OH)_2$$
$$\text{or } 3CaO \cdot Al_2O_3 + XH_2O = 3CaO \cdot Al_2O_3 \cdot XH_2O$$

The extent of hydrolysis of the calcium silicates studied was determined by an indirect method. Since the hydrolysis of the calcium silicates involves the liberation and crystallization of calcium hydroxide, the rate and extent of hydrolysis may be determined by measuring the amount of calcium hydroxide produced at any given time period. This was done by an application of the ammonium acetate method for the determination of uncombined lime (*13*). It was found, however, that the calcium hydroxide crystals were difficultly soluble in the reagents used. Therefore the calcium hydroxide was converted to the oxide by heating to a temperature somewhat above 530° C. (986° F.), the dissociation temperature of calcium hydroxide, for one hour. The hydrated calcium silicate residue was found not to be dissociated by this treatment. The lime resulting from the dissociation of calcium hydroxide could then be determined readily.

The above procedure could not be applied to the compounds containing alumina. When the hydration products derived from $3CaO \cdot Al_2O_3$, $5CaO \cdot 3Al_2O_3$, or $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ are heated to 400° C. (752° F.) or above, they break down with the liberation of calcium oxide. This has been found to be due to the formation of tricalcium aluminate hydrate when any of those compounds are treated with water, and the subsequent breakdown of that hydrate, on heating to 400° C. to form anhydrous $5CaO \cdot 3Al_2O_3$ and lime. The evidence for the hydration in that manner of these calcium aluminates will be given later. The decomposition of the tricalcium aluminate hydrate at 400° C. to $5CaO \cdot 3Al_2O_3$ and lime was demonstrated by both microscopic and x-ray examination, and the amount of lime formed during the heating indicates that the reaction proceeds practically to completion (*20*).

Because of the above reactions the extent of hydrolysis of the calcium silicates could not be determined in the presence of any of the alumina-containing materials.

The loss in weight obtained on heating to 1000° C. (1832° F.) a sample of the material which previously had been pulverized and dried at 105° C. (221° F.) for 24 hours is referred to in this paper as fixed water. The value obtained is not to be regarded as the total combined water of the sample, for it is probable that much of the water driven off at 105° C. is in some form of combination.

In some cases the fixed water of hydration was determined by noting the difference between the fixed water and the water of hydrolysis, which in this case is assumed to be the water combined as calcium hydroxide alone.

The heat treatment at 105° C. for 24 hours is sufficient to convert the gypsum almost, if not completely, to the anhydrous calcium sulfate (*16*).

Microscopic examinations of the hydrating materials were made at the end of 1, 3, 6, 12 months, and 2 years.

TABLE I. HYDROLYSIS OF CALCIUM SILICATES

COMPOUND		1 DAY	3 DAYS	7 DAYS	28 DAYS	3 MO.	6 MO.	1 YR.	2 YR.
C_3S	CaO in the form of $Ca(OH)_2$, %	11.3	15.2	17.2	18.0	18.1	19.3	19.1	19.2
	Hydrolysis, %	15.5	20.8	23.5	24.7	24.8	26.4	26.2	26.3
$\beta\ C_2S$	CaO in the form of $Ca(OH)_2$, %	0.1	0.1	0.2	0.5	0.5	0.3	0.6	0.6
	Hydrolysis, %	0.1	0.1	0.3	0.8	0.8	0.5	0.9	0.9
$\gamma\ C_2S$	CaO in the form of $Ca(OH)_2$, %	0.1	0.1	0.1	0.1	0.1	0.3	0.3	0.3
	Hydrolysis, %	0.1	0.1	0.1	0.1	0.1	0.5	0.5	0.5

TABLE II. FIXED WATER OF CEMENT COMPOUNDS CALCULATED AS PERCENTAGE OF ORIGINAL ANHYDROUS MATERIAL

COMPOUND	GYPSUM ADDED %		1 DAY	3 DAYS	7 DAYS	28 DAYS	3 MO.	6 MO.	1 YR.	2 YR.
C_3S	0	Fixed water	8.6	10.3	12.0	14.6	15.2	15.0	19.0	18.6
		Water in $Ca(OH)_2$	3.6	4.9	5.5	5.8	5.8	6.2	6.1	6.2
		Fixed water of hydration	5.0	5.4	6.5	8.8	9.4	8.8	12.9	12.4
		Same calcd. to silicate residue	5.6	6.4	7.9	10.8	11.5	10.9	15.9	15.4
	5	Fixed water	11.7	11.8	12.9	15.0	15.9	15.1	19.2	18.9
$\beta\ C_2S$	0	Fixed water	0.8	1.2	1.7	3.4	8.9	10.8	12.2	12.1
		Water in $Ca(OH)_2$	0.1	0.1	0.1	0.2	0.2	0.1	0.2	0.2
		Fixed water of hydration	0.7	1.2	1.7	3.2	8.8	10.7	12.0	11.9
		Same calcd. to silicate residue	0.7	1.2	1.7	3.2	8.8	10.7	12.1	12.0
	5	Fixed water	1.2	1.4	1.8	3.8	7.0	8.7	11.2	11.6
$\gamma\ C_2S$	0	Fixed water	0.4	0.4	0.5	1.0	1.3	1.9	2.4	3.4
	5	Fixed water	1.0	1.1	1.6	1.5	2.4	3.2	3.9	5.0
C_3A	0	Fixed water	30.2	31.4	32.4	34.9	36.7	36.2	36.9	38.5
	15	Fixed water	25.8	27.6	29.3	29.6	32.7	32.3	35.5	39.0
C_3A_3	0	Fixed water	32.5	35.6	35.4	35.5	36.8	37.1	40.7	40.7
	15	Fixed water	27.1	29.8	28.4	34.0	36.4	32.8	37.2	37.8
C_2F	0	Fixed water	5.7	5.9	5.7	5.8	6.2	6.6	7.1	7.6
	5	Fixed water	9.4	9.0	9.2	10.4	11.0	12.7	13.6	14.1
C_4AF	0	Fixed water	25.7	26.7	27.1	27.9	28.7	28.8	29.4	30.1
	15	Fixed water	22.0	23.5	24.0	25.6	30.4	30.0	31.6	31.9

X-ray diffraction patterns (powder method) were obtained and compared with patterns of the anhydrous compounds which previously had been studied (*6*). By this procedure it was possible to demonstrate the presence or absence of unhydrated compounds.

Tests of compressive strength of the neat materials were carried out as follows:

The glass around the specimens was broken away, the cylinders were placed in a clamp, and the ends were ground down to give a cylinder one inch long. These were then tested for compressive strength in duplicate at the ages of 1, 3, 7, 28 days, 3, 6, 12 months, and 2 years. Where the values obtained on duplicate specimens differed by more than 10 per cent, a third specimen was broken. The results given in the tables have been calculated to pounds per square inch.

The time of set and soundness (*2*) were determined with neat pats of the pure materials and with the same to which 5 per cent of gypsum had been added. The normal consistencies (*2*) were not determined, but the amount of water used in each case for these tests was the least quantity practicable for the preparation of a good pat and is indicated in the tables.

Calcium Silicates

Hydrolysis. The data obtained on the hydrolysis of the silicates by measuring the calcium hydroxide produced are given in Table I. In one day the tricalcium silicate had become about 15 per cent hydrolyzed (that is, the reaction,

$$3\ CaO{\cdot}SiO_2 + XH_2O = 3\ Ca(OH)_2 + SiO_2{\cdot}XH_2O$$

had proceeded 15 per cent towards completion) leaving a hydrated amorphous material of lower basicity than the original $3CaO{\cdot}SiO_2$. At 7 days the value of the hydrolysis had reached 23 per cent, and at 6 months, 26 per cent. After 6 months no further hydrolysis was observed up to 2 years.

The rate of hydrolysis of the dicalcium silicates was exceedingly slow. Scarcely over 0.1 per cent was hydrolyzed at one day. The beta dicalcium silicate was still under one per cent hydrolyzed at the end of a year and had advanced no farther at 2 years. The gamma dicalcium silicate was only 0.5 per cent hydrolyzed at 6 months and remained in that condition up to the 2-year period.

A microscopic examination of the tricalcium silicate hydrate at one month showed only a few grains of the original material, and at 3 months none of the anhydrous silicate could be found. The products were crystalline calcium hydroxide and an amorphous calcium silicate. Some of the crystals of calcium hydroxide were large enough to be identified by index determinations, but the greater number of them were present as extremely fine crystals dispersed through the amorphous material.

In the case of the hydrated dicalcium silicates, however, an abundance of unaltered beta or gamma material was found, even at the end of 2 years, by both the microscopic and the x-ray methods. Only traces of calcium hydroxide were found, and no other crystalline phase was observed.

These results on hydrolysis confirmed by further tests (not here recorded) indicate that the hydrolytic reactions do not proceed so far in pastes which are allowed to set to hard bodies as in powdered compounds that are held in suspension in large excesses of water. Previous studies (*14*), in which large excesses of water were used, have shown that the tricalcium silicate gives rise to a growth of crystals of calcium hydroxide within 24 hours and that hydrolysis continues until the composition of the residue is close to $3CaO{\cdot}2SiO_2$. The dicalcium silicates also were found to produce crystals of calcium hydroxide in 10 to 12 weeks and, somewhat more slowly than the tricalcium silicate, to approach the same composition of residue.

In the cement pastes reported in this investigation, however, the hydrolyses have advanced only a part of the distance to the above equilibrium composition. For the conversion of $3CaO{\cdot}SiO_2$ to the composition $3CaO{\cdot}2SiO_2$, 36.5 per cent of lime would be released to form calcium hydroxide and the percentage hydrolysis would be 50. For the conversion of $3CaO{\cdot}SiO_2$ to the composition of $2CaO{\cdot}SiO_2$, 24.3 per cent of lime would be released, and the percentage hydrolysis would be 33.3. The figures obtained (Table I) show but 19.3 per cent lime as calcium hydroxide, equivalent to 26.4 per cent hydrolysis, after 6 months with no further change at 2 years. Thus the tricalcium silicate, in the pastes used, hydrolyzed to a composition somewhat more basic than $2CaO{\cdot}SiO_2{\cdot}XH_2O$, an amount only 53 per cent of its equilibrium value (i. e., $3CaO{\cdot}2SiO_2{\cdot}XH_2O$) based on the above assumptions. In a similar way it was shown that the beta dicalcium silicate hydrolyzed to only 3.7 per cent of its equilibrium value in 2 years.

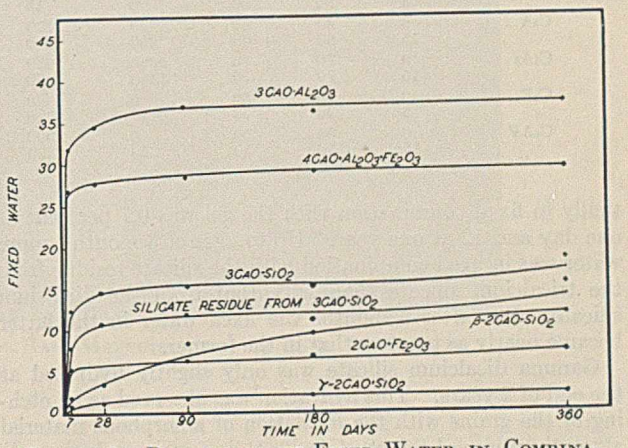


Figure 1. Percentage of Fixed Water in Combination with Pure Compounds

Hydration. The data on fixed water of hydration are given in Table II and Figure 1. The tricalcium silicate has taken up in some form of fixed combination over 8 per cent of water in one day and 19 per cent at the end of a year. When the amount of water combined in these samples as calcium hydroxide, shown in the second line of Table II (calculated from the data in Table I) is subtracted from the total fixed water, the values given in the third line are obtained. These values represent the fixed water of hydration in combination with the calcium silicate residue; they are recalculated in the fourth line to show the percentage of fixed water of hydration on the basis of 100 per cent silicate residue. That is, the lime which has been broken off by hydrolysis, and is thus combined as calcium hydroxide, is subtracted from the original weight of calcium silicate. The difference is referred to as silicate residue. The water combined with this residue divided by the weight of the residue, multiplied by 100, gives the values of the fourth line. These values increase from 5.6 per cent at one day to 15.9 at one year.

Beta dicalcium silicate hydrated very slowly. At the end of one month the grains appeared only slightly etched with an amorphous layer forming around the edges. At the later periods the amount of amorphous material increased and the amount of unhydrated beta dicalcium silicate decreased, but at the end of 2 years there still remained a large amount of the unhydrated material. Not more than a trace of calcium hydroxide could be identified in these samples and no other new crystal phase appeared.

The amount of water combined with the lime in the hydration products of the beta dicalcium silicate is almost negligible. In the case of this silicate the amount of water ac-

TABLE III. COMPRESSIVE STRENGTH OF CEMENT COMPOUNDS

(Calculated from cylinders 15/16 × 1 inch)

Compound	Gypsum Added	Mixing Water	Total Water Used	Compressive Strengths (Average of Two Specimens Only)							
				1 day	3 days	7 days	28 days	3 mo.	6 mo.	1 yr.	2 yr.
	%	%	%	Pounds per square inch							
C_3S	0	35	50	1450	2800	5960	7100	7100	9690	10,300	11,300
	5	35	50	1770	2780	5830	6760	6330	8700	9,800	11,300
β C_2S	0	30	50	0	60	140	910	5160	7560	10,250	14,350
	5	30	50	0	90	220	1200	3900	7700	9,800	12,600
γ C_2S	0	50	50	0	15	15	40	70	100	130	330
	5	50	50	0	15	15	40	60	140	190	480
C_3A	0	60	60	30	170	250	600	670	890	1,090	800
	15	60	60	600	900	1000	1580	1280	1770	1,320	1,330
C_3A_3	0	70	70	680	930	1620	1900	2000	1910	2,020	1,900
	15	70	70	1480	1670	..	1860	1860	1970	2,090	2,000
C_2F	0	30	50	0	0	0	0	0	0	0	0
	5	30	50	0	0	0	0	0	0	0	0
C_4AF	0	50	50	0	300	290	360	380	580	650	720
	15	50	50	20	390	440	720	1110	1330	1,420	1,500

tually in fixed combination with the gel was 0.7 per cent at one day and 12 at one year. Up to ages of 3 months, more water was in fixed combination with the silicate residue from the tricalcium silicate than with that from the dicalcium silicate. But after 6 months the fixed water in the latter became nearly as great as that in the former.

Gamma dicalcium silicate was only slightly hydrated at the end of 2 years. This hydration was observed as an etching of the grains with the formation of amorphous material along the edges of the crystals.

An examination of the hydrated calcium silicates which remained following the reactions with water indicated that they were quite amorphous. The index of refraction was not constant but appeared to vary with the method of drying. Since some investigators (*7*, *18*) have reported that fine needle-like crystals are produced on the hydration of the calcium silicates, a special search was made for such crystals, using a paraboloid condenser with a dark-field illumination. The calcium silicates used throughout this study were examined and also a number of samples especially prepared on glass slides. These samples, mixed with various amounts of water, were allowed to hydrate on the slides for periods of 7 days to 4 months. In no case could any hydrated crystalline calcium silicate be found.

The x-ray diffraction patterns of these hydrates showed no lines to indicate a new crystalline structure of the hydrate at any age up to 2 years.

ACTION OF GYPSUM ON CALCIUM SILICATES. When 5 per cent of gypsum is added to the calcium silicates, the rate of hydration is somewhat accelerated, especially during the first few days. This relation is shown in Table II.

CEMENTING PROPERTIES. The results obtained on the compressive strengths and other cementing properties of the neat cylinders (Tables III and IV) agree well with results previously obtained by Bates and Klein (*4*). Tricalcium silicate was found to set in a manner similar to normal Portland cement and to give good compressive strengths at early ages. The strength increased slowly after 28 days. The beta dicalcium silicate had very low strength at 7 days, but after a month the strength increased steadily, the two silicates having strengths of the same general order at one year. The gamma dicalcium silicate remained soft and weak at all ages up to 2 years. These data are plotted in Figure 2.

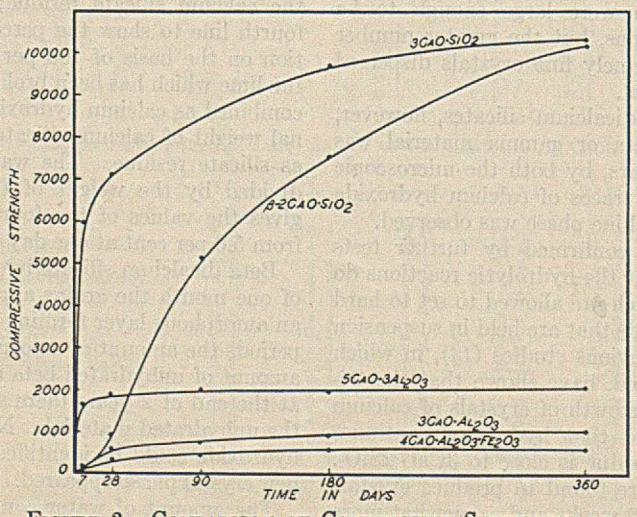


FIGURE 2. COMPARISON OF COMPRESSIVE STRENGTHS OF CEMENT COMPOUNDS

(In pounds per square inch)

TABLE IV. TIME OF SET BY GILLMORE NEEDLES AND SOUNDNESS OF CEMENT COMPOUNDS

Compound	Gypsum Added	Water Used	Initial Set	Final Set	Steam Test
	%	%	Hours	Hours	
C_3S	0	30	3.7	6.0	OK
	5	30	4.2	6.0	OK
β C_2S	0	22	4.7	24.0	OK
	5	22	4.5	24.0	OK
γ C_2S	0		Does not set		
	5		Does not set		
C_3A	0		Not determinable		
	15	45	2.3	6.0	OK
C_3A_3	0	45	0.1	0.3	OK
	15	45	0.1	0.3	OK
C_2F	0	20	0.3	1.0	Flaked
	5	20	0.5	6.0	OK
C_4AF	0	43	0.1	0.3	OK
	15	43	1.5	2.8	OK

The addition of 5 per cent of gypsum somewhat retarded the initial set of the $3CaO \cdot SiO_2$ and improved its one-day strength but showed no certain effect on the strengths at later ages.

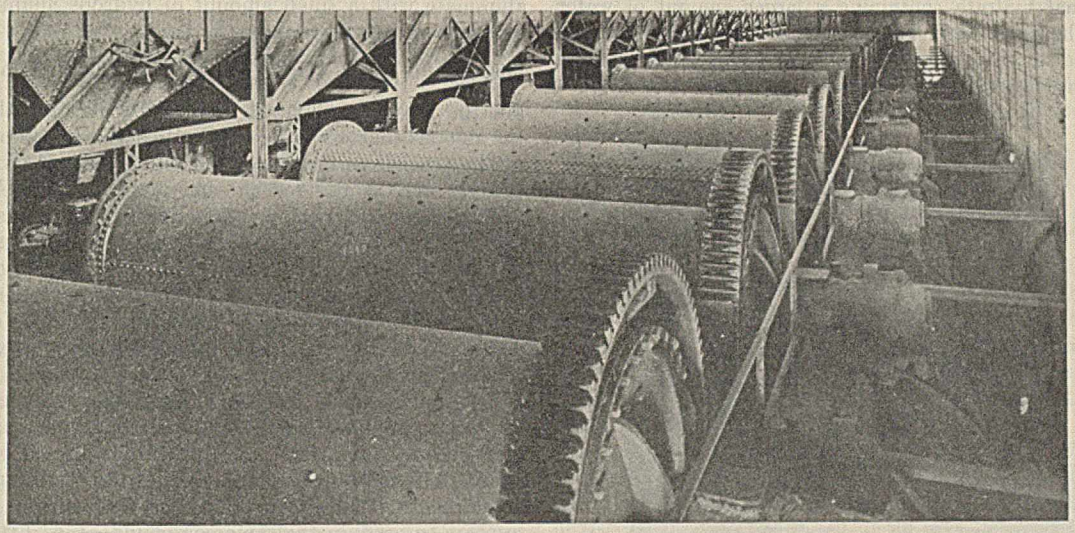
It will be recalled that these specimens were protected from the air; hence the setting and hardening were not influenced by the carbon dioxide. Richardson (*17*) had suggested that carbon dioxide is necessary to the hardening of beta dicalcium silicate.

The observations described above bring out some indications of special interest:

(1) The compressive strengths developed by the calcium silicates of Portland cement appear to be brought about chiefly by the formation of the colloidal calcium silicate hydrate, but there is some indication that calcium hydroxide may contribute somewhat to the strengths developed.

(2) The strength increases are not proportional to the hydrolysis of the calcium silicates, for the $2CaO \cdot SiO_2$ hydrolyzes only slightly up to 1 or 2 years but develops high strength in that time.

(3) The strength increases are not strictly proportional to the total combined water or water of hydration, for the calcium silicates show no appreciable change in the fixed water or the fixed water of hydration between 1 and 2 years, whereas the strengths,



BATTERY OF TUBE MILLS FOR GRINDING RAW MATERIALS AND CLINKER

especially of the $2CaO \cdot SiO_2$, increase during that period. During the earlier periods, however, there is some similarity between the rate of development of strength and the water of hydration of the two calcium silicates.

It seems probable that the strength which may be developed by the colloidal silicate hydrate is determined by the structure and the nature of hydration of the gel. The structure is established by the fineness of the original solid phase and the amount of water present in the paste at the time of set. The density will increase and the pore space of the paste will decrease as the fineness is increased and the water content decreased. Greater compressive strengths result.

Some unpublished data from this laboratory have revealed something of the nature of the hydration of the calcium silicate grains. When water comes in contact with the grain, a film of hydrated calcium silicate is formed. Further hydration of the inner portions of the grain can then be accomplished only by the passage of water through the membrane or the reaction of the unhydrated, or lesser hydrated, material with water which already is combined near the surface as more highly hydrated silicate. Thus it appears that there may be a gradation in degree of hydration of a given grain from highly hydrated material at the surface to unhydrated crystals or partially hydrated amorphous material towards the center of the grain. A condition may obtain between two given time periods during which no appreciable change has occurred in the total combined water (water retained at 105° C. or 221° F.) but pronounced changes have occurred in the distribution of the remaining water (water liberated at 105° C.). At the earlier time the water may have been combined as a highly hydrated product near the surface of the grain and a slightly hydrated product at the center. At the later time the water may have penetrated deeper, leaving the entire grain in a more uniform state of hydration. Such a withdrawal of water from the surface to the interior also would make the bond between grains more rigid and probably result in greater strengths but would not be indicated by changes in the fixed water of hydration or water of hydrolysis.

Although the data obtained in the present study do not bear directly on the above hypothesis, it is felt that they strengthen the viewpoint that the compressive strength which may be developed by the calcium silicates is determined by the structure and the nature of the hydration of the colloidal calcium silicate gel.

CALCIUM ALUMINATES

THE PASTE. Tricalcium aluminate, by itself and with 10 per cent added lime, reacted vigorously with water, producing a rapid rise in temperature until the paste was steaming hot. This resulted in considerable drying, owing to loss of water as steam, and was accompanied by a flash set, but on the addition of more water and rapid working the paste became plastic and did not again assume a rapid set (*4*). In these cases the amount of water present with the material when placed in the vials was 60 per cent, as determined by ignition loss.

Tricalcium aluminate with 15 per cent of added gypsum acted very differently; there was only a slight rise in temperature, the addition of 60 per cent of water produced the desired plasticity, and there was no evidence of a flash set. The paste worked very much like the calcium silicates.

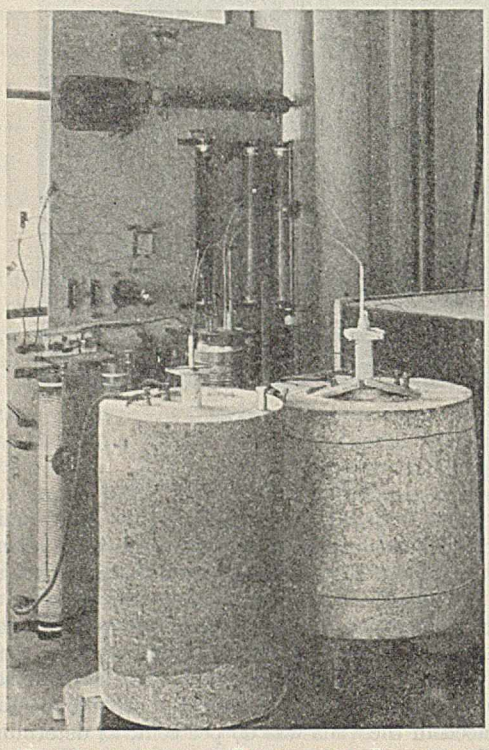
The 5–3 calcium aluminate required 70 per cent of water. This paste stiffened rapidly and gave only a slight rise in temperature. The addition of 15 per cent of gypsum produced no noticeable change in the rate of set of this compound.

HYDRATION. The aluminates hydrated very rapidly as shown in Table II and Figure 1. At one day the fixed water of the tricalcium aluminate had reached about 30 per cent. This increased to 35 per cent at one month and 38 per cent at 2 years. The values obtained for the $5CaO \cdot 3Al_2O_3$ were of the same order. In both cases the anhydrous phase could no longer be identified at the end of one month. The addition of 15 per cent of gypsum reduced the percentage of fixed water about 5 per cent with both aluminates at one day, and a somewhat lesser amount at later ages.

The product of hydration of the tricalcium aluminate was composed of fluffy aggregates of very fine crystalline grains of poor definition. These aggregates were isotropic, having a definite index of refraction of 1.605 ± 0.003. Klein and Phillips (*8*) allowed an excess of water to react with tricalcium aluminate on a microscope slide. Under those conditions they found the hydrated material to consist of hexagonal birefracting plates having refractive indices (*3*) of ω_D 1.520 ± 0.003 and ϵ_D 1.504 ± 0.003. In the neat pastes used in the experiments reported here, only a few such birefracting plates were found.

Thorvaldson, Grace, and Vigfusson (*20*) found that, when tricalcium aluminate is hydrated in water at room temperature, or hydrated in steam at 150° C. (302° F.), an isotropic hydrate is formed having the composition $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

A hexagonal hydrate containing a larger amount of water of crystallization could be formed at lower temperatures but tended to revert to the isotropic form. The hydrate obtained in this study was identified as $3CaO \cdot Al_2O_3 \cdot 6H_2O$.



FURNACES FOR THE EQUILIBRIUM STUDY OF CEMENT COMPOUNDS

The chemical nature of the isotropic grains was investigated by several means. The x-ray diffraction pattern showed a well-developed crystalline structure indicated by a number of strong lines. This pattern did not contain either the lines characteristic of unhydrated tricalcium aluminate or 5–3 calcium aluminate, or the lines of calcium hydroxide. However, the pattern obtained with the hydrated tricalcium aluminate, following heating to 600° C. (1112° F.) for an hour, showed that it had been converted to anhydrous 5–3 calcium aluminate and lime.

The absence of aluminum hydroxide in the hydration product of tricalcium aluminate was assumed by noting the solubility in dilute hydrochloric acid. The isotropic crystals dissolved completely. The product of hydration from the 5–3 calcium aluminate, however, gave by this test an amount of aluminum hydroxide which was nearly equivalent to that which would be liberated by the reaction:

$$3(5CaO \cdot 3Al_2O_3) + XH_2O = 5(3CaO \cdot Al_2O_3 \cdot XH_2O) + 4Al_2O_3 \cdot XH_2O$$

The x-ray pattern obtained on hydrated 5–3 calcium aluminate was identical with that of hydrated tricalcium aluminate except that the lines of hydrous alumina were present.

Some authors have suggested that, when tricalcium aluminate is hydrated in the presence of a saturated solution of calcium hydroxide, a tetracalcium aluminate is formed. Kuhl and Thuring (*9*) held that view, and Lafuma (*10*) concluded that in the hydration of tricalcium aluminate two new hydrated phases are formed—a hydrated tetracalcium aluminate and a hydrated dicalcium aluminate. He believed these to be formed in equal amounts and to coexist in equilibrium with each other. Lafuma considered the hydration product of 5–3 calcium aluminate to be essentially dicalcium aluminate with a small amount of hydrous alumina, in accordance with the reaction,

$$2(5CaO \cdot 3Al_2O_3) + XH_2O \longrightarrow 5(2CaO \cdot Al_2O_3) + Al_2O_3 \cdot XH_2O$$

but the insoluble alumina, as noted above, greatly exceeds the amount that would be obtained by this reaction.

The possible formation of the tetrabasic and dibasic compounds were considered in this investigation. A mixture was prepared of tricalcium aluminate with 10 per cent of lime. This was somewhat less than the theoretical amount of lime which would be required for the complete conversion of the tricalcium aluminate to hydrated tetracalcium aluminate. After 2 years no new phase was found by either microscopic or x-ray methods, but calcium hydroxide could readily be observed.

Thus by chemical, microscopic, and x-ray evidence, there appears to be but one product, crystalline isotropic hydrated tricalcium aluminate, $3CaO \cdot Al_2O_3 \cdot 6H_2O$, formed on the hydration of tricalcium aluminate under the conditions of these experiments. The hydration of the 5–3 calcium aluminate appears to produce the same compound—i. e., hydrated tricalcium aluminate, with the additional formation of hydrous alumina. The amount of this alumina formed is about the amount which would be required for such a reaction but is greatly in excess of that which would be produced if $2CaO \cdot Al_2O_3$ and hydrous alumina were formed, as suggested by Lafuma.

ACTION OF GYPSUM ON CALCIUM ALUMINATES. The hydration products of the calcium aluminates with added gypsum contained the isotropic aggregates as in the material without gypsum. Neither gypsum nor calcium sulfoaluminate was identified by x-ray or microscopic methods. It has been found difficult, however, to obtain a satisfactory x-ray pattern of calcium sulfoaluminate in the presence of $3CaO \cdot Al_2O_3$ hydrate, and it has been shown (*12*) that calcium sulfoaluminate may develop in a submicroscopic form, making microscopic identification impossible. In order to ascertain if the latter had occurred in this instance, samples at one year were pulverized and placed in distilled water. After a week the solution was filtered off and found on analysis to contain 0.006 per cent sulfur trioxide, a value which represents approximately the solubility of calcium sulfoaluminate. The solubility of gypsum is about 0.1 per cent sulfur trioxide. The fact that the tricalcium aluminate, hydrated with gypsum, gave on treating with water a solution with a sulfur trioxide concentration equivalent only to that of the calcium sulfoaluminate, indicates that the latter compound was probably formed even though its presence could not be demonstrated by microscopic means.

It appears that the marked influence of gypsum in retarding the set of tricalcium aluminate is due to the development of calcium sulfoaluminate. Because of the high insolubility of that compound, a large part of the calcium aluminate which enters the solution is withdrawn from it. That process continues until the sulfate ions have been exhausted and so delays the development of the crystalline hydrated tricalcium aluminate.

The failure of gypsum to retard the set of 5–3 calcium aluminate may be explained on the basis of the relative amounts of lime and alumina that enter into solution. It previously has been shown (*12*) that the rate of formation of calcium sulfoaluminate increases with increasing concentration of calcium hydroxide in the solution. But a larger amount of calcium hydroxide (a higher pH) is formed in a solution at equilibrium with $3CaO \cdot Al_2O_3$ than in a solution at equilibrium with $5CaO \cdot 3Al_2O_3$ (*14*). Also, the alumina liberated from the $5CaO \cdot 3Al_2O_3$ may tend to keep the pH of the solution in a sufficiently low range so that the formation of calcium sulfoaluminate will be retarded.

CEMENTING PROPERTIES. The compressive strengths of the calcium aluminates were low (Figure 2). Tricalcium aluminate in the absence of gypsum developed a strength of about 1090 pounds per square inch at a year, while with 15 per cent of gypsum a strength of 600 pounds was reached in one day and 1770 pounds in 6 months. The 5–3 calcium aluminate developed slightly greater strengths than the tribasic compound. Without gypsum it rose from 680 pounds at one day to 2020 pounds at a year. With 15 per cent gypsum the values were 1480 pounds at one day and 2090 pounds at one year.

COMPOUNDS CONTAINING FERRIC OXIDE

THE PASTE. The dicalcium ferrite required about 30 per cent of water to form a plastic paste, but no stiffening or temperature changes were observed.

The compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ required 50 per cent of water, and the mixture became somewhat granular because of agglomeration into balls. These appeared to hydrate rapidly on the exterior with the formation of an impervious layer which hindered the further penetration of water. There was a pronounced evolution of heat but not sufficient to cause steaming. In this respect the compound was similar to the 5–3 calcium aluminate. With the addition of gypsum the compound still required 50 per cent of water, but the mixture was smooth and there was no agglomeration. The paste showed a decided tendency to stiffen rapidly, but the evolution of heat appeared to be somewhat delayed.

HYDRATION. The dicalcium ferrite was found to hydrate only to a limited degree; even after 2 years only 7 per cent of water had entered into fixed combination with the ferrite, and a large amount of unhydrated material remained. Both microscopic and x-ray examinations indicated that the hydrate which is formed is amorphous. The refractive index was found to be about 1.70.

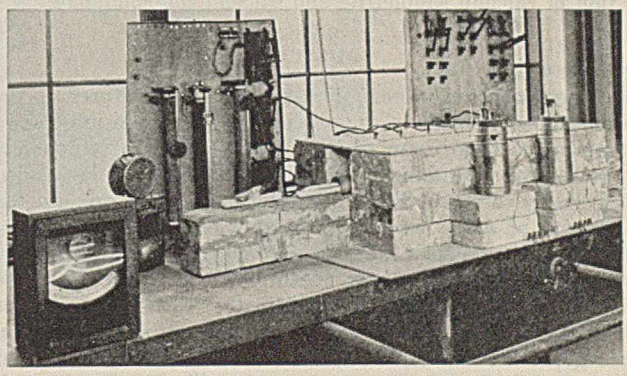
It seems probable that the product of hydration of dicalcium ferrite is an amorphous dicalcium ferrite hydrate. The evidence is not direct but is based on the following considerations: If there were formed some hydrated calcium ferrites more basic than dicalcium ferrite, they probably would be decomposed on heating to the temperature of dehydration (600° C. or 1112° F.) since no anhydrous calcium ferrites more basic than the dicalcium ferrite are known to exist (*19*). The breakdown of such polybasic ferrites would result in the liberation of some lime. When the product of hydration of the dicalcium ferrite was heated to dehydration and examined, no uncombined lime could be found. If hydrolysis occurred, on the other hand, with the formation of a less basic calcium ferrite, calcium hydroxide would be formed as the other end product. Calcium hydroxide could not be found in the hydration product, however, by either microscopic or x-ray examinations, or by an uncombined lime determination of the dehydrated material. The molar concentration of water contained in this hydrate cannot be determined at the present time because the reaction, which has been in progress for 2 years, is still far from complete.

The compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ hydrated rapidly, and at the end of one month the anhydrous phase had disappeared. The compound absorbed in fixed combination about 25 per cent of water in one day; this increased slightly, reaching 29 per cent at one year (Figure 1).

The hydrated product of the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ consisted of a crystalline phase and an amorphous phase. The crystalline material was isotropic and had an index of refraction of 1.640 ± 0.005, somewhat higher than that (1.605 ± 0.003) obtained for the tricalcium aluminate hydrate. The x-ray diffraction pattern, however, appeared to be identical with the pattern obtained with the tricalcium aluminate hydrate. It seems from this information that the crystalline hydration product of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is essentially tricalcium aluminate hydrate since identical x-ray patterns, without shift in position, indicate identical compounds. The raised indices are probably due to some of the hydrated, amorphous ferric oxide–containing material adhering to the surface of the crystals.

The amorphous phase formed on the hydration of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ has not been identified. The material is of reddish brown color because of the presence of the iron compound. If the crystalline hydration product is hydrated $3CaO \cdot Al_2O_3$, the composition of the residue will be one mole each of lime and ferric oxide. Since no crystalline calcium hydroxide has been observed in the hydration products of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and the x-ray pattern shows no evidence of the presence of hydrous ferric oxide, it seems probable that the residue consists of hydrated amorphous monocalcium ferrite.

ACTION OF GYPSUM ON COMPOUNDS CONTAINING FERRIC OXIDE. The addition of gypsum to the dicalcium ferrite resulted in an increase in the rate of hydration. The amount of fixed water was increased at all ages, and the rate with which the unhydrated material disappeared from the specimens was accelerated. In the neat pastes, however, no new compound could be found which might aid in an understanding of the accelerated hydration of the dicalcium ferrite. In order further to study the reaction, a small quantity of dicalcium ferrite was placed in a large excess of calcium sulfate solution. After a year a new crystalline phase was found to be present which did not occur when the dicalcium ferrite was placed in water. These crystals were short, broad, hexagonal, colorless prisms, indices $\alpha = 1.486 \pm 0.003$, $\gamma = 1.492 \pm 0.003$, parallel extinction, positive elongation, and uniaxial positive. These optical properties agree very well with those of the crystals observed by MacIntire and Shaw (*15*) to which they assigned the composition $3CaO \cdot Fe_2O_3 \cdot 3CaSO_4 \cdot XH_2O$. The similar crystals obtained in this study have not been sufficiently free from other products to warrant a chemical analysis, but the similarity in optical properties suggests that they may be the same as those reported by MacIntire and Shaw. The above formula was assigned by those authors by analogy with $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot XH_2O$, but no analyses could be made by them because of contamination with unreacted ferric oxide. Hence the exact composition is unknown.



LABORATORY FURNACE FOR THE PRODUCTION OF CEMENT

It is probable that this compound, which will be referred to as calcium sulfoferrite, has formed also in the neat pastes. It appears, therefore, that the more rapid hydration of the dicalcium ferrite in the presence of gypsum may be associated with the formation of finely crystalline calcium sulfoferrite.

The addition of gypsum to the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ resulted

in a decrease in fixed water for one month, beyond which time there was a slight increase. That is about the effect that would be anticipated if it were postulated that the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ on hydration broke down into tricalcium aluminate hydrate and a calcium ferrite hydrate. It is recalled that gypsum retards the hydration of the $3CaO \cdot Al_2O_3$ but accelerates the hydration of the $2CaO \cdot Fe_2O_3$. The order of values obtained when gypsum is added to $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is intermediate between those obtained with the above two compounds.

CEMENTING PROPERTIES. Dicalcium ferrite stiffened sufficiently to support the needles, indicating an initial and final set, in a short time. The pat, however, did not harden and the material failed to develop any appreciable strength at any age.

The addition of gypsum to the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ retarded the initial and final set of that compound. In the absence of gypsum a compressive strength of 650 pounds per square inch was obtained at one year, and in the presence of gypsum the compressive strength was raised at all ages, reaching 1420 pounds per square inch at one year. It appears probable that the increased strength of the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in the presence of gypsum may be associated with the formation of calcium sulfoferrite and calcium sulfoaluminate.

MIXTURES

GENERAL RELATIONS. The properties of mixtures of the cement compounds in the absence of gypsum in most cases represented the mean of the properties of the compounds which they contained. The addition of gypsum tended generally to retard the evolution of heat and to reduce the amount of water necessary to form a plastic paste.

The times of set (Table V) were not materially altered by the addition of gypsum to mixtures of the silicates or of the silicates with 5–3 calcium aluminate. The initial set was retarded, but the final set was accelerated by the addition of gypsum to mixtures of the silicates with $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The final set was likewise accelerated, but the initial set was unaffected, by the addition of gypsum to a mixture of the silicates with $2CaO \cdot Fe_2O_3$.

A few of the pats from compositions containing ferric oxide which showed an abnormally slow final set did not pass a satisfactory steam test. The pats, however, were not unsound in the true sense of the term; their condition was due rather to the abnormal set (*11*). The surface of the pats had dried and carbonated sufficiently to form a dense outer shell while the interior of the pat had not set. In the steam test this outer shell chipped and cracked, and the interior of the pat became honeycombed. With the addition of gypsum these same compositions gave satisfactory pats.

TABLE V. TIME OF SET BY GILLMORE NEEDLES AND SOUNDNESS OF MIXTURES

COMPOSITION	GYPSUM ADDED	WATER ADDED	INITIAL SET	FINAL SET	STEAM TEST
	%	%	*Hours*	*Hours*	
C_3S 50, βC_2S 50	0	25	3.9	6.3	OK
	5	25	3.9	6.3	OK
C_3S 42.5, βC_2S 42.5, C_4AF 15.0	0	28	1.5	24.0	Flaked
	5	26	3.5	5.8	OK
C_3S 42.5, βC_2S 42.5, C_2F 15.0	0	27	5.5	24.0	Flaked
	5	27	5.5	8.0	OK
C_3S 42.5, βC_2S 42.5, C_3A 15.0	0	32	0.4	6.3	OK
	5	29	3.0	5.5	OK
C_3S 42.5, βC_2S 42.5, C_5A_3 15.0	0	28	0.2	1.3	OK
	5	26	0.2	1.3	OK
C_3S 50, γC_2S 50	0	38	5.3	9.3	OK
	5	37	5.0	9.0	OK

The identification of the hydration products from the mixtures and laboratory cements was difficult because of the heterogeneous mixture of crystalline and amorphous materials present. In general, the microscopic and x-ray examinations indicated that the reaction products formed by the hydration of the mixtures are the same as would be expected from the pure compounds present. Crystalline calcium hydroxide could be identified by microscopic and x-ray methods in all compositions containing tricalcium silicate. Crystalline hydrated tricalcium aluminate could be identified in the compositions containing large amounts of alumina, either as a calcium aluminate or as $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

Compositions containing dicalcium silicate or dicalcium ferrite still contained some of those constituents in the unhydrated condition after 2 years. In most other cases the original constituents had disappeared at much earlier periods.

The factors which determine the compressive strengths that are developed in a mixture of materials are not, however, solely the additive values of the compressive strengths of the respective constituents. Many cases presented themselves in this investigation, as shown by the data in Table VI, in which the strength developed by a given mixture was not

TABLE VI. COMPRESSIVE STRENGTHS OF MIXTURES

(Calculated from cylinders $^{15}/_{16} \times 1$ inch)

COMPOSITION	GYPSUM ADDED	MIXING WATER	TOTAL WATER USED	COMPRESSIVE STRENGTHS (AVERAGE OF TWO SPECIMENS ONLY)							
				1 day	3 days	7 days	28 days	3 mo.	6 mo.	1 yr.	2 yr.
	%	%	%	*Pounds per square inch*							
C_3S, 85; C_3A, 15	0	46	50	2030	3620	5680	5730	5800	6,740	7,160	6,800
C_3S, 85; C_5A_3, 15	0	49	50	1360	2000	2580	2910	3320	3,030	3,650	3,580
βC_2S, 85; C_3A, 15	0	50	50	30	100	160	710	1710	2,680	3,090	3,700
βC_2S, 85; C_5A_3, 15	0	50	50	170	260	260	350	1140	4,930	5,000	6,460
C_3S, 50; βC_2S, 50	0	30	50	170	830	1530	5440	9280	11,500	11,900	12,600
	5	30	50	350	1000	1520	4930	8840	10,900	11,500	12,200
C_3S, 42.5; βC_2S, 42.5; C_4AF, 15.0	0	30	50	0	610	1000	2830	7540	9,060	9,300	9,500
	5	30	50	380	830	1290	3400	7900	10,200	10,700	11,100
C_3S, 42.5; βC_2S, 42.5; C_2F, 15.0	0	30	50	0	0	1130	2900	7600	9,900	10,200	10,500
	5	30	50	290	960	1770	5560	8050	9,720	10,500	11,000

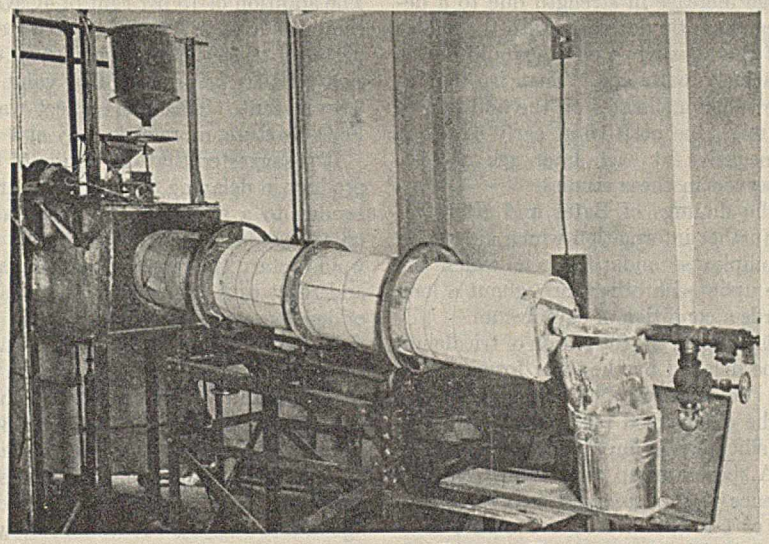
TABLE VII. FIXED WATER OF MIXTURES, COMPUTED AS PERCENTAGE OF ORIGINAL ANHYDROUS MATERIAL

COMPOSITION	GYPSUM ADDED	FIXED WATER							
		1 day	3 days	7 days	28 days	3 mo.	6 mo.	1 yr.	2 yr.
	%	%							
C_3S, 85; C_3A, 15	0	11.4	13.9	15.0	16.5	18.2	18.2	21.3	21.2
C_3S, 85; C_5A_3, 15	0	12.2	14.3	15.0	16.1	18.3	18.5	20.4	20.4
βC_2S, 85; C_3A, 15	0	4.3	4.8	5.1	7.4	12.2	13.9	17.0	18.8
βC_2S, 85; C_5A_3, 15	0	6.8	6.9	7.4	8.6	9.9	12.1	16.5	18.7
C_3S, 50; βC_2S, 50	0	4.6	6.6	6.9	9.9	11.5	13.0	14.9	15.3
	5	6.0	7.5	7.9	9.7	10.8	13.1	15.0	15.4
C_3S, 42.5; βC_2S, 42.5; C_4AF, 15.0	0	1.8	6.3	6.8	9.5	10.3	12.8	13.3	14.1
	5	5.3	6.4	7.2	9.3	11.3	13.5	15.2	15.7
C_3S, 42.5; βC_2S, 42.5; C_2F, 15.0	0	1.5	2.3	6.8	9.2	11.6	14.0	14.7	15.0
	5	5.5	7.0	7.6	9.9	11.2	14.4	15.2	15.8

the mean of the strengths of the constituent materials. An understanding of the underlying bases of these apparent inconsistencies would furnish an essential link in the interpretation of the strength of cement mixtures in terms of composition, in the absence of a retarder.

INFLUENCE OF ALUMINATES ON SILICATES. In the first two lines of Table VI are shown the strengths resulting from the addition of 15 per cent of $3CaO \cdot Al_2O_3$ and 15 per cent $5CaO \cdot 3Al_2O_3$, respectively, to $3CaO \cdot SiO_2$, in the absence of a retarder. In the third and fourth lines the strengths are shown resulting from the introduction of the same materials into β $2CaO \cdot SiO_2$. A comparison of these data with the strengths obtained on the pure $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ (Table III) shows the following effects:

1. The addition of 15 per cent of $3CaO \cdot Al_2O_3$ raises the strengths of $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ for 1 and 3 days but greatly reduces the strengths of the calcium silicates at later ages.
2. The presence of $5CaO \cdot 3Al_2O_3$ has a similar effect on the $2CaO \cdot SiO_2$ but lowers the strengths of the $3CaO \cdot SiO_2$ at all ages.



EXPERIMENTAL ROTARY CEMENT KILN

No difficulty arises in an understanding of the increase in early strength of $2CaO \cdot SiO_2$ on the addition of the aluminates, because the latter possess more strength than the $2CaO \cdot SiO_2$ for several weeks. But in the case of the mixture of $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ a strength is attained at early ages greater than that of either component compound.

The rapid combination of the aluminates with water decreases the amount of water that otherwise could be available to the silicates. A reduction in the water to cement ratio is known to increase strengths (*1*). Since the tricalcium silicate is the chief early strength-imparting compound, it is probable that a reduction in the water to silicates ratio likewise will tend to increase the strengths, especially at early ages.

The data given in Table VII show that the fixed water of the mixtures is essentially the algebraic mean of the fixed water of the constituent compounds at the several ages. Hence the effect of the calcium aluminates on the compressive strength of the calcium silicates in the absence of gypsum cannot be accounted for on the basis of a changed mean rate of hydration. Neither can it be accounted for on the basis of retarded hydrolysis, since the strength of the beta dicalcium silicate, which undergoes only slight hydrolysis, is also greatly affected by the presence of the calcium aluminates.

A few tests were made to learn if the presence of 15 per cent of $3CaO \cdot Al_2O_3$ produced an appreciable rise in the temperature of the paste. It was found that, in the small vials used, the dissipation of heat was sufficiently rapid to prevent a noticeable temperature rise because of the presence of the $3CaO \cdot Al_2O_3$. Hence the effect of the calcium aluminates cannot be accounted for on the basis of differences in the temperature of the pastes.

Some observations were made which suggest that the amount of hydrated tricalcium aluminate formed may be a factor in determining the strength of the mixtures. Tricalcium aluminate on hydrating in water or in calcium hydroxide solution probably combines directly with water as follows:

$$3CaO \cdot Al_2O_3 + XH_2O = 3CaO \cdot Al_2O_3 \cdot XH_2O$$

But $5CaO \cdot 3Al_2O_3$ hydrates to $3CaO \cdot Al_2O_3 \cdot XH_2O$ and $Al_2O_3 \cdot XH_2O$. The $Al_2O_3 \cdot XH_2O$ combines with lime, when available, to form an additional quantity of $3CaO \cdot Al_2O_3 \cdot XH_2O$. Hence in the presence of $3CaO \cdot SiO$ (or more specifically, the lime liberated from the $3CaO \cdot SiO_2$ on hydrolysis), the hydration of $5CaO \cdot 3Al_2O_3$ proceeds as follows:

$$5CaO \cdot 3Al_2O_3 + 4CaO + XH_2O = 3(3CaO \cdot Al_2O_3) \cdot XH_2O$$

Omitting water of hydration, 100 grams (3.5 ounces) of tricalcium aluminate will give 100 grams of tricalcium aluminate hydrate, whereas 100 grams of 5–3 calcium aluminate will give 138 grams (4.9 ounces) of tricalcium aluminate hydrate, when both are hydrated in calcium hydroxide solution—i.e., in mixture with $3CaO \cdot SiO_2$. The greater reduction in late strengths of $3CaO \cdot SiO_2$ obtained with the 5–3 calcium aluminate over that obtained with the tricalcium aluminate suggests that the late strength reduction is a function of the tricalcium aluminate hydrate formed.

This view is further corroborated by an examination of the influence of the aluminates on the beta dicalcium silicate. The dicalcium silicate has been shown to hydrolyze but very slightly under the conditions of these experiments. Hence, very little calcium hydroxide is formed. When $5CaO \cdot 3Al_2O_3$ hydrates in water, 100 grams of $5CaO \cdot 3Al_2O_3$ will form 77 grams (2.7 ounces) of hydrated tricalcium aluminate, if the water of hydration is neglected. Thus, in a mixture of $2CaO \cdot SiO_2$ with $5CaO \cdot 3Al_2O_3$, it would be expected that less hydrated tricalcium aluminate would be formed than from a similar mixture of the $2CaO \cdot SiO_2$ with $3CaO \cdot Al_2O_3$. The data obtained, as seen in Table VI, show that a greater reduction in the strength of the dicalcium silicate results from the addition of $3CaO \cdot Al_2O_3$ than from the addition of $5CaO \cdot 3Al_2O_3$.

From the above results it appears that the formation of the tricalcium aluminate hydrate may bear some relation to the lowering in the late compressive strengths of the calcium silicates which follows the addition of these calcium aluminates in the absence of gypsum.

In explanation of that influence, it is noted that the tricalcium aluminate hydrate crystallizes rapidly from the solution, which is supersaturated with respect to the hydrate, forming a fluffy structure of increased volume. A visual inspection of the set material shows also a rather open and porous structure in contrast to the more dense structure of the calcium silicate pastes. In a mixture of $3CaO \cdot Al_2O_3$ with the calcium silicates, water causes first the hydration of the aluminate, as it has been shown that this reaction is much more rapid than the hydration of the silicates. The formation of the relatively open structure, due to the crystalliza-

tion of tricalcium aluminate hydrate, in the absence of a retarding material, may be expected to separate the grains of the silicates and prevent the close contacts which are necessary for maximum adhesion or cohesion per unit of area. The results will be indicated by reduced strengths.

From the above discussion, it is suggested that the formation of tricalcium aluminate hydrate produces a structure, under the conditions of these tests in the absence of a retarder, which tends to reduce the strengths that otherwise would result from the hydration of the calcium silicates. The observed increases in strength at early ages may be accounted for by the reduced water available to the $3CaO \cdot SiO_2$ due to the presence of the more active $3CaO \cdot Al_2O_3$. It has been noted that the percentage increase in strength due to a decrease in the water to cement ratio decreases with the age at test. Hence the sum of the above two effects would be expected to increase negatively with age. That is, the increase in strength of the calcium silicates on the addition of the calcium aluminates might be positive at early ages but would be increasingly negative at each later age of test. This effect has been observed in these studies.

These data confirm the findings of Bates and Klein reported in 1917 and add further information which aids in an understanding of the complex secondary effects which the cement compounds have upon each other throughout a long period of approach towards a condition of equilibrium.

When calcium sulfate is present, the formation of tricalcium aluminate hydrate will be delayed by the prior formation of calcium sulfoaluminate. In this case the structure of the set material appears to be determined primarily by the hydration of the tricalcium silicate, and improved strengths may be expected to result. A special group of tests was selected to determine if the presence of gypsum confirmed these predictions. Mortar cubes of 1 to 3 mixtures of the pure compounds with sand, with and without gypsum, were prepared. These were mixed with equal quantities of water, cured in the moist closet 1 day, then stored in water and tested in compression at ages of 3, 7, 28 days, 3, 6, and 12 months. The data are given in Table VIII.

TABLE VIII. COMPRESSIVE STRENGTHS OF MIXTURES OF CEMENT COMPOUNDS

Composition		Gypsum Added	Water Used	Compressive Strengths (Av. of Two Specimens Only)					
				3 days	7 days	28 days	3 mo.	6 mo.	1 yr.
%		%	%	Pounds per square inch					
C_3S	85	0	40	1750	2300	4050	4700	5000	5300
βC_2S	15	4.3	40	2040	2620	4100	4600	4960	5260
C_3S	85	0	40	1700	2900	3700	3900	4100	4300
C_3A	15	4.3	40	1720	2650	3850	4200	4600	4950
C_3S	85	0	40	1090	1600	2150	4100	4400	4220
C_4AF	15	4.3	40	1600	2450	2900	3500	4300	4600

The presence of the gypsum somewhat improves the strengths of mixtures of the two calcium silicates at early ages. An improvement is noted in the strengths of the mixtures of tricalcium silicate with tricalcium aluminate, due to the addition of gypsum, especially at late ages, and in the strengths of the mixtures of that silicate with $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, both at early and at late ages. These data, together with the results of microscopic examinations, tend to confirm the belief that the gypsum permits the structure of the set specimens to be determined by the hydration of the tricalcium silicate. The formation of the tricalcium aluminate hydrate, which occurs later, then takes place by crystallization in the interstices of the silicate structure. The direct contacts are between silicate grains, not between aluminate grains, and the superior strengths in the presence of the gypsum appear to be the result of the prior establishment of the structure by the tricalcium silicate.

INFLUENCE OF FERRIC OXIDE-CONTAINING COMPOUNDS ON SILICATES. When the compounds containing ferric oxide were added to a mixture of tricalcium silicate and beta dicalcium silicate in the absence of a retarder (Table VI), reductions in strength occurred which were greater than could be due to the diluting influence. The effects differed from those of the aluminates in that the reductions occurred at early ages as also at later periods.

In this case it appears that the amorphous hydration product of the ferric oxide may affect the rate of hydration of the silicates. The data (Table V) show that the presence of the compounds containing ferric oxide retards the final set and (Table VII) delays the rate of hydration. For example, the mixture of equal parts of tricalcium silicate and beta dicalcium silicate combines with 6.9 per cent of water in 7 days. The addition of 15 per cent of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, which alone combines with 27.1 per cent of water in 7 days, would be expected to raise the combined water of the mixture at that period to 10.0 per cent. The value obtained, however, was 6.8 per cent. This same effect was found with the $2CaO \cdot Fe_2O_3$ mixture, more especially at 1 and 3 days.

It is suggested that the action of the ferric oxide hydration product in delaying the rate of hydration of the silicates may be due to a precipitation of the amorphous calcium ferrite on the grains of calcium silicate. Such an amorphous film would retard the rate with which water could come in contact and react with the calcium silicates and thus retard the rate of development of strength.

It seems probable that the tricalcium aluminate hydrate which is formed on the hydration of the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ may be equally effective in determining the influence of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ on the silicates as of $3CaO \cdot Al_2O_3$, in proportion to the amount of the hydrate produced. A given percentage of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, however, does not produce as large an amount of tricalcium aluminate hydrate as an equal percentage of $3CaO \cdot Al_2O_3$. It would follow that the influence of the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ should be less than that of $3CaO \cdot Al_2O_3$ at the later ages. This was found to be the case.

The presence of gypsum was found (Tables VI and VIII) to improve the compressive strengths of the mixtures containing ferric oxide compounds, both at early and late ages. The effect of the gypsum on the tricalcium aluminate hydrate component of the hydration product of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is probably identical with its effect on the $3CaO \cdot Al_2O_3$ hydrate formed on the hydration of $3CaO \cdot Al_2O_3$. By delaying the rate of formation of that hydrate through the prior formation of calcium sulfoaluminate, the structure of the set cement may be expected to be determined by the tricalcium silicate. Furthermore, the formation of calcium sulfoferrite, which is crystalline, should hinder or prevent the formation of the colloidal calcium ferrite hydrate. If the latter is responsible, as seems likely, for a delayed impenetration of water to the unhydrated grains, its elimination may be expected to result in a normal hydration and normal development of strength. All of the data bear out this deduction, for both early and late strengths are raised to the order of their normal values by the presence of gypsum.

CONCLUSIONS

The outstanding conclusions that may be drawn from this study are as follows:

1. Results found in the literature are confirmed that tricalcium silicate and beta dicalcium silicate are the compounds chiefly responsible for high compressive strength in Portland cement, gaged with water to make a plastic paste.
2. Tricalcium silicate reacts with water rapidly, both by hydrolysis and hydration; beta dicalcium silicate remains practically unhydrolyzed but combines with water to form fixed water of hydration, very slowly during the first month but approaching the hydration value attained by the tricalcium silicate in a year.

3. The products of the reaction of water on tricalcium silicate, under the conditions of these experiments, are crystalline calcium hydroxide and an amorphous hydrated calcium silicate of composition approaching $2CaO \cdot SiO_2 \cdot XH_2O$. The beta dicalcium silicate hydrates to approximately the same amorphous hydrated silicate, but only traces of crystalline calcium hydroxide have been observed.

4. The rate of development of compressive strength appears not to be determined by hydrolysis or by the total fixed water of hydration. It appears, however, to be established by the structure and nature of hydration of the colloidal calcium silicate hydrate. The distribution of the water is an essential factor as well as the total amount of water in combination.

5. The compounds containing alumina react rapidly with water to form a fluffy crystalline isotropic hydrated calcium aluminate of a composition $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

6. The alumina-containing compounds, mixed with the calcium silicates, in the absence of a retarder tend to raise the early strength and lower the late strength of the mixtures. It is suggested that the reduction in the water available to the $3CaO \cdot SiO_2$, due to the addition of $3CaO \cdot Al_2O_3$, may be responsible for increases in early strength and that the reduction in strength at late ages may be associated with the development in the paste of tricalcium aluminate hydrate. The influence of this compound is attributed to the rapid development of a weak and open structure by the crystalline tricalcium aluminate hydrate, thus preventing optimum contacts of the hydrating calcium silicate grains.

7. The $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ reacts with water to form an amorphous hydrate, the composition of which has not definitely been established, and crystalline $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

8. The $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$, mixed with the calcium silicates, in the absence of a retarder lower the compressive strengths of the mixtures. It is suggested that this may be due in part to the precipitation, upon the grains of the hydrating calcium silicates, of amorphous $CaO \cdot Fe_2O_3$ hydrate, thus retarding the rate of impenetration of water and reducing bonding action.

9. Gypsum reacts with the alumina that enters into solution, with the formation of crystalline calcium sulfoaluminate, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$. This occasions a delay in the development of the crystalline hydrated tricalcium aluminate and so retards the initial set.

10. Gypsum tends to counteract the influence of alumina in lowering the compressive strengths of the calcium silicates. It is suggested that this favorable influence may be associated with a retardation in the development of the tricalcium aluminate hydrate, owing to the prior formation of calcium sulfoaluminate, thus permitting the structure of the set paste to be established by the hydrating tricalcium silicate.

11. Gypsum also tends to counteract the influence of the ferric oxide–containing compounds in lowering the compressive strengths of the calcium silicates. It is suggested that this favorable influence may be associated with the formation not only of calcium sulfoaluminate as above but also of calcium sulfoferrite and the consequent reduction in the amount of the amorphous ferrite hydrate that can be deposited on the grains of the calcium silicates.

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Transmission of Light by Egg Albumen

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THE interpretation which may be placed upon certain phases of the candling appearance of eggs has recently come under widespread question and investigation. It has become clearly evident that an elaboration of the factors which influence the candling appearance of eggs is greatly needed. One of these is the ability of egg albumen to transmit light. It is the purpose of this paper to present results obtained in a study of this property of egg albumen.

Preparation of Samples

Samples were prepared by breaking out twelve eggs singly on screens and separating the three layers of albumen, as described by Almquist and Lorenz (*3*). The outer liquid, middle gelatinous, and inner liquid layers were each thoroughly mixed. Each was placed in a 5-cm. cell, and the transmission of light relative to air determined in a König-Martens spectrophotometer (Franz Schmidt and Haensch). The light source was the yellow line of helium with a wave length of 5876 Å. as obtained from a helium arc. The total percentage of dry matter and the percentage of mucin were also determined in most samples. The latter was obtained by diluting the albumen with five volumes of water, mixing thoroughly, and allowing to stand for 24 hours. The precipitated mucin was washed with dilute salt solution and finally several times with distilled water with the aid of a centrifuge.

The mucin content of the layers was determined because it seemed that there was a distinct influence of the quantity and physical state of this protein on the passage of light. It has been shown by Almquist and Lorenz (*2*) and McNally (*4*) that the mucin is responsible for the chief structural differences between firm and liquid white. Mucin differs from the other proteins in egg white in that it appears to exist in the form of translucent, long fibers, and exhibits a marked tendency to separate as a white solid at the higher hydrogen-ion concentrations of egg albumen. The direct transmission of light through egg albumen probably is affected to a large extent by these semi-solid particles or fibers of mucin.

Light Transmission

The transmission of light in the different layers of albumen does not change in proportion to the percentage of total solids in these layers (Table I). On the other hand, the correlation between the percentage of mucin and the transmission of light is very striking. The coefficient of this correlation was calculated by assuming an equation analogous to Beer's law for solutions. It is recognized, however, that the effect of mucin

on the transmission of light is much more complicated than the effect of a substance in true solution. The equation used was formulated as follows:

$$I/I_0 = 10^{-Kdc}$$

where I = transmitted light
I_0 = incident light
K = a constant
d = distance through which the light passes
c = percentage of mucin as determined by analysis

The ratio I/I_0 is defined as the transmission. It follows from this equation that the concentration of the absorbing substance is directly proportional to the negative logarithm of the transmission. The coefficient of correlation between the percentage of mucin and the negative logarithm of the transmission in twenty-four samples of fresh egg albumen was found to be $+0.82 \pm 0.05$, a value which is highly significant.

Of particular interest is the fact that the cold storage of eggs has a tendency to lower the transmission of light, especially in the middle and inner layers (Table I). The arrangement of these layers is such that the inner and middle layers present the greatest depth through which light must pass when an egg is candled. Since the transmission of light is an exponential function of the depth of the transmitting medium, the relative effect of these layers on the intensity of light passed through the egg from a candling lamp is much greater than the transmission values would indicate. This lowered transmission in the case of stored eggs may account for the common experience that eggs graded soon after removal from cold storage often present a better candling appearance than that of the same eggs when fresh, because of a less prominent yolk shadow.

TABLE I. MEAN VALUES OF LIGHT TRANSMISSION, PERCENTAGE OF MUCIN, AND PERCENTAGE OF TOTAL SOLIDS IN SAMPLES OF FRESH AND STORED ALBUMEN

Layer of Albumen	No. of Samples	Transmission	Standard Deviation of Transmission	Percentage of Mucin	Standard Deviation of Mucin Percentage	Percentage of Total Solids
FRESH EGGS (1 DAY OLD)						
Outer	8	0.915 ± 0.010	0.040	0.145 ± 0.022	0.092	11.70
Middle	8	0.482 ± 0.008	0.032	0.591 ± 0.049	0.205	12.21
Inner	8	0.808 ± 0.010	0.041	0.227 ± 0.027	0.114	12.87
COLD STORAGE EGGS (3 MONTHS OLD)						
Outer	5	0.890 ± 0.010	0.046	0.148[a]	...	12.40[a]
Middle	5	0.343 ± 0.056	0.187	0.768[a]	...	12.84[a]
Inner	5	0.590 ± 0.041	0.136	0.250[a]	...	13.20[a]

[a] Data from three representative samples only.

The translucency of the mucin fibers appears to be controlled by temperature as well as by the hydrogen-ion concentration. At cold storage temperatures and hydrogen-ion concentrations corresponding to pH values of 6 or 7, the mucin can be caused to separate as distinct white fibers. Storing egg albumen in a carbon dioxide atmosphere for a few days was found to cause a marked lowering of the transmission of light (in the case of the middle layer almost to zero) and a more opaque or cloudy appearance.

Eggs with relative impervious shells, such as the "glassy" shells described by Almquist and Burmester (*1*) or very fresh eggs which have been oil-dipped, retain more carbon dioxide than do normal eggs and show a marked tendency to develop a cloudy albumen in cold storage, a fact which may be ascribed to the low temperature and relatively low pH. If the cloudy condition has not existed for a long period of time, it will be found to decrease slowly when the albumen is removed from the shell and allowed to warm to room temperatures and to lose carbon dioxide. Cold storage eggs which are regraded several days after removal from storage often show surprising differences in comparison with their candling appearance immediately after removal; this may be ascribed, in part, to a decrease in the opacity of the mucin caused by increased temperature and increased opportunity for the loss of carbon dioxide. This increased light transmission, and consequent increased visibility of the yolk, may be the reason, in part, for the common opinion that cold storage eggs deteriorate rapidly when removed from storage.

Storing egg albumen in the presence of ammonia gas caused a marked increase in the transmission of light, especially in the middle and inner layers. Almost no mucin could be obtained from this alkaline albumen. It is well known that newly laid eggs have appreciable amounts of carbon dioxide in the albumen but that this tends to escape rapidly through the shell while, and at the same time the albumen becomes more alkaline (*5*). In alkaline albumen a slow destruction of the mucin probably takes place.

The values for the percentage of mucin in the inner layers are, on the average, greater than those obtained from the outer layers, a fact which does not agree with the report of McNally (*4*) that the inner layer contains only relatively minute quantities of mucin.

SUMMARY

The transmission of light varies in different layers of egg albumen, being lowest for the firm or gelatinous layer. The transmission of light is correlated with the percentage of mucin in the albumen and varies with the temperature and pH, which affect the physical condition of the mucin. The changes in the transmission of light due to these factors cause differences in the candling appearance of eggs, which are not necessarily correlated with changes in interior quality.

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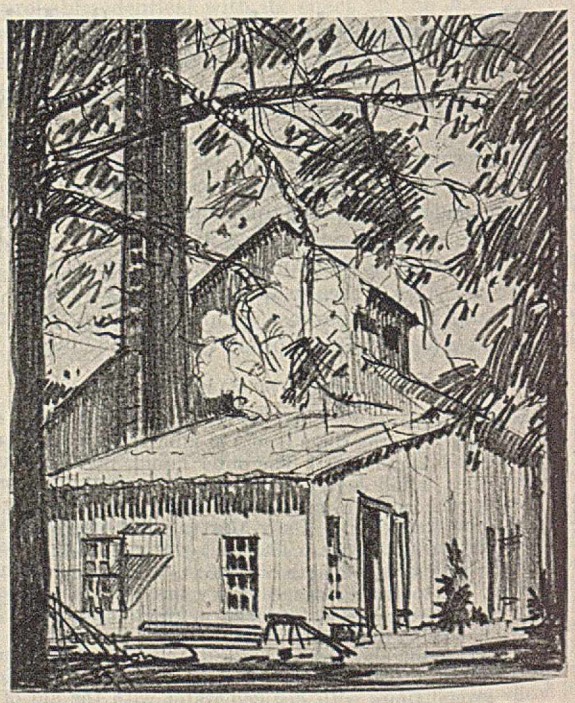

DU PONT POWDER MILLS, MOOSIC, PA., POWER PLANT

Removal of Fluorides from Drinking Water

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Fluorides in drinking water have been shown to be the cause of mottled enamel on teeth in America, England, Africa, and elsewhere. The present authors have developed a method of removing fluorides from potable water by adsorption by carbon. The process, however, has the handicap that at the time of treatment the water must be at a pH of 3 or less.

THE first reference to mottled enamel of teeth was made in 1901 in a report by Eager (*7*). Since then many articles have been written on the subject (*1, 6, 11, 12, 16–19*). However, it was not until 1931, when Churchill (*5*) indicated that fluorine might be the cause of the trouble, that this element was determined in water from endemic areas. The work of McKay (*13*) and the Smiths in Arizona (*6, 16, 19*) has definitely confirmed the fact that fluorine is the cause of the difficulty.

An article by Boruff (*2*) is the only one that has dealt with methods of removing fluorine from water. One criticism that may be made of his work is that no concentration in excess of 5.0 parts per million of fluorine was used, and even at this concentration the removals were not satisfactory. Many waters from western endemic areas vary from 5 to 8 p. p. m., and cases are known in which it is as high as 16.8 p. p. m., so that a limit of 5.0 p. p. m. is felt to be low.

Methods of Analysis

There are several suggested methods of analysis for small amounts of fluorine (*4, 10, 15*), but each had some objectionable features which made it unsuitable for use in the present experiments. The method outlined by Fairchild (*8*) and modified by Churchill (*5*) was followed in the first part of this investigation and has proved fairly satisfactory.

Since this work was started, other methods of analysis for small amounts of fluorine have appeared (*3, 9, 20, 21*).

In order to obtain satisfactory results with a fluorine range of 1 to 10 p. p. m., it was necessary to modify Churchill's method slightly. It was found that the ferric chloride solution could be reduced to one-third its original strength—i. e., to 0.00533 *M*—and still give satisfactory results, but that no dilution could be made in the thiosulfate solution.

Churchill stated that the flasks should be heated for 30 minutes to complete the liberation of the iodine, but it was found that this was not important, as variations of from 30 to 60 minutes in the time of heating at 38° C. did not appreciably alter the results.

Since the waters from the American endemic areas are alkaline, the "synthetic water" used in this work was New York city water to which was added the desired amount of sodium fluoride and which was made alkaline with 0.272 gram of sodium acid carbonate per liter, which is an average figure found in analyses of such waters. This amount of bicarbonate produced a pH of 8.3 but had no effect on the titration, as the increased amount of sodium thiosulfate consumed was within the limit of error of the method, being less than 0.10 cc.

All determinations were run in duplicate. Portions (250 cc.) of the synthetic potable water containing fluorine were measured out, and the required amount of acid and adsorbent was added. This gave sufficient volume so that, on filtering off the adsorbent and rejecting the first portion of the filtrate, there would still be over 200 cc. left—enough to pipet the two 100-cc. portions required for the duplicate analyses. Blanks were similarly put through but without any adsorbent, and the difference between the two titrations gave the amount of fluorine adsorbed.

Attempts were first made to remove the fluorine with iron and aluminum sulfates, but neither was of value. The amount of iron salt varied from 17 to 165 p. p. m. and the time of contact ranged from 30 minutes to 48 hours. In the case of the aluminum salt 83 p. p. m. were added and left in contact with the solution for 48 hours. In these experiments the reduction of fluorine was only 0.25 p. p. m. which was within the limits of error of the method. Boruff (*2*) showed that with aluminum sulfate there was a reduction of slightly more than 1.0 p. p. m. of fluorine at a pH of 8.0. The present lower removal may be explained by a different type of stirring. Boruff states that this is important. The authors used only the slightly alkaline water (pH, 8.3) for these salts, whereas Boruff varied his pH considerably. It was thought that, since ferric fluoride is nonionized, it might be more easily adsorbed. Therefore, a ferric salt was added to an acid solution of the water containing sodium fluoride. After a few minutes sufficient sodium carbonate was added to make the water alkaline again, the precipitate of ferric hydroxide was filtered off, and the filtrate was tested for fluorine, but there was no reduction.

The siliceous adsorbents used were two grades of Wyoming bentonite and one each of fuller's earth, H. S. C. Celite, and silica gel. To samples of the synthetic water 0.2 per cent by weight of adsorbent on the weight of the water was added. The material was left in the water for 16 hours and shaken from time to time. The adsorbent was then filtered off and the filtrate tested for fluorine. In no case was any of the fluorine removed. In these experiments the adsorbent was added to the water without changing its pH.

The next step was to add various amounts of acid and adsorbent. The pH of the original water was 8.3 which was reduced in small steps to 2.5. There was no removal of fluorine until the acidity had reached a pH of 3.6, and at 2.5 approximately one-half of the amount originally present was removed. While this was the first promising lead, it was far from the desired removal.

Removal by Carbon

The following four different carbons were next tested: (A) Norit, a commercial carbon produced from the charcoal of the European pine; (B) the residual carbon discarded by the soda pulp industry; (C) the same as carbon B activated with acid (*14*); (D) a war gas type of adsorbent carbon which is an anthracite coal activated with hot carbon dioxide gas.

No fluorine was removed by the A or D carbon. In fact, with carbon A the blank in all cases gave a higher thiosulfate consumption than the sample with the carbon. This indicated that something was leached out of this carbon which reacted with the thiosulfate.

Carbon B removed about half the fluorine at a pH of less than 3.0.

Carbon C showed real promise, and the greater part of the work was devoted to its study. Here, also, there was little removal of fluorine until the pH had been reduced to 3.6, and between this and 2.5 the removal of fluorine increased from approximately 30 per cent to complete adsorption,

TABLE I. RUNS IN THE CONTINUOUS APPARATUS

	Run 1, C Carbon		Run 2, C Carbon		Run 3, C Carbon		Run 4, B Carbon		Run 5, B Carbon		Run 6, B Carbon		Run 7,[a] B Carbon	
	pH	*P. p. m.*	*pH*	*P. p. m.*	*pH*	*P. p. m.*	*pH*	*P. p. m.*	*pH*	*P. p. m.*	*pH*	*P. p. m.*	*pH*	*P. p. m.*
Water	8.3	8.0	5.7	8.0	3.1	8.0	3.0	8.0	5.2	8.0	4.4	8.0	5.4	8.0
FILTRATE *Liters*														
0–2	6.6	6.0	6.7	6.0	6.4	2.0	6.6	4.0	6.4	8.0	6.7	8.0	6.7	8.0
3–4	6.8	...	6.2	8.0	3.3	...	5.7	0.0	6.1	...	6.3	5.0	6.5	...
5–6	7.0	8.0	6.1	8.0	3.1	0.5	4.8	0.0	6.0	8.0	6.2	5.0	6.3	6.0
7–8	7.2	...	6.5	...	3.1	...	4.5	0.0	5.9	...	6.1	...	6.3	...
9–10	7.3	8.0	5.9	8.0	3.1	1.0	4.2	...	5.9	6.0	6.1	5.0	6.1	5.0
11–12	7.5	...	6.7	...	3.1	...	3.8	...	5.9	...	6.1	...	6.1	...
13–14	7.4	8.0	5.8	8.0	3.1	3.0	3.5	0.5	5.9	5.0	6.1	5.0	6.3	7.0
15–16	7.4	...	7.1	...	3.1	...	3.3	0.5	5.9	...	6.0	...	6.5	...
17–18	7.5	8.0	7.3	8.0	3.1	4.0	3.3	...	5.9	6.0	5.9	5.0	6.4	6.0

[a] Ferric chloride (185 p. p. m.) was added to the water.

using the customary 0.2 per cent carbon based on water taken.

The efficiency of adsorption in relation to the pH of the solution is as follows, where 8.0 p. p. m. of fluorine was added:

pH	Per Cent Removed	pH	Per Cent Removed
6.90	4	2.53	99
3.57	49	2.38	99
3.16	88	2.25	100
3.01	100		

Thus complete removal is obtained at a pH of 3.0 or less, as the 99 per cent values may be taken as complete removal of the fluorine.

The efficiency of fluorine removal by the carbon, when only 0.08 per cent by weight of carbon on the weight of water was used, is as follows:

Fluorine Added	Fluorine Removed	Fluorine Added	Fluorine Removed
P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*
10.0	8.45	5.0	4.60
10.0	7.50	2.5	2.75
7.5	7.05		

This shows that 0.08 per cent carbon will remove practically all the fluorine from waters containing up to 7.5 p. p. m., and 80.0 per cent from water with 10.0 p. p. m. One part per million is the maximum that may be allowed in potable water if mottling of children's teeth is to be avoided. Since the majority of waters analyzed from the endemic areas showed 8.0 p. p. m. or less, then 0.08 per cent of carbon C would seem to be sufficient in most cases. This was confirmed by using a water containing 8.0 p. p. m. at a pH of 2.25, where 0.08 per cent carbon removed all the fluorine, but 0.04 per cent removed 76 per cent, and 0.02 per cent only 57 per cent.

The next step was to develop some method of continuous treatment which might have a practical application:

For this purpose a glass tube 40 mm. in diameter and 750 mm. long was filled to a height of 620 mm. with carbon. For these tests a sieved material passing a 16-mesh but held on a 30-mesh screen was used. The water was run in at such a rate that a constant, slight hydrostatic head was maintained during the run. Owing to packing of the carbon, there resulted a slight decrease in the rate of flow during the run. In run 7 there was a marked drop in the rate of flow due to the iron salt added to the water.

In order to follow the rate of adsorption of the fluorine, the effluent water was collected in 2-liter samples which were analyzed. This entailed a large number of analyses, and the Fairchild method would have been too slow. The method outlined by Thompson and Taylor (*21*) seemed satisfactory on test and was adopted with slight changes. The solutions were made up as follows: solution 1, 0.87 gram zirconium nitrate and 100.00 cc. water; solution 2, 0.14 gram alizarin red, 7.50 cc. normal sodium hydroxide solution, and 100.00 cc. water. The two solutions were mixed, allowed to stand for 3 hours, and then filtered. For the analysis 1.0 cc. of the reagent and 1.0 cc. of 5 *N* hydrochloric acid were added to 50.0 cc. of the water. Standard fluorine solutions were made up by increments of 2.0 p. p. m. from none to 10 p. p. m., and 1.0 cc. each of the acid and indicator was added to 50.0 cc. of the standard. There was a range in color from pink with no fluorine to a straw yellow at 6.0 p. p. m. Above this there was no appreciable difference in color. If the unknowns were above 6.0 p. p. m., it was necessary to dilute them in order that they might be compared to the standards. Tests showed that acid in excess of the 1.0 cc. added did not change the color of the standard solutions.

TABLE II. RATES OF FLOW IN THE CONTINUOUS RUNS

Filtrate *Liters*	Run 1	2	3	4	5	6	7
	Minutes						
3–4	..	7.25	7.75	3.5	3.75	4	3
5–6	5.5	..	..	..	..	..	..
9–10	..	8.5	7.75	..	5	5.25	6.5
11–12	6.25	..	..	4.75	..	..	..
15–16	6.5	8.5	9	..	6.25	6	9
17–18	..	..	..	5.75	..	..	..

In comparing Tables I and II with the earlier tables in which the small-scale batch tests were carried out, it will be seen at once that the results are of the same order in both cases—namely, that there is little removal of fluorine until the pH has been reduced to 3.0. In run 3 the poor removal of fluorine after the twelfth liter was run through was due to the fact that the limit of adsorption had been reached. The same 100 grams of carbon had been used for the first three runs of 20 liters each. In the fourth run fresh carbon (B) was taken, and this was effective for the entire 18 liters. As expected, the first few liters of the acidified water activated the carbon and made it effective.

In the five runs made on the acid side, in all cases the first 2 liters were always more alkaline than the rest, with resulting low fluorine removal. This is explained by the small amount of residual alkali present in the carbon resulting from its method of production.

The chief objection to this method of purification is that such a low pH is required before the flourine is removed. It was felt that the nonionized ferric fluoride might be more easily adsorbed. Several attempts were made in the small-scale tests to obviate this difficulty by adding ferric chloride to the water. The results were quite inconclusive. In run 7 three times the amount of ferric chloride required to form ferric fluoride was added, and the water was allowed to stand for 5 hours before passing through the carbon. Once more, with the alkaline solution, almost no fluorine was removed.

SUMMARY

This work has indicated that it is possible to remove the fluorine from water by adsorption. Several different materials have been tested; of these the carbons were the most promising and some were more efficient than others. The chief criticism of this work is that, even with the most efficient carbon, there is no removal of fluorine until the pH of the water has been reduced to about 3.0. Attempts to reduce to 1 p. p. m. or less the fluorine content of the water with a higher pH have been unsuccessful.

ACKNOWLEDGMENT

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Formation of Gas Hydrates in Natural Gas Transmission Lines

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Solid compounds, resembling snow or ice in appearance, are formed with methane, ethane, propane, and isobutane in the presence of water at elevated pressures and temperatures. The melting point of these mixed hydrates in a natural gas mixture depends upon the pressure and varies from about 34° F. at 110 pounds per square inch absolute to about 60° at 800 pounds.

The formation of gas hydrates in natural gas pipe lines depends primarily upon the pressure, temperature, and composition of the gas–water vapor mixture. After these primary conditions are fulfilled, the formation of the hydrates is accelerated by high velocities of the gas stream, pressure pulsations, or inoculation with a small crystal of the hydrate.

At equilibrium conditions the hydrates, because of their lower vapor pressure, cause more water to be removed from the vapor phase than in the case of liquid water at the same temperature and pressure.

THE presence of water vapor in natural gas has always been a source of trouble to the natural gas industry in the measurement and transportation of the gas. One of the chief difficulties has been the interruptions of service due to the liquefaction and subsequent freezing of the water within the system. The solid matter which collects in the pipe line usually resembles ordinary snow in appearance. The movement of the gas through the pipe line tends to collect and compress the snow at low spots until the line may become entirely plugged. The snow is honeycombed with small channels through which the gas passes before the flow is entirely stopped. The cause of this freezing has usually been attributed to subzero ground temperatures or to a combination of low temperatures with pressure fluctuations; the latter causes intermittent liquefaction and vaporization of the more volatile hydrocarbons, such as propane and the butanes.

However, it was discovered, during a series of experiments where natural gas and water vapor were compressed to 800 pounds per square inch, that freezing occurred at higher temperatures than would ordinarily be expected. Later the same observation was made on a commercial scale where the natural gas was compressed to about 600 pounds per square inch and cooled to 40° F. in a refrigeration unit (*1*, *2*) which was designed to remove the excess moisture and oil from the compressed gas.

These observations suggested the possibility of another and probably more general cause of freezing in natural gas systems than had heretofore been recognized. Therefore, the object of this investigation was to determine the causes of freezing at elevated temperatures and pressures together with such other factors as might affect the operation of a natural gas transportation system.

The combination of certain gases with water to form crystalline compounds (hydrates) at elevated pressures and at temperatures above the normal freezing point of water is a phenomenon that has not been generally recognized by the gas industry.

Schroeder (*7*) has reviewed the history of the discovery of gas hydrates: Humphrey Davy, in 1810, discovered the first known gas hydrate, a crystalline compound formed by chlorine and water. Wroblewski, in 1882, reported a carbon dioxide hydrate. Cailletet, in 1878, reported acetylene hydrate and was the first to discover that a sudden decrease in pressure aided in the formation of these crystalline compounds. Woehler, in 1840, reported hydrogen sulfide hydrate. Villard and de Forcrand have worked for more than 40 years on this class of compounds. Villard (*6*, *9*) reported hydrates of methane, ethane, acetylene, and ethylene. Schutzenberger reported the first double hydrate—hydrogen sulfide and carbon disulfide. Double hydrates are definite compounds having a definite melting point and are by no means a mixture of the single hydrates, since the decomposition temperature of the double hydrate may be entirely different from the decomposition temperature of either single hydrate. De Forcrand characterized that product, which was obtained from hydrogen sulfide and aqueous alcohol (Woehler, 1840) as a mixed hydrate of hydrogen sulfide and alcohol, and in addition discovered the great family of "sulfhydrierten" hydrates whereby hydrogen sulfide could be united with a great number of halogen-substitution derivatives of the aliphatic series, in hydrate form. Cailletet and Bordet, in 1882, discovered the double hydrate of carbon dioxide and phosphine. De Forcrand and Sully Thomas, in 1897, found that acetylene and carbon tetrachloride form a double hydrate. They also reported double hydrates of acetylene, ethylene, sulfur dioxide, and carbon dioxide with the following: ethylene chloride, ethylene bromide, methyl iodide, methyl bromide, methylene chloride, and methylene iodide. Hempel and Seidel also reported similar compounds

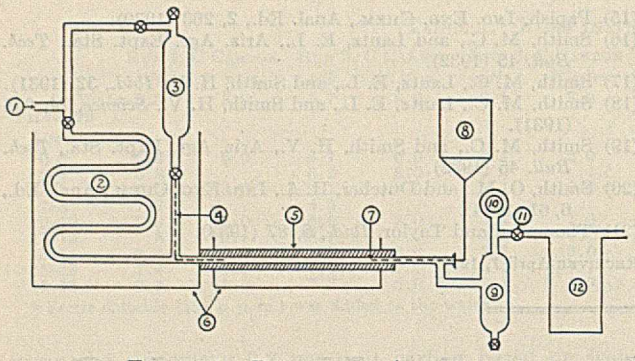


FIGURE 1. DIAGRAM OF APPARATUS

1. Gas inlet
2. 40 feet of 1/4-inch o. d. copper precooling coil
3. Water supply reservoir
4. Copper tube, 1/16 inch i. d., soldered to inlet water valve at one end and discharging into Pyrex glass tube at opposite end
5. Pyrex glass tube, 5/22 inch i. d. and 23/22 inch o. d.
6. Constant-temperature baths
7. Thermocouple junction
8. Millivolt meter
9. Drip
10. Pressure gage
11. Pressure-reducing valve
12. Meter

—e. g., carbon dioxide and ether. A gas hydrate of ammonia also appears to exist. Methyl mercaptan forms a crystalline hydrate with water (*8*).

Apparatus

A diagram of the experimental apparatus is shown in Figure 1:

The compressed gas was passed through a length of copper tubing, 2, which was immersed in a water bath, 6, at the same temperature as the water bath which contained the Pyrex glass tube. This precooling bath allowed the passage of gas through the apparatus at velocities which were comparable to actual operating conditions in pipe lines, and at any desired temperatures. Water was injected from 3 by gravity flow through the internal copper tube, 4, at the inlet of the Pyrex glass tube, 5. The temperature of the gas was measured by means of an iron-constantan thermocouple, 7, which was inserted in the glass tube through a stuffing box arrangement. The gas was vented to atmospheric pressure at 11 through the positive meter, 12. The pressure was measured with a Bourdon tube gage, 10, which had been calibrated by means of a piston gage.

The natural gas that was used for these experiments was taken directly from the pipe line after the gas had passed through (*a*) an oil absorption plant and (*b*) a refrigeration system where the gas was cooled to about 38° F. in order to remove the excess water and oil vapors. For pressures above 600 pounds per square inch, the gas was passed through a small motor-driven compressor, the discharge gas from this compressor being filtered through a plug of cotton in order to prevent the entrainment of lubricating oil.

The composition of this pipe line gas does not vary greatly, as shown by frequent analyses over a 2-year period. Typical analyses are given in Table I.

TABLE I. ANALYSES OF GASES

	Pipe Line Natural Gas		Gas from Pipe Line Snow
	%	%	%
Date sampled	6-8-33	8-28-32	1-3-33
Carbon dioxide	0.20	0.00	0.44
Nitrogen residue	7.19	5.11	6.46
Methane	82.50	82.70	56.95
Ethane	5.99	6.68	5.66
Propane	3.26	4.46	24.97
Isobutane	0.30	0.40	4.69
n-Butane	0.49	0.57	0.83
Pentanes, plus	0.07	0.08	0.00
Tota	100.00	100.00	100.00

Relationship between Pressure and Melting Point of Gas Hydrate

The formation or decomposition of the natural gas hydrate could be observed in glass tube 5 (Figure 1). The appearance of the hydrate usually resembled ordinary snow although at times transparent crystals resembling ice were separated. The transparent crystals formed only when there was no agitation of the melt.

In order to observe the melting point of the hydrate at various pressures, the flow of gas through the tube was stopped, and the gas was vented from the system until the desired pressure was obtained. The temperature of the bath was then slowly increased until the hydrate began to melt. The melting point was fairly sharp (within 1° F.) and duplicate results could be obtained. The temperature as recorded by the thermocouple could be checked during the melting point determinations (i. e., when there was no gas flow through the glass tube) by means of a mercury thermometer placed in the bath, 6.

The following relationship between pressure and melting point of the natural gas hydrate was determined from the experimental data (Figure 2):

$$Y = 8.9X^{0.285}$$

where Y = temp., ° F.
X = abs. pressure, lb./sq. in.

Primary Causes of Hydrate Formation

The formation of natural gas hydrates depends primarily upon the temperature, pressure, and composition of the gas. As shown by the melting point diagram (Figure 2), both high pressures and low temperatures are favorable to the formation of hydrates. In regard to the composition of the gas, water vapor is the only component that can be controlled on a practical basis. However, the removal of the moisture in the gas will of course eliminate the possibility of any hydrate formation. It is not necessary that the gas be entirely free from water vapor since these hydrates cannot form until the dew point of the gas is reached. As a matter of fact, if the partial pressure of the water vapor in the gas is less than the vapor pressure of the gas hydrate, the hydrate will lose water and decompose. This fact was demonstrated by passing some relatively dry gas over some gas hydrate in the glass tube (Figure 1):

The inlet gas had a dew point of approximately 30° F. at a pressure of 600 pounds per square inch. The temperature of the tube was maintained several degrees below the decomposition point of the hydrate or about 47° F. at 600 pounds per square inch. The test was continued for 5 days. A small amount of moisture which was present in the glass tube with the hydrate was removed first. Then the hydrate was slowly removed from the walls of the tube. The removal of the hydrate began at the inlet end of the tube, and there was a sharp line of separation (between the dry tube and the hydrate-coated portion) which marked the progress of the evaporating hydrate along the tube as the gas was passed through.

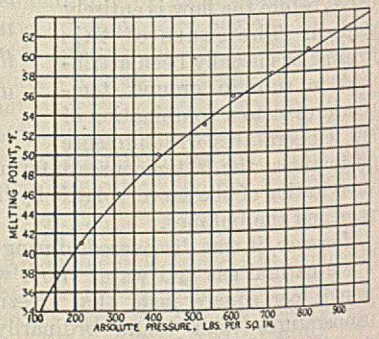
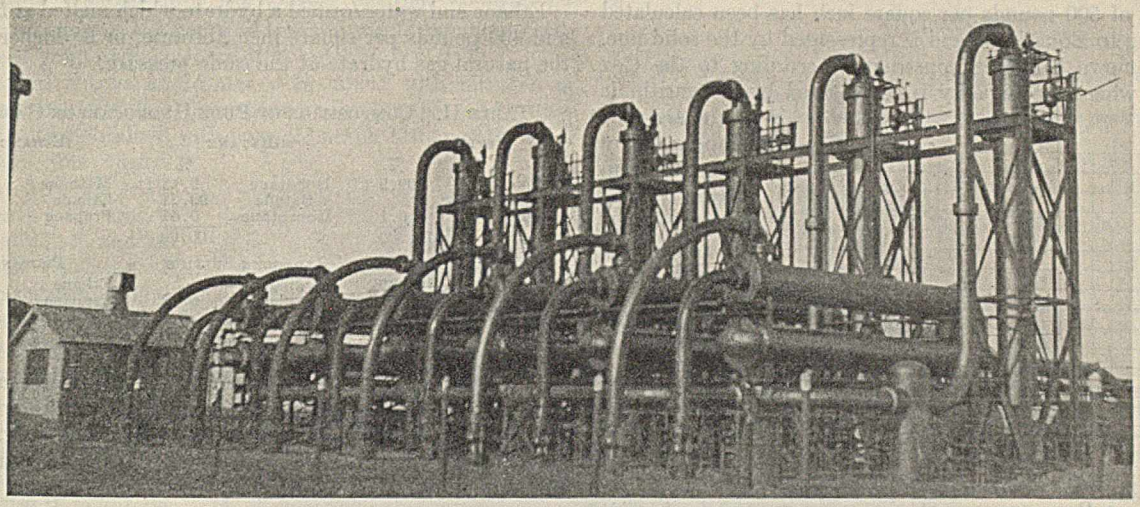


FIGURE 2. MELTING POINT DIAGRAM

Secondary Causes of Hydrate Formation

As stated above, a definite temperature, pressure, and composition are necessary before the gas hydrate is formed. However, even if these conditions are established, it is by no means certain that the hydrate will crystallize out. For example, there was no hydrate formation during a test which was conducted over a 40-hour period while a low flow of gas was passed through the glass tube which contained droplets



REFRIGERATION UNITS

Propane is employed as refrigerant in the vertical columns; the horizontal tubes are heat exchangers.

of water. The temperature was maintained between 32° and 40° F. and the pressure was 600 pounds per square inch absolute; i. e., the conditions were such that the existence of a hydrate was entirely possible.

There are, then, certain other secondary factors which influence the formation of hydrates. For example, it has been found that high velocities of the gas stream, pressure pulsations of the gas stream (due to compressors), or the introduction of a small crystal of the hydrate all hasten the formation of the hydrate. It has been demonstrated under actual operating conditions that the high velocity of the gas in the pipe line furnishes almost ideal conditions for the formation of hydrates, once the proper conditions of pressure, temperature, and composition are established.

These secondary causes of hydrate formation appear to be adequately explained by the general behavior of crystal formation as described by Eucken (*3*): "The formation of a crystal generally requires a certain arrangement and, above all, a definite adjustment of the molecules with respect to each other, the lack of which is characteristic of the liquid phase, and which cannot always be established at once. In general, a certain time elapses before the essential number of molecules come together into correct positions by purely accidental influences. Only after the formation of a small elementary crystal or crystallization nucleus, which then exercises a certain directing force on the neighboring liquid molecules and forces them to join together, does the crystallization proceed smoothly." From this, it appears that hydrate formation should be promoted by any force which tends to mix or stir the melt, because any such agitation increases the probability of bringing the essential number of molecules into the correct position required for crystallization. Both high velocities and pressure pulsations impart a mixing action to the droplets of condensed moisture.

Depression of Dew Point and Calculation of Fugacity of Natural Gas Hydrate

The presence of the gas hydrates in pipe lines causes a definite lowering of the dew point of the gas. This was proved by making a series of dew point determinations upon the exit gas from the refrigeration plant (*2*). The results of this dew point survey are shown in Figure 3 and include the time that the refrigeration unit was first placed in operation until the accumulation of gas hydrate had caused sufficient pressure drop across the unit to require a "defrosting" period. When the minimum temperature of the refrigeration unit was maintained at 38° F., the dew point of the exit gas was 25°; i. e., it was 13° lower than would ordinarily be expected. That this depression of the dew point was caused by the formation of the gas hydrate was proved by raising the temperature of the same unit from 38° to 60° F.—i. e., to a temperature where the gas hydrate could not exist at the operating pressure of 525 pounds per square inch (Figure 2). In this case the dew point of the exit gas was 60° or exactly the same as the minimum temperature to which the unit had been cooled.

The explanation of this apparently abnormal depression of the dew point lies in the fact that the vapor pressure of the gas hydrate is less than the vapor pressure of liquid water at the same temperature. When the water vapor in the gas mixture is in equilibrium with the gas hydrates, the partial pressure of the water vapor is less than it would be if the water vapor were in equilibrium with liquid water. In other words, less water in the vapor phase is required for equilibrium between hydrate and vapor than for equilibrium between liquid water and vapor.

While this depression of dew point increases the efficiency of a refrigeration plant whose purpose it is to remove water vapor from the gas, it is apparent that the same procedure in the pipe line will hasten clogging.

The fugacity of the natural gas hydrate may be calculated from the following observed data that were taken during the normal operation of the refrigeration plant (*1*):

Min. temp. to which gas is cooled, ° F.	38
Dew point of outlet gas—i. e., gas that is in equilibrium with gas hydrate, ° F.	25
Operating pressure, lb./sq. in. abs.	523

The following relationship has been shown (*5*):

$$\ln \frac{f}{p} = \frac{v}{RT}(P - p) \qquad (1)$$

P = total or operating pressure, lb./sq. in. abs.
f_h = fugacity of hydrate at pressure P, lb./sq. in.
f_w = fugacity of water at pressure P, lb./sq. in.
v = molal vol. of liquid (water)
p = normal vapor pressure of water, lb./sq. in.

From the above data the fugacity of the natural gas hydrate at 38° F. is calculated to be $f_h = 0.0685$ pound per square inch. Likewise, the fugacity of water at the same temperature and under the same total gas pressure is $f_w = 0.1157$ pound per square inch.

In Figure 4 the fugacity of water which is under a total

pressure of 500 pounds per square inch has been calculated according to Equation 1 and is represented by the solid line. The f_w curve has been constructed according to the Cox method where the fugacity is represented by a logarithmic scale and the temperature by a nonuniform scale so constructed that the resultant curve will be a straight line (*5*).

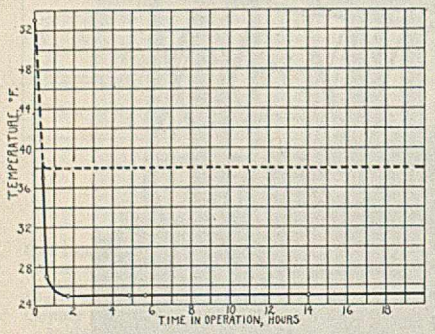


FIGURE 3. RESULTS OF DEW POINT SURVEY OF REFRIGERATION UNIT

Broken line, minimum temperature
Solid line, dew point of gas outlet

The broken line in Figure 4 was drawn parallel to the f_w curve and through the determined point $f_h = 0.0685$ and $t = 38°$ F. It should, therefore, represent the fugacity of the natural gas hydrate as formed from a gas whose composition is similar to that in Table I.

The data for the single determined point on this curve (Figure 4) was checked with three separate commercial refrigeration units, the same results being obtained in all three cases. Furthermore, proof that the fugacity curve for the gas hydrate is parallel to the fugacity curve for water was obtained by subsequent additional observations. These observations cannot be incorporated in the results of Figure 4 because the water in these latter tests was slightly contaminated with calcium chloride, and lower dew points were obtained. However, in these latter tests, dew points were measured at several different temperatures of the commercial unit—e. g., 42°, 46°, 47°, and 52.5° F.—and the results when calculated as in Figure 4 produce a straight line which is parallel to the fugacity curve for water.

CONSTITUENTS OF NATURAL GAS HYDRATES

A sample of pipe line "snow" was obtained by venting a section of pipe line which contained this snow to atmospheric pressure and removing some of the snow to a sample container where it was allowed to melt; the vapors evolved were collected for analysis. While the reduction of the pressure over the snow during the collection of the sample probably altered its composition somewhat, the results of the analysis of the evolved vapors gave some interesting information regarding the composition of the snow. The results of this analysis together with typical analyses of the original gas from the pipe line are shown in Table I. Both propane and isobutane are highly concentrated in the sample of pipe line snow.

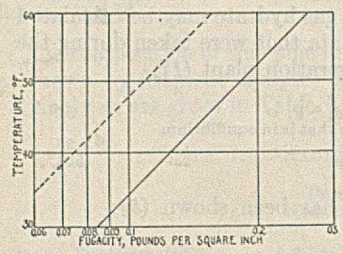


FIGURE 4. FUGACITY CHART

Solid line, fugacity of water at a total pressure of 500 pounds per square inch absolute
Broken line, fugacity of natural gas hydrate

A study was next made with pure hydrocarbon gases and water. The composition of these gases is shown in Table II.

Methane and water formed a hydrate which melted at 54.5° F. and 591 pounds per square inch absolute. This compares with 54.8° on the natural gas hydrate curve (Figure 2).

Ethane and water formed a hydrate which melted at 57° F. and 460 pounds per square inch absolute, or 6° higher than the natural gas hydrate at the same pressure.

TABLE II. COMPOSITION OF PURE HYDROCARBON GASES

METHANE	%	*n*-BUTANE	%	ETHANE	%
Methane	99.9	Isobutane	0.18	Methane	1.0
Ethane + propane	0.1	*n*-Butane	99.21	Ethane	97.0
	100.00	Isopentane	0.61	Propane	2.0
			100.00		100.0
ISOBUTANE		HYDROGEN SULFIDE		PROPANE	
Isobutane	100.00	Hydrogen sulfide	99.7	Ethane	Trace
		Water	0.3	Propane	100.00
			100.0	Isobutane	Ni
					100.0

Propane was mixed with nitrogen gas in order that the total pressure on the apparatus could be increased to conditions approaching actual pipe line operation—e. g., 600 pounds per square inch. The mixture of propane, nitrogen, and water formed a hydrate. The following melting point data were obtained:

PRESSURE	M. P. OF PROPANE HYDRATE	M. P. OF NATURAL GAS HYDRATE[a]
Lb./sq. in.	° F.	° F.
620	54.5	55.5
405	50.0	49.2

[a] From Figure 2.

The nitrogen gas was now purged from the system so that the propane hydrate was in equilibrium with pure propane vapor and water vapor. The melting point of the hydrate under these conditions was determined to be 45° F. at 163 pounds per square inch absolute. (While the vapor pressure of propane at 45° is approximately only 85 pounds per square inch, a total pressure of 163 pounds was possible because the inlet end of the glass tube was in communication with propane that was at room temperature or about 90° F. This condition necessitated the presence of some liquid propane in the glass tube.) This melting point is 7° higher than at the same pressure on the natural gas curve (Figure 2). This increase in melting point might be explained as follows: The hydrate exerts a definite vapor pressure. If an inert gas (nitrogen in this case) is mixed with the propane-water vapor over the hydrate, the same effect is produced as by reducing the pressure in an ordinary distilling flask, and in this way the partial pressure of the hydrate vapor will be reduced so that the hydrate will melt at a lower temperature than if the pure hydrate vapor is in contact with the solid hydrate.

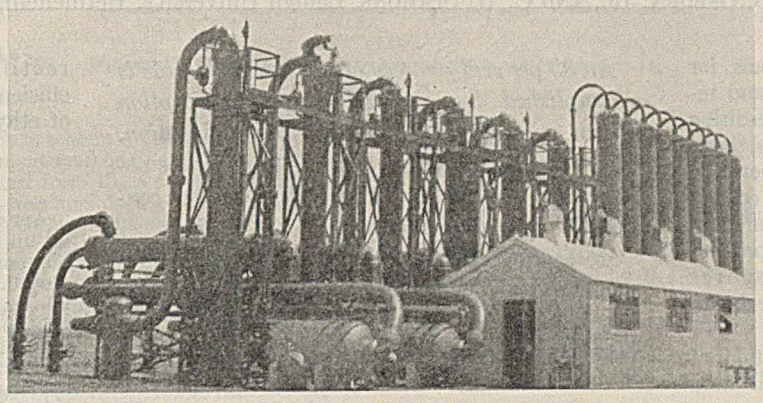
Isobutane and water were also mixed with nitrogen gas in the same manner as propane. It was more difficult to obtain a solid hydrate with isobutane than in the case of methane, ethane, or propane. The following melting point data were obtained:

PRESSURE	M. P. OF ISOBUTANE HYDRATE	M. P. OF NATURAL GAS HYDRATE
Lb./sq. in.	° F.	° F.
833	58	60
617	53.3	55.5

The difficulty in the formation of the isobutane hydrate in this case may be due to the relatively low vapor pressure of isobutane. For example, at 40° F. the vapor pressure of isobutane is roughly one-third as great as propane. Hence at any constant total pressure of a gaseous mixture in which propane and isobutane are constituents, the partial pressure of propane will be about three times greater than isobutane—i. e., the concentration of propane will be approximately three times greater than isobutane, provided there is excess liquid hydrocarbon in contact with the gaseous mixture. Therefore, the probability of bringing the essential number of

molecules together into the correct position required for crystallization of the propane hydrate would be about three times as great as in the case of isobutane.

Normal butane and water were mixed with nitrogen in the same manner as with propane and isobutane. A hydrate could not be obtained with normal butane, although the total pressure was varied from 500 to 800 pounds per square inch at 32° F. and at various velocities of the gas stream. The reason offered for the difficulty with which the isobutane hydrate was formed would also explain the nonformation of a normal butane hydrate. Likewise it might be reasonably assumed that all heavier hydrocarbons of the paraffin series do not form hydrates, at least under the conditions to which they would be subjected in pipe line operations.



Refrigeration Plant with Control Building in Foreground

Gasoline absorbing columns in right rear.

Nitrogen and water, or oxygen gas and water, did not form a hydrate at pressures as high as 900 pounds per square inch and temperatures as low as 32° F.

Table III. Data on Gas Hydrates

	T	T'	Q'	Q	Calcd. Formula	Probable Formula
			From de Forcrand (7)			
A	86	229.2	13.30	6.87	$A + 4.5H_2O$	4 or 5
CH_4	109	244	16.35	7.32	$CH_4 + 6.3H_2O$	6
CO_2	194.8	251.8	16.16	7.55	6	6
N_2O	185	253.7	16.29	7.61	6	6
C_2H_2	188	257.6	15.92	7.73	5.7	6
C_2H_6	185	257.2	17.71	7.71	7	7
C_2H_4	169	259.6	18.34	7.76	7.4	7
PH_3	188	266.6	16.44	8.00	5.9	6
H_2S	211	273.35	16.34	8.20	5.7	6
C_2H_5F	241	276.7	20.12	8.30	8.27	8
SO_2	263	280	19.83	8.40	8	8
CH_3Cl	250	280.5	18.83	8.41	7.2	7
Cl_2	238.4	282.6	18.36	8.48	6.91	7
Br_2	332	>273	?	?	10	10
H_2Se	231	281	16.82	8.43	5.87	6
			Calculated from data of this report			
CH_4	...	265.6	16.73	7.97	6.1	6
C_2H_6	...	266.9	16.92	8.01	6.2	6
C_3H_8	...	267.7	18.19	8.03	7.1	7

When hydrogen sulfide and water were admitted to the apparatus, the glass tube immediately became fouled, and it was impossible to determine visually whether a solid had formed. However a sudden pressure drop of 100 pounds per square inch across the apparatus was fairly conclusive evidence that a hydrate had formed.

Complexity of the Gas Hydrate Molecule

Wroblewski (7) determined the complexity of a number of gas hydrates in an indirect manner by means of gas volumetric measurements where he introduced a small drop of water of known weight into an eudiometer tube which contained the compressed gas at a definite pressure. After reading the volume of the eudiometer tube, the small drop of water was converted to the gas hydrate in which case the same volume of gas exerted a smaller pressure.

While this investigation did not include a study of the composition of gas hydrates, some data were obtained that permit the calculation of several of them according to the method employed by de Forcrand (7) who obtained the results, shown in Table III, by means of the following relationships:

$$Q' = Q + 1.430\,n \qquad (2)$$

or

$$n = \frac{Q' - Q}{1.430} \qquad (3)$$

where

Q' = heat of formation of hydrate (gaseous mol. and liquid water), Cal.

Q = heat of formation of hydrate (gaseous mol. and solid water), Cal.

n = no. of mol. of water in hydrate

1.430 = heat of fusion of 1 mol. of liquid water, Cal.

T' = m. p. of hydrate at atm. pressure, ° absolute

T = normal b. p., ° absolute

P_1 = vapor pressure at T_1

P_2 = vapor pressure at T_2

From Trouton's ratio:

$$Q/T' = K = 0.030 \qquad (4)$$

For a value of $K = 0.030$, de Forcrand claimed an accuracy of 1/15.

If the observed points on the melting point–pressure diagram (Figure 2) are plotted on logarithmic paper, a straight line results. If lines are then drawn through the experimentally determined points for methane, ethane, and propane, parallel to the curve for natural gas hydrate and extended to a pressure of one atmosphere, the value of T' may be read directly and the value of Q calculated from Equation 4.

Q' may be calculated from known vapor pressure data by means of the Clausius-Clapeyron equation which has been integrated by Findlay (4) as follows:

$$Q' = 4.572 \log \frac{P_2(T_1T_2)}{P_1(T_2 - T_1)} \qquad (5)$$

Values of Q' were calculated from data in the International Critical Tables.

The results of these calculations are shown in Table III where it may be seen that the formula for methane hydrate is the same as that calculated by de Forcrand while ethane hydrate contains one less molecule of water. Since propane hydrate has apparently never been reported, no comparisons can be made in this case.

Unfortunately the melting point data for isobutane hydrate cannot be used in the above manner because it was mixed with an indefinite quantity of nitrogen gas prior to the formation of the hydrate.

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Tower Absorption Coefficients

VI. Absorption of Ethylene Dichloride[1]

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An 85 per cent recovery of ethylene dichloride is accomplished by a countercurrent absorption system with kerosene, followed by rectification. In practical application, higher yields can be obtained by providing greater length of time of contact of carrier and extractor.

Absorption coefficients for an ethylene dichloride–kerosene system have been determined and vary with flow ratio, as shown in Figure 1. A logarithmic plot will yield a straight line.

RECOVERY systems for various organic and inorganic vapors, resulting from solvent treatments, have long been under consideration and development. The cost of the necessary equipment and the value of the recovered product are the determining features of the feasibility of reclamation.

A rather simple solution of such a problem is found in a countercurrent absorption system followed by rectification of the extractor. The success of such treatment is determined by the properties of the solvent to be recovered and its relationship to the extractor. Obviously, it is necessary to find an extractor which will easily dissolve the solvent under consideration and at the same time have a low vapor pressure and a boiling point not too close to that of the solvent.

The use of ethylene dichloride as a solvent in various industries results in waste gases containing as high as 10 per cent dichloride. The solvent is a colorless liquid having a specific gravity of 1.265 and a molecular weight of 98.95; it is slightly soluble in water and quite soluble in various organic liquids. The boiling point is 83.5° C.

A good extractor for such a substance is found in kerosene in which it is miscible in all proportions; the kerosene has a low vapor pressure and a boiling point well over 100° C. It is desired to show that a simple countercurrent absorption system of kerosene and ethylene dichloride–air, followed by rectification, provides an efficient means for the recovery of ethylene dichloride.

[1] Previous articles in this series have appeared in Ind. Eng. Chem. as follows: I and II, **19**, 989 and 991 (1927); III, **22**, 718 (1930); IV, **24**, 301 (1932); V, **26**, 529 (1934).

Procedure

Apparatus. An experimental set-up similar to that used by Simmons and Long (*2*) was employed. A Pyrex glass tower 90 cm. long and 7.25 cm. inside diameter was equipped for countercurrent absorption. The tower was packed with glass spheres having an average diameter of 1.85 cm. to a filled height of 68.5 cm. The drain-free volume ratio was determined and checked with previous work at 0.414, giving a gross volume of 2.83 liters and a drain-free volume of 1.175 liters. The wash oil used was kerosene of the following specifications:

Density at 20° C., gram per cc.	0.808
Molecular weight	168
Universal-Saybolt viscosity (21° C.), seconds	34

Air was supplied at constant pressure through a wet test meter, carefully dried in a large calcium chloride tube, passed through an electric furnace, and finally bubbled through ethylene dichloride. The amount vaporized depended upon the sensible heat of the air. Hence, careful control of the air temperature in the heater made it possible to produce any desired concentration of ethylene dichloride.

The air mixture was tested for ethylene dichloride before and after scrubbing by means of a bleeding system running directly to a modified Orsat.

The combustion of ethylene dichloride in excess oxygen is represented by the following equation:

$$2C_2H_4Cl_2 + 5O_2 \longrightarrow 4CO_2 + 4HCl + 2H_2O$$

A mixture of the ethylene dichloride with air was led into the usual measuring cylinder and ignited in a combustion chamber with excess oxygen; the products of combustion then passed

Table I. Absorption of Ethylene Dichloride

Test	$C_2H_4Cl_2$ In	$C_2H_4Cl_2$ Out	Extractor	Carrier	Mole Flow Ratio, f	Av. Pressure	Temperature Gas in	Temperature Extractor out	Operating Free Vol.	Absorption Coefficient, K
	%	%	*Gram-moles per min.*			*Mm. Hg*	° *C.*	° *C.*	*Liters*	
1	3.5	0.448	8.58	0.930	9.23	760.15	23.7	29.1	0.967	47.1
2	4.4	0.512	9.62	0.975	9.87	760.15	23.7	29.0	0.941	52.2
3	6.3	0.913	7.54	0.933	8.08	760.3	23.7	29.1	0.992	43.4
4	7.4	0.991	6.92	0.930	7.45	760.4	23.6	29.1	1.008	41.6
5	5.3	0.600	6.71	0.931	7.21	760.7	23.7	29.1	1.012	41.2
6	4.9	0.519	9.11	0.930	9.78	760.0	23.5	29.0	0.953	47.2
7	5.7	0.991	6.51	0.931	7.00	760.0	23.5	29.0	1.017	39.1
8	0.45	0.073	6.72	0.931	7.22	760.0	23.7	29.2	1.007	40.1
9	5.5	0.871	7.28	0.930	7.83	760.0	23.6	29.2	1.003	41.8
10	2.6	0.532	6.62	1.012	6.53	759.1	23.7	29.2	1.014	38.3
11	3.0	0.621	6.27	1.000	6.27	759.1	23.6	29.2	1.022	37.3
12	4.1	0.639	9.01	1.000	9.01	759.1	23.7	29.1	0.957	46.0
13	4.7	0.721	7.56	0.931	8.13	759.8	23.8	29.1	0.992	42.2
14	5.7	0.834	7.67	0.935	8.21	759.8	23.8	29.1	0.984	43.1
15	5.2	0.761	8.31	0.951	8.75	758.3	23.8	29.1	0.973	25.0
16	3.4	0.753	5.74	0.956	6.00	761.1	23.6	29.0	0.936	37.1
17	4.3	0.781	5.55	0.971	5.72	758.3	23.6	29.0	1.040	36.9
18	2.3	0.932	1.13	0.952	1.19	758.3	23.6	29.0	0.900	30.7
19	1.0	0.416	1.10	0.987	1.11	761.1	23.7	29.0	0.907	30.4
20	3.1	0.713	1.87	0.930	2.01	761.1	23.6	29.1	1.060	31.5
21	3.7	0.762	5.28	0.971	5.44	758.1	23.8	29.1	1.047	35.7
22	4.1	0.931	4.05	0.971	4.17	758.5	23.6	29.2	1.076	34.2
23	3.9	0.876	3.41	0.971	3.51	758.5	23.8	29.0	1.092	33.4
24	1.8	0.312	5.72	0.930	6.15	761.1	23.7	29.2	1.047	27.1
25	2.0	0.300	7.57	0.999	7.58	761.3	23.6	29.1	1.090	41.1
26	2.6	0.410	7.41	1.012	7.31	761.3	23.8	29.1	1.094	40.3
27	4.8	0.760	9.24	1.012	9.12	761.3	23.6	29.1	0.950	46.2
28	2.01	0.310	9.46	1.012	9.36	761.3	23.7	29.1	0.939	27.5
29	2.3	0.425	11.90	1.252	9.50	760.0	23.7	29.0	1.009	48.9
30	1.0	0.210	12.05	1.252	9.63	760.0	23.7	29.0	0.931	49.2

through water to remove the hydrochloric acid and water vapor, and the remaining carbon dioxide was absorbed in potassium hydroxide. This provided a quick method for determining the ethylene dichloride concentration in the air, as it is easily calculated directly from the carbon dioxide formed.

In order to determine the accuracy of this method, a measured quantity of air was bubbled through the dichloride in the bubble tower for one hour. The amount vaporized was determined by replacement method and the composition of the air mixture was calculated from these determinations. The Orsat analyses run on this mixture during the hour remained substantially constant and checked the determination by the method just described to two decimals in percentage composition.

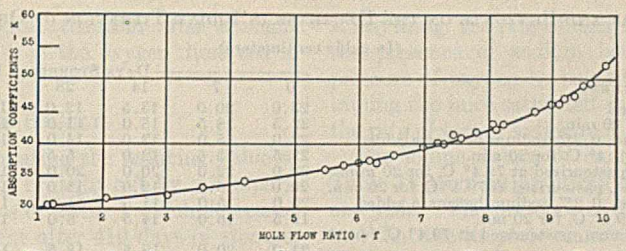

FIGURE 1. ABSORPTION COEFFICIENTS FOR ETHYLENE DICHLORIDE

The air supplied through the wet test meter had an average humidity of 26 per cent at 20° C. and corrections were made for this in determining the dry volumes used in the calculations. Each run was in operation for 30 minutes before any data were taken. These data, together with calculated values and absorption coefficients obtainable from the equation of Bennetch and Simmons (*1*), are listed in Table I. The coefficients have been plotted against mole flow ratio in Figure 1.

Rectification of the extractor containing various amounts of ethylene dichloride produced distillates with a maximum concentration of 0.02 per cent kerosene in the dichloride.

ACKNOWLEDGMENT

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Iodine Reducing Value of Orange Juice

Effect of Sodium Benzoate and Heat

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SINCE the report of Williams and Corran (*5*), based on biological assay, that sodium benzoate and various other substances which had a preservative action against gross fermentation of lemon juice exerted a destructive effect on vitamin C, two additional papers in which practically the same conclusion is reached have appeared. Bennett and Tarbert (*1*) claim as a result of very limited investigations that the use of any preservative which is efficient in preventing fermentation is followed by a decrease and eventually a disappearance of the indophenol reducing power of lemon juice. They conclude that in untreated juice the reducing factor is protected from atmospheric oxidation by the action of an enzyme which, if inhibited or destroyed by the usual means, results in rapid loss of reducing power. Cultrera (*2*) presents data based on 2,6-dichlorophenol–indophenol titration and on biological assay indicating that lemon juice preserved with 350 p. p. m. of sulfur dioxide rapidly loses its antiscorbutic power, thus confirming in part the findings of Bennett and Tarbert. Although it was early shown that vitamin C is readily destroyed by oxidation, especially at high temperatures and high pH values, the idea that commonly used food preservatives, such as sodium benzoate and sulfites, actually destroy antiscorbutic vitamin is novel and, if true, of great concern to the industry. The results of the above investigators, however, are contrary to those obtained by Morgan et al. (*4*) which indicated that sodium benzoate in concentration of 0.10 per cent was without effect on the vitamin C potency of sweetened orange juice. Certain results obtained in the course of this study of the changes occurring during the deterioration of orange juice seem to indicate that the destruction of reducing value and vitamin C content observed in preserved juices is due to oxidation rather than to some little-understood effect of the preservative. Prolonged storage studies made to determine the factors involved in the darkening of bottled orange juice indicated that the iodine reducing power of the juice was more rapidly lost under certain storage conditions than under others. Some of the early data obtained on the rate of loss of iodine reducing power of the juice has some bearing on this particular problem, and it is therefore presented at this time. Although the iodine reducing value may not be as specific a measure of ascorbic acid content of orange juice as 2,6-dichlorophenol–indophenol titration, it has recently been shown that it is fairly reliable in indicating relative changes in ascorbic acid content of orange juice exposed to air (*3*) as in the present investigation. If this is true, the results reported here indicate that destruc-

Data reported here show that the iodine reducing power of orange juices does not diminish a great deal in storage in the absence or presence of preservatives and/or heat treatment, provided oxidation is retarded or prevented from occurring by such procedures as vacuum-sealing or canning. In samples exposed to air the reducing factor is rapidly oxidized. The amount of loss of reducing value occurring is conditioned by the amount of available oxygen.

The writers believe that an enzyme protecting the reducing factor from atmospheric oxidation does not exist in fresh orange juice but that such a protective agency may be elaborated in fermented juice by the causative organisms.

It is concluded that the loss in reducing value of orange juice is due to oxidation and that preservatives of the benzoate type or heat treatment in the absence of air have no destructive action on the reducing power.

TABLE I. EFFECT OF HEAT AND BENZOATE ON THE DECREASE IN IODINE TITRATION OF ORANGE JUICE WITH STORAGE

(In cubic centimeters)

SAMPLE	TREATMENT	DAYS STORED AT ROOM TEMPERATURE 0	7	14	28	42	63	178	316	410
A	0.2% sodium benzoate added	23.0	20.0	13.5	12.0	13.5	8.5	15.0	14.0	7.0
B	Pasteurized at 79.4° C. for 20 min.	22.5	18.5	15.0	11.0	10.0	8.5	9.5	8.5	6.0
C	Pasteurized as above, opened, 0.2% sodium benzoate added	22.0	15.0	13.0	14.0	14.5	11.0	8.0	9.5	4.0
D	Deaërated, pasteurized at 79.4° C. for 20 min.	22.5	15.5	12.0	5.5	8.0	5.5	7.5	..	..
E	Deaërated, vacuum-sealed, pasteurized at 79.4° C. for 20 min.	23.0	22.0	20.0	20.0	19.5	20.0	17.5	16.5	14.5
G	0.2% sodium benzoate added, pasteurized at 79.4° C. for 20 min.	20.0	15.0	12.0	11.0	11.0	10.0	8.0	9.0	6.0
H	Pasteurized as above, opened, 0.2% sodium benzoate added	20.0	15.0	11.5	11.5	11.0	9.0	7.5	7.0	..
I	Deaërated, pasteurized at 79.4° C. for 20 min.	19.5	16.0	14.5	8.0	11.0	9.5	7.0	6.5	4.5
J	Deaërated, closed under vacuum, pasteurized at 79.4° C. for 20 min.	21.0	20.0	19.5	18.5	18.5	20.0	18.5	16.5	14.5

TABLE II. EFFECT OF EXCESSIVE AMOUNTS OF SODIUM BENZOATE AND OF TEMPERATURE OF HEATING ON THE DECREASE IN IODINE TITRATION

(In cubic centimeters)

SAMPLE	TREATMENT	DAYS STORED AT ROOM TEMPERATURE 0	7	14	21	28	42	81	274
L	2.0% sodium benzoate added	28.7	22.2	15.9	12.9	11.0	7.8	5.6	5.2
M	Pasteurized at 79.4° C. for 25 min.	27.8	16.5	13.6	8.5	8.0	6.3	3.3	3.2
N	Pasteurized at 100° C. for 25 min.	26.5	21.6	13.8	8.5	6.1	4.2	2.5	2.5

tion of ascorbic acid in preserved juices is due chiefly to oxidation.

In studying the effect of pasteurization and sodium benzoate upon the color changes occurring in orange juice stored in glass containers, the iodine reducing value was determined on the various samples at periodic intervals throughout the duration of the test. These values, recorded in Table I, represent the amount of 0.01 *N* iodine required to oxidize the reducing materials present in 50 cc. of orange juice.

The orange juice was extracted from fruit of the Valencia variety obtained from the Citrus Experiment Station at Riverside, Calif. Two lots of fruit at different stages of maturity, of the following analysis, were used:

	FIRST LOT	SECOND LOT
Total titratable acidity as % citric	0.852	0.656
Balling degree, 20° C.	12.50	12.70
Ratio, Balling/acid	14.7:1	19.4:1
Original iodine value, cc. 0.01 *N* I_2/50 cc. juice	23.0	21.0

Samples A to E in Table I were prepared from the first lot, and samples G to J from the second. Samples A, B, and C consisted of 200-cc. portions of strained juice placed in 225-cc. crown-capped glass bottles. Sample D consisted of 100-cc. portions in 225-cc. bottles. Sample E consisted of 100-cc. portions of juice packed in 120-cc. wide-mouth jars and sealed with an Anchor closure under a pressure of 15.2 cm. of mercury in a machine designed for this purpose. The size and style of bottles and the quantities of juice in samples G to I were similar to those of A, B, and C, while J corresponded to E in these respects. One bottle of juice was sampled at each time of analysis.

In order to confirm and extend the results obtained in the first test, a second series of samples was prepared one year later. In this test 100-cc. portions of Valencia juice were packed in 195-cc. crown-capped bottles and treated as shown in Table II. A large amount of sodium benzoate, ten times that added in the previous test and about twenty times that ordinarily used for preservative purposes, was added to lot L in order to accentuate its effect.

In a series of tests conducted to determine the effect of various metallic ions on the flavor and color of orange juice, it was observed that certain cations had a marked effect on color. Some tended to increase the rate of browning and others exerted an inhibitory effect toward color change. Chief among those increasing the rate of browning was Fe^{++}, while Sn^{++} protected orange juice from color change for longer periods of time. The decrease in iodine reducing values of juices containing 200 p. p. m. of Fe^{++} added as ferrous sulfate and 200 p. p. m. of Sn^{++} added as stannous chloride, in comparison with an untreated sample, is shown in Table III. The samples consisted of 130-cc. portions of filtered Valencia orange juice containing 0.2 per cent sodium benzoate, stored in cotton-stoppered 4-liter bottles at room temperature. The initial iodine titration on all three lots was 19.4; and the addition of Fe^{++} caused a definite initial decrease, whereas the presence of Sn^{++} resulted in an increase due to its iodine reducing effect. A 50-cc. portion was withdrawn periodically for titration.

The iodine reducing values of a set of experimentally canned Valencia orange juice samples after storage at room temperature and at 0° C. are shown in Table IV. The juice, after deaëration, was flash-pasteurized by passing it through an aluminum coil surrounded by hot water a few degrees higher than the temperature to which it was desired to bring the juice. The time of exposure to the various temperatures was less than one minute; the cans were completely filled with the hot juice, sealed, and cooled in running water.

Since it was noted that the rate of decrease in iodine reducing value, when all other conditions were constant, was limited by the availability and rate of solution of oxygen, a detailed study was made of the kinetics of the oxidation of juice as determined by iodine titration. Fifty-cc. portions of centrifugalized, freshly extracted Valencia orange juice were shaken in tightly stoppered 250-cc. Erlenmeyer flasks in a head space of air and of oxygen in a thermostat at 25° C. The iodine titrations were made periodically. Care was taken to maintain constant conditions of shaking and exposure. The juice for these tests was stored in partly filled 120-cc. containers closed under a pressure of 15.2 to 25.3 cm. of mercury for a few days at room temperature and afterwards at 0° C. Since only 70 cc. of benzoated juice were in each container, some oxidation took place. Thus, the iodine titration decreased from 32.9 to 31.2 in 5 days and remained constant on 4 succeeding days, after which it was used in these tests. Storage at 0° C. for 157 days resulted in a further slight decrease to 29.0. The results obtained are shown in Figure 1, based on titrations in duplicate or triplicate.

A comparison of the decrease in iodine reducing value of freshly extracted navel orange juice, of the same juice after addition of 0.2 per cent sodium benzoate, and after heating at 100° C. for 3 minutes was made in the same manner by shaking 50-cc. portions of the juice with oxygen for 6 hours. No marked difference between the rates of oxidation of these lots of juice was obtained; the values agreed within the experimenal error. Some difficulty was experienced in titrating the oxidized, strained navel juice in the presence of added acid since the end point was green rather than the blue of the starch-iodine.

Further tests with samples of benzoates or pasteurized orange juice stored in completely filled bottles did not give

any appreciable decrease in iodine titration after a slight initial decrease, probably because of the oxygen dissolved in the juice.

Discussion of Results

The role oxygen plays in decreasing the reducing value of orange juice in glass is strikingly brought out by a comparison of the vacuum-sealed samples of Table I which decreased in reducing value only 35 per cent after 410 days of storage, while all other samples except A decreased in reducing value by approximately 65 per cent after 63 days of storage. The variations in the titrations noted for A are, as explained below, ascribable to the presence of mold in certain samples. Slight changes in iodine value occurred in all pasteurized samples during the heating process, except in those which were vacuum-sealed. The greatest reduction in iodine value thereafter occurred during the first 14 days of storage. The limit to which the loss in iodine reducing value occurred was determined by the apparent removal of oxygen from the head space of the bottle. All the samples sealed at atmospheric pressure at the time of preparation were under from 2.5 to 7.5 cm. of vacuum when tested on the sixty-third day of storage. Further evidence that loss in iodine reducing value is an oxidative process was also furnished at this sampling period. It was noticed that certain samples of A and C were lighter in color than other members of the same series. Examination showed that these samples had considerable mold growth on the inside cork surface of the crown seal. When the iodine values of the light colored samples were compared with those of the dark colored samples they were found to be considerably higher—e. g., 16.5 for the former and 9.5 for the latter. The mold in this case had apparently competed with the reducing factor for the oxygen in the head space, and this accounted for the observed slower rate of oxidation.

The rate and amount of loss in reducing value was also controlled by the amount of oxygen present—that is, by the size of the head space. Samples A, B, and C, as already stated, contained 200 cc. of juice, allowing 25 cc. head space, while sample D, on the other hand, contained only 100 cc. of juice, allowing 125 cc. head space. Sample D, which was deaërated by subjecting the juice to a vacuum of 73.7 cm. for 10 minutes prior to treatment, in order to remove entrapped and dissolved oxygen gained during the extraction operation, darkened at a faster rate and to a slightly greater extent than A, B, or C.

This evidence indicates that decrease in iodine number is caused not so much by heating or sodium benzoate as by the oxygen in the head space of the container. Increasing the head space increases the rate of diminution of iodine reducing substances as shown in Table II. Large amounts of sodium benzoate had no more pronounced effect on loss of reducing value of the juice than did pasteurization. If anything, the rate of decrease in iodine number was less in the presence of sodium benzoate. Increasing the partial pressure of oxygen by substituting oxygen for air and maintaining the juice saturated with oxygen by shaking, increased the rate of loss of iodine reducing value as shown in Figure 1.

The iodine values of canned orange juices, as shown in Table IV, remain practically constant even after storage for one year. The presence of dissolved tin in the juice and the fact that the tin plate maintains a reducing atmosphere in the can probably account for this. Increase in iodine number due to the presence of dissolved stannous salts is responsible for the relatively high iodine reducing number of canned juice packed in plain tin cans. Increase in temperature of processing had little effect on the change of iodine reducing value.

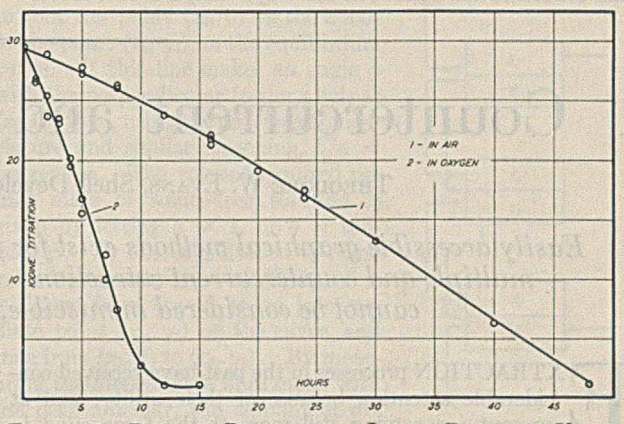

Figure 1. Rate of Decrease in Iodine Reducing Value of Orange Juice Shaken with Ample Supply of Air or Oxygen

Exposure of a large surface to air resulted in a more rapid rate of decrease in reducing value. Thus, in the data reported in Table III the presence of a good supply of air resulted in a more rapid rate of decrease in iodine reducing value, even in the presence of tin, than was found in Tables I and II for closed containers.

The previous investigators apparently did not control the oxidation of their samples during their tests. They do not indicate whether or not the juices were freed of oxygen and stored out of contact with air. The fact that their preserved juices actually decreased in reducing value indicates that oxidation probably took place. Their use of fermented or fermented and moldy samples as controls may be criticized on the basis that the elaboration of reducing principles by these organisms, the presence of carbon dioxide in the juice, or removal of dissolved oxygen from the juice by these organisms causes the conditions of oxidation in the control to

Table III. Effect of Iron and Tin Cations on Decrease in Iodine Reducing Value of Orange Juice in Open Containers

(In cubic centimeters)

Treatment	Days Stored at Room Temperature						
	0	1	3	5	7	9	17
Clarified, 0.2% sodium benzoate added	19.4	16.5	12.0	6.5	3.0	2.5	2.5
Clarified, 0.2% sodium benzoate plus 200 p. p. m. Fe^{++} added	17.0	13.0	9.5	5.5	3.5	2.5	2.5
Clarified, 0.2% sodium benzoate plus 200 p. p. m. Sn^{++} added	29.0	24.0	18.0	12.0	7.0	3.5	2.5

Table IV. Changes in Iodine Titration of Canned Orange Juice

(In cubic centimeters)

Sample No.	Treatment	Days Stored				
		0	9	115	242	367
1	Deaërated, flashed at 85° C.; plain tin cans	40.5[a]	33.5	33.5 (34.0)[b]	39.0 (36.5)	37.0 (37.0)
2	Deaërated, flashed at 79.4° C.; plain tin cans	34.0[a]	33.0	36.0 (33.0)	40.5 (36.0)	42.0 (37.5)
3	Deaërated, flashed at 73.9° C.; plain tin cans	35.5[a]	34.0	36.0 (34.0)	41.5 (36.5)	46.0 (38.0)
4	Deaërated, flashed at 85° C.; ordinary enamel cans	31.5	30.0	27.5 (29.0)	27.0 (31.0)	26.0 (31.0)
5	Deaërated, flashed at 85° C.; charcoal plate cans	32.0	33.0	30.0 (29.5)	32.5 (36.0)	30.5 (32.5)
6	Deaërated, flashed at 85° C.; dark colored citrus enamel cans	30.0	29.0	26.0 (28.0)	28.5 (30.5)	27.5 (30.5)

[a] Values may be high; about 2 hours elapsed after the opening of the cans and the iodine titration, during which time the plain tin cans became markedly detinned. In all subsequent tests the juice was removed to glass as soon as the tins were opened.

[b] Values in parentheses indicate samples stored at 0° C.; all others were stored at room temperature.

differ from that in the preserved samples. The presence of these organisms and spoilage of juice merely inhibited oxidation which was allowed to occur in the preserved samples. The authors have also observed the loss of reducing value in fermented orange juice exposed to oxidation after the discharge of the carbon dioxide by filtration by suction.

In the presence of reducing substances more readily oxidized by air than ascorbic acid, destruction by oxidation of vitamin C is inhibited until these are used up. From preliminary data it would appear that Sn^{++} and sulfites at certain concentration behave in this way. Experiments are now under way to determine the extent and nature of their protective action.

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Countercurrent and Multiple Extraction

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Easily accessible graphical methods exist for the calculation of theoretical efficiencies in both multiple and countercurrent extraction. These methods vary as the solvents can or cannot be considered immiscible, being simpler in the former case.

EXTRACTION processes in the past have received considerable attention because of their utility, and at present are coming still more to the foreground in various industries. There are two general methods of operation—multiple extraction, in which the solution to be extracted is contacted with successive lots of fresh solvent, and true countercurrent extraction. It is generally recognized that of the two the latter is by far more efficient but, at the same time, more difficult to realize. Thus, equipment for multiple extraction is relatively simple, the minimum requirement being only an agitator which can also serve as a settler and separator, so that the solution may be easily treated any number of times in the one piece of equipment. For countercurrent extraction, on the other hand, an extensive outlay is required to convey the layers from mixer to mixer, as well as a mixer for each stage. While towers can be substituted for mixers, they seem in general to be equivalent to a relatively small number of perfect plates or mixers. Consequently, in order to balance the relative merits of the two methods, it is desirable to have some simple and rapid means by which, knowing the feeds and equilibria involved, the effects of a definite number of stages of both multiple and countercurrent extraction can be calculated. In this way the relative results and efficiencies to be expected can be estimated and a decision made as to which will be preferable in practice, or whether either will be feasible.

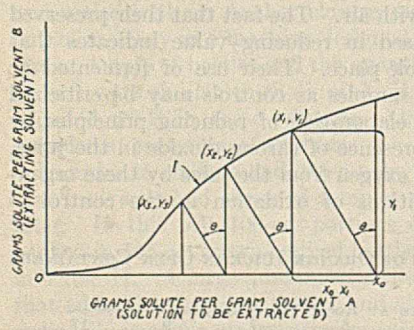

Figure 1. Multiple Extraction for Immiscible Solvents

The literature in this field is widely scattered. The problem for multiple extraction in case the solvents are immiscible and the partition law holds has been explicitly solved for some time, as well as the corresponding countercurrent situation (*1*, *3*, *4*, *5*, *8*, *9*). For partially miscible solvents, or in case the partition law does not hold, explicit solutions are apparently not available, although Friedrichs (*2*), Sanders (*7*), and Walker, Lewis, and McAdams (*10*) treat these cases with certain restrictions. The analogy between distillation and extraction has been extensively developed by Saal and van Dyck (*6*) in one of the most important papers in this field. They show that similar methods of computation can be employed in both processes. Their methods have recently been discussed by Hunter and Nash (*5*).

Because of the importance and utility of the subject, it seems worth while to collect in one easily accessible place the various methods of solution. As a start in this direction, the following graphical methods of treating present the different situations. These methods are independent of the form of the distribution curve but require a knowledge of the equilibrium distribution curve for the system under consideration. The case in which the solvents can be considered immiscible is probably of greatest interest, since many practical systems can be so considered for purposes of preliminary calculation. By making this approximation, the results are obtained rapidly, and in any case they can serve as tentative figures. The multiple extraction method developed here seems to be novel, while the countercurrent extraction method is a generalization of the work of Sanders (*7*).

For the sake of completeness the corresponding cases of partially miscible solvents are also considered. The multiple extraction here is but a statement of the elementary properties of the triangular graphs, while the countercurrent extraction is a somewhat detailed exposition of the method outlined by Saal and van Dyck (*6*). These more involved methods may be used when greater precision than can be obtained by the foregoing approximations is desired.

Multiple Extraction, Immiscible Solvents

In this method of operation the solution to be extracted is treated with a portion of the extracting solvent, the extract removed, and the resulting extracted solution again treated with fresh solvent, etc.

In Figure 1 let curve I represent the distributional equilibria existing between solutions of a common solute in solvents A and B, the compositions being taken on the basis of grams solute per gram of solute-free solvent. Suppose an initial solution of a grams of solvent A containing x_0 grams of solute per gram of solvent A is to be extracted three times, each time with b grams of pure solvent B. Denoting the concentrations in the two phases at equilibrium at the end of the ith extraction by (x_i, y_i), the material balance equations are:

$$ax_1 + by_1 = ax_0$$
$$ax_2 + by_2 = ax_1$$
$$ax_3 + by_3 = ax_2$$

From these equations we have by rearrangement:

$$\frac{x_0 - x_1}{y_1} = \frac{b}{a}$$

or, generally

$$\frac{x_{i-1} - x_i}{y_i} = \frac{b}{a}$$

By means of these relations we can easily determine the composition of the solution at each step as follows: Referring to Figure 1, the point $(x_0, 0)$ on the x axis gives the composition of the initial solution before extraction. The point (x_1, y_1) (which is temporarily unlocated) represents the composition in the solution (x_1) and extract (y_1) at the end of the first extraction of the solution by pure solvent B. Since these two phases are in equilibrium, (x_1, y_1) lies on curve I. Assuming for the moment that the location of (x_1, y_1) is known, draw the line from $(x_0, 0)$ to (x_1, y_1), making the angle Θ with the perpendicular at $(x_0, 0)$ to the x axis.

Still referring to this construction, it is seen that, from the definition of the tangent of an angle, the tangent of angle Θ is given by $(x_0 - x_1)/y_1$. But $(x_0 - x_1)/y_1 = b/a$, and b and a are known under the conditions of the problem. Hence Θ can be determined from trigonometrical tables. Consequently, to locate (x_1, y_1), a line is drawn through $(x_0, 0)$ such that tangent $\Theta = b/a$. The intersection of this line with I will give (x_1, y_1), since this point (x_1, y_1) will satisfy all the conditions imposed on it by the problem—namely, that it lie on I, and that $(x_0 - x_1)/y_1 = b/a$.

Proceeding similarly from the point $(x_1, 0)$, the next point (x_2, y_2) is secured, etc. In case different amounts of solvent are used in the different stages, then the ratio b/a varies from point to point, and with it the angle Θ, but the relation tangent $\Theta = b/a$ will always hold for each point.

It may happen that, instead of using pure solvent B to extract the solution in A, recovered solvent B, which is not entirely solute-free, will be employed. Suppose this to be the case and that solvent B contains m grams of solute per gram of solvent. In this case the material balance equation becomes

$$ax_1 + by_1 = ax_0 + bm$$

$$\text{or} \quad \frac{x_0 - x_1}{y_1 - m} = \frac{b}{a}$$

By precisely the same reasoning as before it is readily seen that the only effect this has on the geometrical construction is to replace the x axis as the starting line by a parallel line located m units higher—namely, the line $y = m$. In other words, instead of the first line being laid off through the point $(x_0, 0)$, it is laid off through (x_0, m), still making an angle Θ such that tangent $\Theta = b/a$ with the perpendicular at that point.

The foregoing argument tacitly presupposes that the same scale is used on both x and y axes. This is, of course, not always convenient. Suppose, for example, that 1 cm. on the x axis corresponds to 0.01 gram of solute per gram of solvent A, whereas 1 cm. on the y axis corresponds to 0.02 gram of solute per gram of solvent B. The relation $(x_0 - x_1)/y_1 = b/a$ still holds, in that to compute $x_0 - x_1$ the numerical value of x_1 is subtracted from that of x_2, etc. On the other hand, looking solely at the graph, the ratio $(x_0 - x_1)/y_1$ as determined by dividing the distance in centimeters between the points $(x_0, 0)$ and $(x_1, 0)$ by the distance in centimeters between (x_1, y_1) and $(x_1, 0)$ will evidently be twice that determined in the true fashion by considering the magnitudes of the points. In other words, the angle Θ must now be taken such that tangent $\Theta = 2\,b/a$. A similar formula is obvious for any other ratio between the two scales.

The above process is also easily reversed; that is, given a solution of a certain concentration, the amount of extracting solvent required to reduce it to any desired concentration in one or more steps can be readily determined. To illustrate this, suppose it is desired to reduce the concentration of the solution in Figure 1 from x_0 to x_3 in one step. To calculate the mass of extracting solvent required per unit mass of solute-free solution, it is necessary only to join the point $(x_0, 0)$ on the x axis to the point (x_3, y_3) on the equilibrium curve. If this line makes an angle ϕ with the perpendicular to the x axis at $(x_0, 0)$, then, using the previous nomenclature and similar reasoning, $b/a =$ tangent ϕ. The solvent required per unit mass of solute-free solution is given by letting $a = 1$, or $b =$ tangent ϕ. In case it is desired to reach x_3 by two successive extractions, a line is drawn from $(x_0, 0)$ to an intermediate point (x_1, y_1) on the curve, and then from $(x_1, 0)$ to (x_3, y_3). By measuring the angles these lines make with the perpendicular, the amount of extracting solvent needed at each stage is determined.

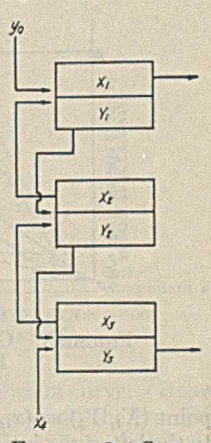

FIGURE 2. SCHEMATIC COUNTERCURRENT TOWER

In case the equilibrium curve is a straight line, it has been shown that maximum efficiency is achieved by taking this point (x_2, y_2) so that equal amounts of solvent are used in each step; there is no reason to suppose that a similar rule holds if the equilibrium curve is not a straight line. In this case only trial and error can decide which is the most favorable division of the solvent.

COUNTERCURRENT EXTRACTION, IMMISCIBLE SOLVENTS

In Figure 2 is shown a schematic diagram of the apparatus. For simplicity three plates are considered. It will be clear that this is no restriction. Assume a solution of L grams of solvent, containing y_0 grams of solute per gram of solute-free solvent, is extracted with U grams of another solvent containing x_4 grams of solute per gram of solute-free solvent. In case pure solvent is used, then $x_4 = 0$. Similarly let x_n be the grams of solute per gram of solvent at equilibrium in the extracting solvent in the nth mixer (the solution to be extracted enters the first mixer), and y_n the corresponding figure for the solution being extracted. With this nomenclature the necessary and sufficient conditions for the operation of the apparatus are: (1) At every stage x and y satisfy the experimentally determined equilibrium relations; (2) the material balance equations are:

$$Ly_0 + Ux_2 = Ux_1 + Ly_1 \text{ for the first stage}$$
$$Ly_1 + Ux_3 = Ux_2 + Ly_2 \text{ for the second stage}$$
$$Ly_2 + Ux_4 = Ux_3 + Ly_3 \text{ for the third stage}$$

Rewriting the last equations:

$$L(y_0 - y_1) = U(x_1 - x_2)$$
$$L(y_1 - y_2) = U(x_2 - x_3)$$
$$L(y_2 - y_3) = U(x_3 - x_4)$$

If now, for convenience, we use the notation $(X_n, Y_n) \equiv (x_n, y_{n-1})$ it is seen from the last set of equations that the points (X_n, Y_n) fall on a straight line of slope U/L, since we have:

$$\frac{Y_1 - Y_2}{X_1 - X_2} = \frac{Y_2 - Y_3}{X_2 - X_3} = \frac{Y_3 - Y_4}{X_3 - X_4} = \frac{U}{L}$$

Now, in Figure 3, let x and X, y and Y be plotted on the same axes. Let curve I represent the experimentally determined equilibrium relation which exists between x and y. (If the familiar distribution law holds, I is a straight line.) The analyses of the feeds, y_0 and x_4, are shown. The only thing left to determine is the locus of (X, Y). It is known to be a straight line of definite slope, but so far its position is not fixed. To locate it, a trial and error method is employed. Inasmuch as its intersection with $y = y_0$ gives the

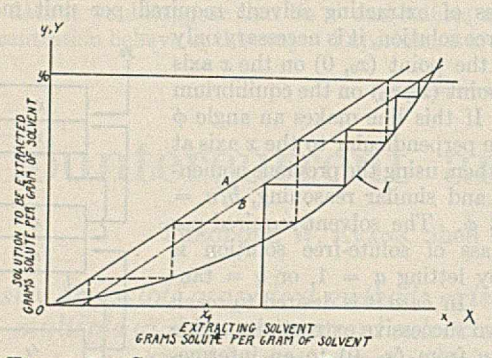

FIGURE 3. COUNTERCURRENT EXTRACTION FOR IMMISCIBLE SOLVENTS

point $(X_1, Y_1) \equiv (x_1, y_0)$, this intersection must lie somewhere to the left of the intersection of I and $y = y_0$. This is readily seen to be true since x_1 is the concentration of the extracting solution as it leaves the apparatus, and x_1 can never exceed the equilibrium value (x_0) corresponding to y_0 in the solution to be extracted; i. e., x_1 must be less than the value of x on curve I (x_0) corresponding to the value y_0 on this curve. As a first trial, assume A is the correct line. From its intersection with $y = y_0$, x_1 is determined and hence y_1 by dropping to curve I, since (x_1, y_1) by definition lies on I.

Now by crossing to A on $y = y_1$, (X_2, Y_2) and hence x_2 are secured, etc. If A is the correct line, we should arrive at the true value of x_4 by this process. As it is, we do not but end far to the left on line A for the point $(X_4, Y_4) \equiv (x_4, y_3)$. Hence in choosing A, it was placed too far to the left. Now try B. It, on the other hand, proves to be somewhat to the right of the true value. Hence the true line lies between A and B. Consequently the value of x_1—i. e., the composition of the extract from the apparatus—lies between the values of x corresponding to the intersections of A and B with the line $y = y_0$. Now by drawing a line C midway between A and B, line C will similarly be found either too far to the right or left. Assuming it too far to the left, then x_1 is restricted to the region between the intersections of C and B with $y = y_0$; in other words, its range has been cut in half. Similarly, placing a line midway between C and B again restricts it farther, etc. Thus the value of x_1 is rapidly established to as narrow a range as desired. Thus, supposing A and B initially determine that x_1 lies between 10 and 20 grams of solute per 100 grams of solvent (i. e., $x_1 = 15 \pm 5$), then C will cut the variation to $\pm$ 2.5 at the most, and the next line to $\pm$ 1.25. This assumes the most unfavorable case—namely, that the successive lines have been spaced equally without attempt at judging the most likely position for the succeeding lines. At first sight the method may appear a bit cumbersome, but in reality it is rapid. By means of several large graphs of curve I with only two trial lines on each graph, a high degree of accuracy can be reached in a few minutes.

MULTIPLE EXTRACTION, SOLVENTS PARTIALLY MISCIBLE

In Figure 4 let A and B represent the composition of solution and solvent, respectively, and let m_A and m_B be their masses. Assume three successive extractions are to be made. For the first operation m_A grams of solution of composition A are mixed with m_B grams of solution of composition B, and the mixture is stratified and separated. To establish the composition of the resulting phases, the following fundamental properties of these triangular graphs are employed:

(1) When two solutions are mixed, the point representing the over-all composition of the mixture lies on the line joining the points representing the compositions of the original solutions (*1*). Its location is so related to the masses of the solutions taken that, denoting it by C, in the present example:

$$\frac{AC}{CB} = \frac{m_B}{m_A}$$

where AC and CB represent the distances from A to C and C to B.

These distances are to be taken in the sense of directed lengths; that is, if we agree to call the direction from A to C positive, then AC is a plus length, whereas CA is a minus length $(AC = -CA)$. With this same convention that the direction from A to C is positive, then CB is a positive distance if, in going from C to B, one travels in the same direction as from A to C; if one travels in the opposite direction, then CB is a negative distance.

(2) In case point C represents a composition which cannot exist as a single phase, then the mixture separates into two conjugate phases whose compositions are given by the extremities of the tie line passing through C.

In the present case then, point C, lying on AB, is located either by direct calculation of the over-all composition of the mixture of m_A and m_B, or from the fact that $AC/CB = m_B/m_A$. Once C is located, the tie line through it is drawn, thus securing D and E. For this first operation, then, two solutions are secured, the one an extract of composition E, the other the partially extracted solution of composition D. The masses of these solutions are obtained from the relations:

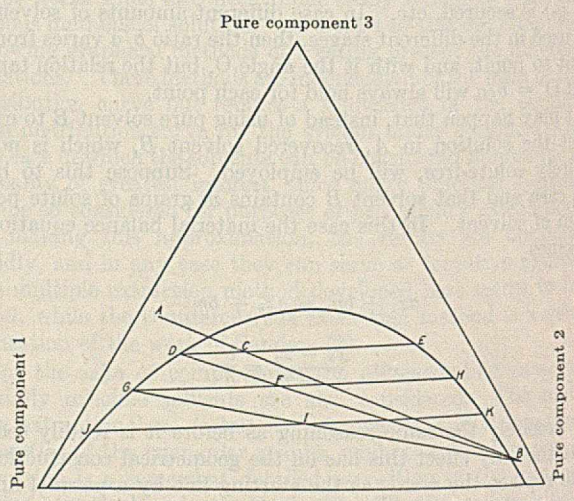

FIGURE 4. MULTIPLE EXTRACTION FOR PARTIALLY MISCIBLE SOLVENTS

$$m_D + m_E = m_A + m_B$$

$$\frac{m_D}{m_E} = \frac{EC}{CD}$$

The m_D grams of solution of composition D are then treated exactly as the original m_A grams of composition A, etc. The final products are, therefore, a residual extracted solution of composition J and mass m_J, and the three extracts of composition E, H, K, and masses m_E, m_H, m_K.

It should be noted in passing that property 1 is somewhat more general than is indicated here. Since this property is derived by algebraic processes, it applies equally well to subtraction of solutions as addition; i. e., in place of adding m_A grams of A to m_B grams of B, we may consider the effect of subtracting m_A grams of A from m_B grams of B (that is, adding $-m_A$ grams). The statement in property 1 still holds for this case—namely, that the point representing the over-all composition of the mixture lies on AB, and at such a point that $AC/CB = m_B/-m_A$. However, interpreting this geometrically, it is seen that, while in the addition of the solutions C lies between A and B, in the case of subtraction C must lie beyond either A or B to make the ratio AC/CB negative. Thus in the following line the ratio AC/CB is negative (note $AC = -CA$, etc.) since AC and CB are measured in opposite directions:

$$\overline{C \qquad\qquad A \qquad\qquad B}$$

In the systems under consideration it may even happen that C falls outside the triangle. This is readily explained, however, by the fact that these "solutions" are in reality only formal mathematical means of arriving at the ultimate physical solutions. Thus, the result of subtracting 200 grams of a solution of composition (50, 10, 40) from 100 grams of a solution of composition (40, 50, 10) is -100 grams of solution containing -60, $+30$, and -70 grams of the three constituents, or, -100 grams of a solution of composition 60, -30, and 70 per cent of the three components. The practical utility of this will be evident in the next section.

Countercurrent Extraction, Solvents Partially Miscible

The case of three mixers or plates will be considered. It will be evident that the choice of three imposes no limitations.

In Figure 5 let A represent the composition of the solution to be extracted, B that of the extracting solvent. If the solvent is pure, B coincides with the corner of the triangle. Let m_A grams of solution A be fed into the apparatus (to mixer one) along with m_B grams of B (to mixer 3). Let F, H, E and D, I, G represent the compositions of solution and extract at equilibrium in the three mixers. In relation to Figure 3 we have the following correspondence: y_0 and A, (x_1, y_1) and (D, F), (x_2, y_2) and (I, H), (x_3, y_3) and (G, E), x_4 and B. Let the masses of the solutions be m_D, m_E, etc., the end products are then m_D grams of extract of composition D and m_E grams of extracted solution of composition E.

As before, the conditions for a steady state of the apparatus are: (1) F and D, H and I, etc., are conjugate phases; (2) the material balance equations are:

$$\begin{aligned} m_AA + m_II &= m_FF + m_DD \text{ for the first stage} \\ m_FF + m_GG &= m_HH + m_II \text{ for the second stage} \\ m_HH + m_BB &= m_EE + m_GG \text{ for the third stage} \end{aligned}$$

Rewriting this set of equations;

$$m_AA - m_DD = m_FF - m_II \quad (1)$$
$$m_EF - m_II = m_HH - m_GG \quad (2)$$
$$m_HH - m_GG = m_EE - m_BB \quad (3)$$

or

$$m_AA - m_DD = m_FF - m_II =$$
$$m_HH - m_GG = m_EE - m_BB \quad (4)$$

To locate these points, a trial and error method similar to that previously used is employed. Let point C represent the over-all composition of the mixture of $m_A + m_B$. The tie line through C would evidently give the compositions of the product from a one-stage apparatus by virtue of the properties previously given. In the present case we have a three-stage apparatus; hence, the extract must be richer than it would be from a one-stage process. Therefore D must lie somewhat above the tie line through C. As a first choice let us arbitrarily choose it as is shown in Figure 5. From an over-all material balance $m_AA + m_BB = m_DD + m_EE$. Since $m_AA + m_BB$ gives a "solution" of composition C, so must $m_DD + m_EE$. Therefore E must lie on the same line as D and C, since otherwise a mixture of E and D could

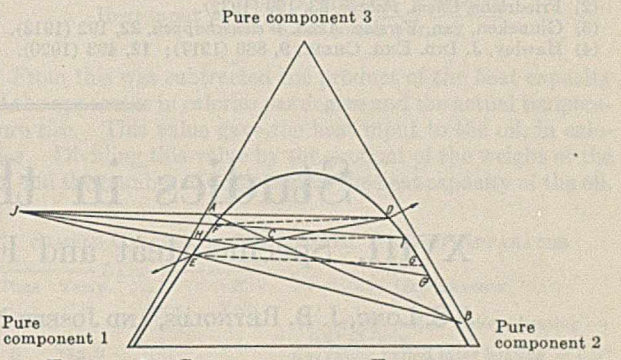

Figure 5. Countercurrent Extraction for Partially Miscible Solvents

not give C. But D also lies on the equilibrium curve. Hence it is given by the intersection of the curve and the line DC. Now from D and E the points F and G are immediately located as the extremities of tie lines (shown as broken lines), since D and F, E and G are conjugate phases.

To locate the remaining points, recourse is had to the material balance equations. The left side of Equation 1 ($m_AA - m_DD$) is equal to the right side of Equation 3 ($m_EE - m_BB$); i. e., in case of any number of mixers, consider the first and last of this set of equations. Let J represent the composition of this "solution" represented by $m_AA - m_DD$. By the fundamental properties of these diagrams J must lie on the line DA, and it must also lie on the line BE. Hence J is given as the intersection of these lines. Having located J, we are now able to locate the other points easily. By the first equation, $m_FF - m_II$ also gives a solution of composition J. Hence J, F, and I lie on the same line. We know J and F; hence I is given as the intersection JF with the curve. Knowing I, H is immediately given as the extremity of the tie line through I. By drawing JH we obtain the next point, etc. In the present case this next point represents the composition in the final mixer, G^1. But we have already fixed this point G in fixing D. Hence, if D has been chosen properly G and G^1 coincide. If they do coincide, then obviously D represents the correct solution of the problem, and m_D and m_E can be calculated, since

$$m_A + m_B = m_D + m_E$$
$$\frac{m_D}{m_E} = \frac{EC}{\overline{CD}}$$

In the present case, however, G^1 does not coincide with G but falls below it. This means that in choosing D we have placed it too low on the curve. Therefore we next try a new D at a point somewhat above our first choice. This will, in general, be chosen sufficiently high so that now the new G^1 will fall above the new G. Therefore the true value of D will be between these first two choices. By taking a third point midway between these two points, the location of D is restricted to half its former range, and by continuing this process it can be located to as high a degree of precision as desired.

It will be observed that only one calculation is required—namely, the location of C, a point dependent solely on the feeds of the apparatus. Once C is located, a few trials in-

volving only the drawing of certain lines will fix D as closely as desired. Hence the method, while not so rapid as for the immiscible solvents, is nevertheless reasonably rapid and easy of application.

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Studies in the Drying Oils

XVIII. Specific Heat and Features of Heating Drying Oils

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The specific heats of linseed oil, China wood oil, and soy-bean oil have been determined over much of the temperature range employed in heating them to make industrial products.

Mathematical design of a kettle is given to maintain substantially constant ratio of air-oil interface to volume of oil, irrespective of the quantity of oil in the kettle. The matter of kettle design for specific objectives, which has been somewhat neglected, is indicated.

Heat-bodying of drying oils over hot direct fires with little agitation yields products which are not homogeneous but which are dispersions of highly associated molecules in liquid containing molecules in much lower state of association or aggregation.

DRYING oils are heated in kettles to produce oils thickened or bodied to various extents for use in paints, varnishes, enamels, coated fabrics, inks, and other materials. Certain features of a rather extensive study of this process are presented here. Calculation of the quantity of heat actually absorbed by the oil involves knowledge of (*a*) the quantity of oil, (*b*) the temperature, and (*c*) the specific heat of the oil. Despite the fact that many millions of gallons of oil have been heat-bodied, data could not be found in the literature on the specific heats of the drying oils that are most generally heated. Accordingly the specific heats of these materials have been determined over most of the temperature range employed.

The shape or design of kettles in which to heat the oils has also been somewhat neglected. Certain standard shapes which have developed on the basis of expediency or which are convenient to handle have been widely adopted, often with very little consideration of the mechanism of reactions occurring in them, as influenced by kettle design or method of heating. It should be kept in mind that the heat-bodying of drying oils involves chemical reactions.

The variety of objectives for which oils are heat-bodied precludes the advisability of attempting to design one ideal kettle. This paper will attempt to show that by the application of ordinary mathematics it is possible to calculate designs to fulfil desired objectives. The particular case chosen is that of maintaining a constant ratio of oil volume to the area of oil exposed to the air. In heat-bodying oil for patent leather, it has been customary to cook small batches of 30 to 50 gallons, and it was believed that, when larger batches were cooked, a product was obtained which had very different properties. In tackling the problem of cooking large batches, due consideration has been given to the viewpoint of the past, and, instead of simply increasing the size of a batch in a kettle with, for example, vertical sides, a large kettle has been designed to maintain approximately the same ratio of air surface to volume of oil, irrespective of the quantity of oil put in the kettle. In cases considered up to the present, it has been unnecessary to adhere rigidly to the strictly theoretical shape of the kettle. Shapes approximating this on the basis of practicability of fabrication usually fulfil the objective.

The literature on the heat-bodying of drying oils is voluminous. The process is broadly considered as polymerization or, more accurately, molecular association. This is a progressive process and passes through a series of degrees of association. The highly associated molecules are relatively insoluble in the matrix liquid. The bodied product contains molecules of various degrees of association. The molecular weight figure represents an average.

When a large kettle of oil is heated over a hot fire, it is likely that the oil in contact with the sides of the kettle will be heated to temperatures considerably higher than those shown by the thermometer immersed in the oil. The association or polymerization reactions are a function of temperature and are therefore facilitated at the hot walls and bottom of the kettle. Convection currents lead to some degree of motion of the oil, even in an unstirred kettle, but in many cases it is largely a matter of chance rather than design, if the oil diffuses rapidly enough to prevent local overassociation at the hot bottom and sides. What might be called the "high polymers" or more highly associated molecules thus produced diffuse and disperse in the rest of the oil at first, but as time goes on the entire mass of oil is also bodying at the temperatures used, and the molecules are building up progressively in size and weight. These larger molecules undergo further local overheating at the hot sides and in the face of decreased mobility as their weight increases. It is quite logical, therefore, that particles are formed locally on the bottom and sides which become insoluble in the remainder of the liquid before it has reached the desired body or viscosity. This is, of course, particularly true in unstirred kettles over very hot fires and at high temperatures. The insoluble particles thus produced are not necessarily very large. They often escape detection except by later laboratory tests or abnormal be-

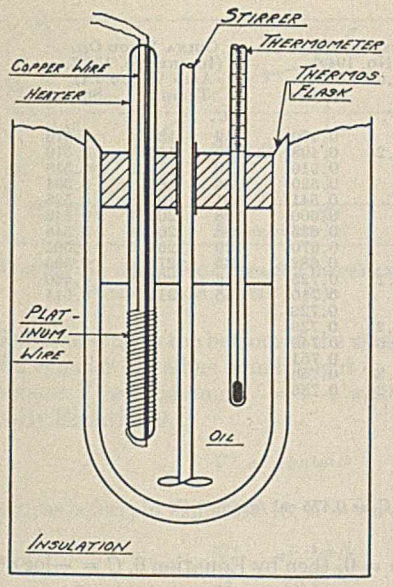

FIGURE 1. APPARATUS FOR SPECIFIC HEAT DETERMINATIONS

havior of the products. In some cases, however, a percentage of them reaches the open-air surface of the oil, is chilled, and sets to a gel or skin. Some data are given later in the paper to bring out this point, and it is felt that consideration of this feature of oil-bodying with consequent (*a*) general lowering of temperatures, (*b*) agitation where possible, and (*c*) changes in kettle design, will lead to improvement in the quality of bodied oils and decrease in the abnormalities arising from this source. Indirect heating by circulating hot petroleum oils, diphenyl, and other liquids is indicated for some cases and will probably have a place in the development of the next decade.

SPECIFIC HEATS OF DRYING OILS (C_p)

PROCEDURE. The apparatus (Figure 1) consisted of a well-insulated thermos flask of such size as to contain 150 to 200 grams of oil and leave an air space of approximately 200 cc. above the surface of the oil. A three-holed cork stopper was used to seal the flask. Through the center hole was fitted a glass stirrer, which was driven by an electric motor. A thermometer, with the bulb immersed midway in the body of the oil was inserted through another hole, while the third hole contained the leads of a platinum-wire resistance heater which was totally immersed in the oil. The heater had a resistance of approximately one ohm and was heated with direct current from storage batteries. A voltmeter was connected across the terminals of the heater. In series with the heater were a rheostat and an ammeter.

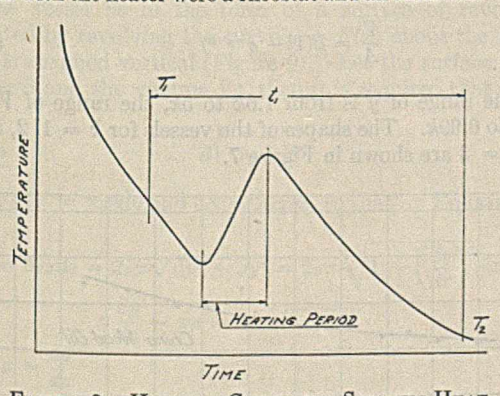

FIGURE 2. HEATING CURVE FOR SPECIFIC HEAT DETERMINATIONS

A sample of oil weighing from 150 to 200 grams was placed in the flask, and the stopper, fitted with stirrer, heater, and thermometer, was inserted. The stirrer was then started and current applied to the resistance heater. When the temperature had reached a value several degrees above the desired point, the heating was discontinued and the rate of cooling was determined. Heat was then applied for one or more minutes, the time being accurately measured by a stop watch, to produce a temperature rise of 1° or 2° C. The heating was then discontinued and another rating period obtained. Readings of temperatures during the entire run were made at one-minute intervals, and readings of current and voltage were taken at regular intervals during the heating period.

METHOD OF CALCULATIONS. The rating periods were obtained before and after the heating, and averaged. Points T_1 and T_2 (Figure 2) were selected on the constant-slope portions of the rating periods before and after heating. Then, (t_1 × average cooling rate) − ($T_1 - T_2$) = actual temperature rise, due to heat energy supplied. The heat input was then obtained by the equation:

$$\text{Heat input} = \frac{\text{volts} \times \text{amperes} \times \text{seconds}}{4.182 \text{ joules per cal.}}$$

From this was subtracted the product of the heat capacity of the apparatus in calories per degree and the actual temperature rise. This value gave the heat input to the oil, in calories. Dividing this value by the product of the weight of the oil and the number of degrees gave the heat capacity of the oil.

SAMPLE CALCULATION OF SPECIFIC HEAT OF APPARATUS

Time	Temp. °C.	DATA I Amp.	DATA E Volts	CALCULATION
				Av. rating period before heating = 0.9° C./min.
0	135.9			
1	135.0			Av. rating period after heating = 0.9° C./min.
2	134.1			Total av. = 0.9° C./min.
3	133.2			Take the time interval from 3 to 13 min., a 10-min. interval. Without heating, the temp. drop would be 10 × 0.9° = 9° C. Actually it was 133.2 − 129 = 4.2° C. So the actual temp. rise due to heating was 9.0 − 4.2 = 4.8° C. Total heat input = $\frac{4.05 \text{ volts} \times 4.79 \text{ amp.} \times 120 \text{ sec.}}{4.182 \text{ joules/cal.}}$ = 556 cal.
4	132.3			
5	131.4			
6	130.5	4.05	4.79	
Heating begun				
7	131.3	4.05	4.79	
8	132.9	4.05	4.79	
Heating discontinued				
9	132.5			
10	131.7			
12	129.9			
13	129.0			
14	128.1			
				Heat input to apparatus = 17 × 4.8 = 82 cal.
				Then 556 − 82 = 474 cal. = heat input to oleic acid

Heat capacity of apparatus = 17 cal./° C.
Oleic acid sample = 167 grams

Then $\frac{474 \text{ cal.}}{167 \text{ grams} \times 4.8° \text{ C.}}$ = 0.591 = sp. heat, cal./gram/° C.

SAMPLE CALCULATION OF HEAT CAPACITY OF APPARATUS

162-gram sample of diphenyl
Temp. of run = 94° C.
Sp. heat of diphenyl at 94° C. = 0.442 cal./gram/° C.
Actual temp. rise due to heating = 6.04° C. (see above)
Current = 4.753 amp.
Time of heating = 2 min.
Voltage = 3.9

Electrical heat input = $\frac{4.753 \times 3.9 \times 120 \text{ sec.}}{4.182 \text{ joules/cal.}}$ = 532 cal.

Input to diphenyl = 6.04° C. × 162 grams × 0.442 cal./gram/° C. = 432 cal.
Input to apparatus = 532 − 432 = 100 cal.
Heat capacity of apparatus = 100/6.04 = 16.6 cal./° C.

Av. of several determinations was 17 cal./° C.

Data on the specific heats of several oils are shown in Table I and Figures 3 to 5.

DESIGN OF A KETTLE

The object of the first part of this section is to discover what form of vessel will give (*a*) an approximately constant ratio, (*b*) an exactly constant ratio between the volume of liquid contained and the surface to the air, or (*c*) a constant ratio of heated surface to volume. Let the constant ratio be k; that is:

$$V = kA \qquad (1)$$

This means that the volume of liquid at any time is equivalent to that of a cylinder of base A and of height k when A is the area of the exposed surface of the liquid.

(*a*) Let the surface of the vessel be formed by the revolution of the curve $y = f(x)$ about the Y axis (Figure 6), which is assumed to be vertical. Let ΔV be the volume added by increasing the depth from y to $y + \Delta y$. Then, approximately,

TABLE I. SPECIFIC HEATS OF DRYING OILS

Alkali-Refined Linseed Oil (Iodine No. 181.3)			Soy-Bean Oil (Iodine No. 134, Acid Value 2.3)			Oleic Acid (Iodine No. 89.9)			Raw Linseed Oil (Iodine No. 194, Acid Value 1.53)			China Wood Oil (Iodine No. 156.7, Acid Value 3.1)		
Temp.		Sp. heat	Temp.		Sp. heat	Temp.		Sp. heat	Temp.		Sp. heat	Temp.		Sp. heat
° C.	° F.		° C.	° F.		° C.	° F.		° C.	° F.		° C.	° F.	
75	167	0.504	75	167	0.568	27	80.6	0.460[a]	80	176	0.470	69	156.2	0.516
89	192.2	0.499	85	185	0.579	29	84.2	0.483	99	210.2	0.498	70	158	0.510
89	192.2	0.474	130	266	0.582	31	87.8	0.450	110	230	0.510	79	174.2	0.516
95	203	0.502	140	284	0.591	38	100.4	0.487	120	248	0.529	85	185	0.534
98	208.4	0.504	140	284	0.606	38	100.4	0.477	130	266	0.541	91	195.8	0.528
102	215.6	0.493	151	303.8	0.589	39	102.2	0.451	140	284	0.600	98	208.4	0.542
121	249.8	0.498	159	318.2	0.596	132	269.6	0.580	150	302	0.625	98	208.4	0.546
142	287.6	0.513	161	321.8	0.597	141	285.8	0.592	160	320	0.670	129	264.2	0.595
152	305.6	0.540	171	339.8	0.603	151	303.8	0.630	170	338	0.682	135	275	0.596
162	323.6	0.539	181	357.8	0.623	171	339.8	0.664	189	372.2	0.725	146	294.8	0.630
172	341.6	0.563	190	374.0	0.640	180	356	0.662	220	428	0.710	155	311	0.644
190	374	0.605	193	379.4	0.630	201	393.8	0.699	230	446	0.722			
200	392	0.627	220	428.0	0.618	210	410	0.684	239	462.2	0.739			
219	426.2	0.664	230	446	0.655	210	410	0.670	252	485.6	0.740			
255	491	0.663	240	464	0.681	222	431.6	0.680	265	509	0.751			
256	492.8	0.660	250	482	0.682	242	467.6	7.20	276	528.8	0.756			
276	528.8	0.680	250	482	0.698	250	482.0	0.700	289	552.2	0.736			
290	554	0.665	280	536	0.759	252	485.6	0.718						
			287	548.6	0.765	258	496.4	0.709						
						260	500	0.710						
						271	519.8	0.748						
						285	545	0.776						
						285	545	0.799						

[a] International Critical Tables, Vol. II, p. 210, gives the specific heat of oleic acid (C_p) between 20° and 30° C. as 0.475 cal./gram/° C.

$$\Delta V = \pi x^2 \Delta y \tag{2}$$

where x = the radius of the vessel corresponding to a horizontal section through the point (x, y) on the curve $y = f(x)$.

Let ΔA be the increase in the area of the exposed surface,

$$\Delta A = \pi[(x + \Delta x)^2 - x^2] \tag{3}$$

From Equation 1 we have:

$$\Delta V = k \Delta A \tag{4}$$

Equations 2, 3, and 4 lead to the approximate relation,

$$\pi x^2 \Delta y = k\pi[(x + \Delta x)^2 - x^2] = k\pi[2x \Delta x + (\Delta x)^2]$$

which yields the exact differential equation,

$$x^2 \frac{dy}{dx} = 2kx \text{ or } \frac{dy}{k} = 2\frac{dx}{x} \tag{5}$$

Upon integrating we have:

$$\frac{y}{k} = \log x^2 + C \tag{6}$$

where C is a constant to be determined.

For Equation 1 to hold, V and A must be simultaneously zero and hence the curve $y = f(x)$ must pass through a point where $x = 0$. This condition cannot be met by Equation 6 since $\log 0 = -\infty$. However, we can obtain a ratio of V to A that is nearly constant, especially for considerable volumes.

Suppose $x = a$ when $y = 0$, then by Equation 6, $C = -\log a^2$ and:

$$\frac{y}{k} = \log \frac{x^2}{a^2} \tag{7}$$

$$\text{or } x^2 = a^2 e^{y/k} \tag{8}$$

We wish now to see how nearly $V/A = k$ for a vessel formed by revolving Equation 8 about the Y axis. The volume is given by

$$V = \pi \int_0^y x^2 dy = \pi \int_0^y a^2 e^{y/k}\, dy = \pi k a^2 e^{y/k} \Big|_0^y$$

$$\text{or } V = \pi k a^2 (e^{y/k} - 1) \tag{9}$$

where y = depth of liquid in the vessel

Now we have

$$A = \pi x^2 = \pi a^2 e^{y/k} \tag{10}$$

so that by Equations 9 and 10

$$\frac{V}{A} = k(1 - e^{-y/k}) \tag{11}$$

If the range of y is from $1.6k$ to $5k$, the range of V/A is $0.80k$ to $0.99k$. The shapes of the vessels for $k = 1, 2$, and 3, and $a = 3$ are shown in Figure 7.

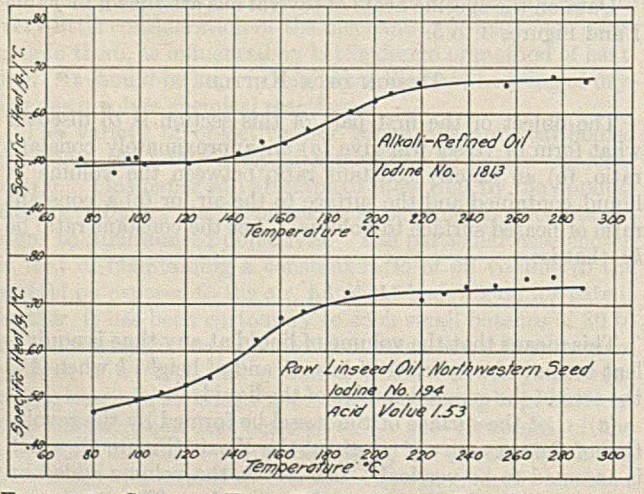

FIGURE 3. SPECIFIC HEAT–TEMPERATURE CURVES FOR LINSEED OILS

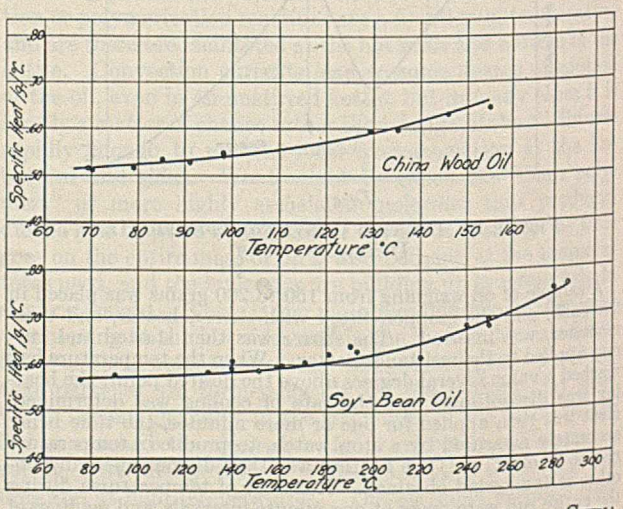

FIGURE 4. SPECIFIC HEAT–TEMPERATURE CURVES FOR CHINA WOOD AND SOY-BEAN OILS

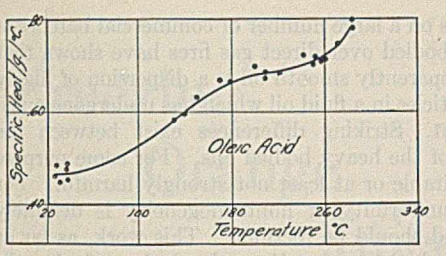

FIGURE 5. SPECIFIC HEAT-TEMPERATURE CURVE FOR OLEIC ACID

The shape of vessel best for any given operation would depend upon the range of the quantity of liquid likely to be used.

(*b*) The ratio $V'/A = k$ can be exactly satisfied by adding to the bottom of the vessel as pictured in Figure 7 a cylinder of radius a and height k; with this addition the volume V' will become $V' = V + \pi ka^2$ (Figure 8).

By Equation 9,

$$V' = \pi ka^2 e^{y/k} \tag{12}$$

and, as before, in Equation 10, $A = \pi a^2 e^{y/k}$. Hence:

$$\frac{V'}{A} = \frac{\pi ka^2 e^{y/k}}{\pi a^2 e^{y/k}} = k$$

Thus, if the vessel is always used with the surface of the liquid at or above the top of the cylindrical portion, the ratio of the volume to the exposed area will always be k and the desired conditions will be met.

It does not matter what shape the addition made to the bottom of the vessel is given, provided only that its capacity is πka^2. Other shapes might be more convenient for heating than the cylindrical one.

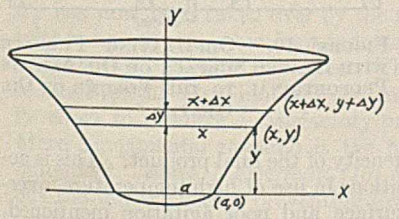

FIGURE 6

(*c*) Finally, the shape of vessel will be discussed which will give a constant ratio, k, of the volume to the curved surface which is supposed to be exposed to heat.

Let the vessel be in the form of a surface of revolution generated by revolving the curve $y = F(x)$ about the Y axis which is assumed vertical (Figure 9). Let the surface generated be S and the volume V; then it is required that:

$$V = kS \tag{13}$$

whence

$$dV = kdS \tag{14}$$

Now, $dV = \pi x^2 dy$ and $dS = 2\pi x ds$, so that by Equation 14:

$$\pi x^2 dy = 2\pi x ds = 2\pi x\sqrt{dx^2 + dy^2} = 2\pi x\sqrt{1 + \left(\frac{dy}{dx}\right)^2}\,dx$$

$$x\frac{dy}{dx} = xp = 2k\sqrt{1 + p^2} \tag{15}$$

where $p = \frac{dy}{dx}$

Then,

$$x^2p^2 = 4k^2 + 4k^2p^2$$
$$(x^2 - 4k^2)p^2 = 4k^2$$

$$p = \frac{dy}{dx} = \frac{2k}{\sqrt{x^2 - 4k^2}}$$

$$\frac{2kdx}{\sqrt{x^2 - 4k^2}} = dy \tag{16}$$

and upon integrating, we have

$$\cosh^{-1}\frac{(x)}{2k} = \frac{y}{2k} + C \tag{17}$$

or

$$x = 2k\cosh\left(\frac{y}{2k} + C\right) \tag{18}$$

The constant, C, is determinable by Equation 18 as soon as the radius, r, of the base of the vessel is decided upon, for this gives the value of x for $y = 0$, and hence $C = \cosh^{-1}(r/2k)$. If a vessel of this shape is uniformly heated over the curved surface, the ratio of the heated surface to the volume of liquid will remain constant for different depths of liquid. Figure 10 shows a possible scheme for accomplishing this. The full curve is plotted for $k = \frac{3}{4}$ and $C = 0$; the dotted one for $k = \frac{1}{2}$ and $C = 0$. The curve is easily plotted for any values of k and C by means of a table of hyperbolic functions, C being determined by the width of the bottom of the vessel which must not be less than $4k$. Nearly the same purpose as that served by the heat chamber could be accomplished by having gas jets distributed uniformly under the curved surface and using only those up to the height of the surface of the liquid.

SKINNING OF LINSEED OIL UPON HEATING

NO DRIERS PRESENT. Three hundred cubic centimeters of alkali-refined linseed oil were heated by direct fire in a monel metal beaker to 300° C. (572° F.) in a half-hour and held at this temperature until skinning appeared. The oil was not stirred.

Skinning began 2 hours and 20 minutes after reaching 300° C. A sample of the oil was taken as skinning started. The skin was pulled off with a pair of forceps, dipped for about 10 seconds in ether to wash it free from adhering oil, and then put in an oven for 10 seconds at 100° C. to drive off the ether. The dry skin was then put in a vial and an ultimate analysis run on it immediately:

	C	H	O
	%	%	%
Oil	77.3	10.6	12.1
Skin	77.0	10.6	12.4

DRIERS PRESENT. Two hundred and fifty grams of alkali-refined linseed oil were heated with no agitation to 293° C. (560° F.) in a half-hour in a monel metal beaker with the following driers incorporated: 0.5 per cent lead as linoleate, 0.05 per cent cobalt as linoleate, 0.05 per cent manganese as linoleate, and 0.5 per cent iron as linoleate.

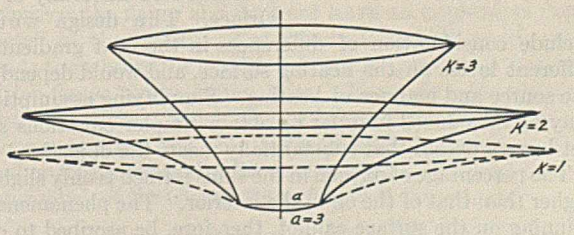

FIGURE 7. APPROXIMATE DESIGN TO SATISFY $V = kA$

The oil was held at 293° C. until a skin appeared. Samples of skin were taken from the side and center of the beaker and a sample of the oil was taken when skinning occurred. The oil skinned about one hour after reaching temperature. The skins were washed in ether, dried, and analyzed as before:

	C	H	O
	%	%	%
Skin from center	77.2	10.4	12.4
Skin from edge	77.2	10.7	12.1
Oil	77.6	10.4	12.0

DISCUSSION OF RESULTS

The curves show that the heat capacity is a linear function of the temperature in the lower ranges of temperature from 70° to about 170° C. There is then a sharp increase in heat

capacity and subsequently a flattening out of the curve. The accuracy of the heat capacities at the higher temperatures is doubtful, because of the fact that the radiation increases considerably in that range, and the cooling rate is no longer linear. This influences the method of calculation of results. Since the heating period is only 2 minutes, and the temperature rise 3° or 4° C., an error of 0.2° C. in calculating the temperature rise means an error of 15 or more per cent in the heat capacity. In the lower ranges, however, the results are reasonably correct. This is somewhat confirmed by the agreement of the authors' data for oleic acid with that given in International Critical Tables for the same temperature range.

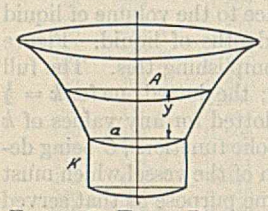

FIGURE 8. EXACT DESIGN TO SATISFY $V=kA$

China wood oil gelled rapidly when held for a time above 230° C., and also became bodied when heated at lower temperatures.

The value for the heat capacity of the apparatus was obtained by using the known specific heat of diphenyl, and making runs similar to those using oils. The specific heat of diphenyl was checked using water at temperatures below 100° C.

The rather sharp rises in the specific heat curves of linseed oil at temperatures between 140° and 200° C. suggest that at these temperatures heat is being absorbed to start chemical reactions, and at higher temperatures the reactions become exothermic and cause the curves to flatten out. This suggests more exact and detailed repetition of this work in an attempt to obtain information on the reactions occurring at the various stages.

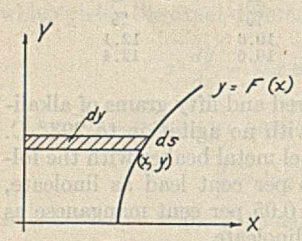

FIGURE 9

A most interesting case for study in connection with kettle design is that of maintaining a constant heating rate, irrespective of the volume of oil in the kettle. This does not reduce simply to maintaining a constant ratio of heating surface to volume unless the heat can be distributed uniformly to the surface. The design would include consideration of differences in the heat gradient at different levels on the heating surface, and would depend on the source and manner of heating. Simplifying assumptions may be introduced in order to obtain simpler equations and yet have a design that substantially meets the objective.

The percentage of oxygen in the skins formed is only slightly higher than that of the oil in the interior. The phenomena of skinning on the surface cannot, therefore, be ascribed to oxidation. This holds, whether or not driers are present. The skin forms as a result of the chilling of thin films of the oil in the form of bubbles at the air interface, after the oil has been bodied to a considerable extent.

Repeated tests on a large number of commercial batches of linseed oil heat-bodied over direct gas fires have shown that the thick and apparently smooth oil is a dispersion of highly polymerized particles in a fluid oil which has undergone much less development. Striking differences exist between the separable parts of the heavy bodied oils. For some purpose this may be desirable or at least not strongly harmful. For others this nonuniformity or nonhomogeneity is definitely objectionable and should be rectified. This work, as far as it has been carried, shows that if we simply heat drying oils over a hot direct fire with little or no agitation until a certain viscosity is attained as measured by some simple test, the product is a mixture or dispersion containing highly and slightly associated molecules. The properties of the product will be affected by this fact and some of the effects are undesirable for certain uses. Skinning, livering, and settling are features somewhat involved in this process. More indirect heating with lower temperature gradients and also oil-bodying at lower temperatures are of real help in achieving a higher degree of uniformity in the product. Agitation where feasible is another obvious advantage. Where for some reason gel lumps in a liquid matrix are desirable, high temperatures over hot, direct fires will accentuate this effect.

Oil mixtures such as China wood with linseed, perilla with soy-bean, China wood with soy-bean, and others, contain ingredients whose molecules at best associate or polymerize at different rates when heat-bodied and therefore lead to nonhomogeneity of the final product. This is accentuated by the conditions in use of high temperature, overheating at the kettle surface, and poor agitation mentioned. Films made from bodied oils which contain any considerable proportion of gel in relatively thin liquid matrix are not as tough as those made from oils in which the degree of association is more nearly the same throughout the oil.

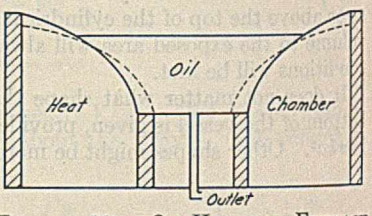

FIGURE 10. OIL-HEATING FURNACE WITH HEATED SURFACE OF OIL ALWAYS PROPORTIONAL TO THE VOLUME OF OIL HEATED

ACKNOWLEDGMENT

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EXPORTS OF AMERICAN PHARMACEUTICALS AND PROPRIETARY MEDICINES INCREASE. Exports of American medicinals, particularly proprietary medicines, pharmaceuticals (both liquid and dry) and staple household remedies in small packages, were valued at $3,430,000 for the first four months of 1934 (not counting those to Alaska, Hawaii, and Puerto Rico), an increase of 6 per cent over the foreign sales of $3,250,000 during the corresponding period of 1933. This represents the best general upturn in the foreign trade that has been noted for many months. The export value was more than five times that of the imports ($645,000).

Increases were recorded in thirteen of the twenty-four different classes of medicinals exported. While decreases were registered in eleven classes, in three of them the decreases were slight. Making up the export total were proprietary medicines $1,790,000, or $190,000 more than during the first four months of 1933; official and nonofficial galenicals and pharmaceuticals and household staple drugs $1,000,000, an increase of $71,500 over the corresponding period; biologicals (serums, antitoxins, and vaccines) for human and animal use $553,000, a reduction of $93,000; and castor oil and white mineral oil $85,000, which was $11,700 more than during the first four months of 1933.

Germany is the world's principal supplier of medicinals, having exported $20,500,000 worth in 1932. The United States was second, with $11,500,000; France, third, with $9,920,000; and the United Kingdom a close fourth, with $9,280,000.

Freezing Orange Juice

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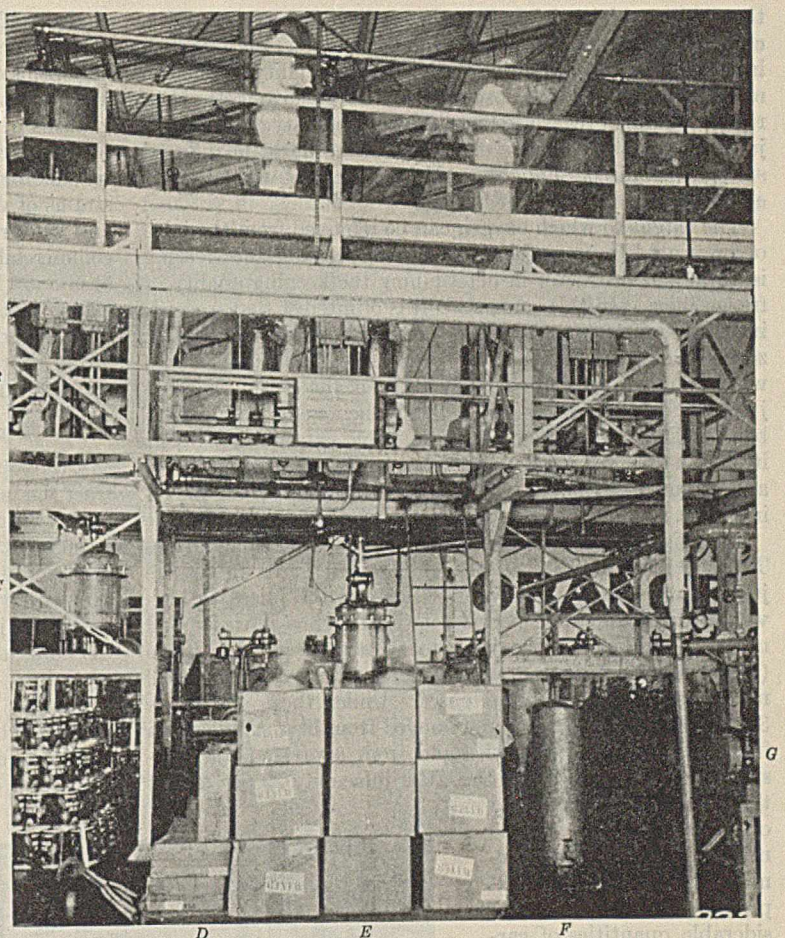


Photo by Food Industries

Deaëating Freezing Plant

A. Orange juice storage tanks to supply freezers
B. Freezers
C. Can filler
D. Container cap sealer
E. Container filler
F. Vapor trap in vacuum line from freezers to vacuum pump G

FOR a score of years the food industry has been endeavoring to pack fruit juices without impairment of their natural qualities. Chief among these have been the pineapple and citrus industries. While they have been struggling to produce satisfactory products, the tomato juice producers have stepped in and made the nation tomato-juice-minded in a short time. Already much of the market that used to belong almost exclusively to the citrus industry has now been taken over by the tomato juice industry, and other fruit industries are endeavoring to secure footholds. The only recourse for the citrus industry is to intensify its effort to produce a satisfactory product. More fundamental research is the first requirement. Since McDermott (*10*) pointed out the importance of preventing oxidation for the packing of a high quality of orange juice, a long period elapsed before the citrus industry recognized that in the newer refrigeration technology it had found an opportunity to take the next great step forward toward the goal of producing a satisfactory preserved orange juice. A better juice is produced by freezing preservation than by any other method which we have seen. However, the product is not uniformly satisfactory and never tastes just like fresh orange juice. The very fact that the citrus industry is still struggling toward this goal is eloquent testimony that the reward for its attainment is considered to be large.

The published work and the commercial developments in the field of the preservation of orange juice by freezing are reviewed. The several methods used and the results of commercial experience with them are discussed. In brief, the variety of orange may be a more important consideration than the effect of the process used. From the manufacturing standpoint, the greatest difficulty lay in securing uniformity of stock. In the marketing of the frozen orange juice, price considerations were the dominant factor. Almost equally important was the requirement of the housewife for the juice to be in usable form for breakfast. Delivery from milk wagons was practical and feasible in some markets. The frozen juice did not lose its vitamin C strength during storage for a year. Excellent flavors were found when the frozen juice was stored for over two years.

Chemical and Physical Observations

We may consider that the orange consists of an outside rind, the flavedo, an inner layer of a white pithy substance, the albedo, and a mass of cells and cell walls, the pulp. The flavedo contains most of the essential oils which, when present in an amount greater than 0.05 per cent, impart a strong terpene flavor to juice. The presence of 0.01 to 0.03 per cent improves the flavor and does not leave an unpleasant "aftertaste" in the mouth. The albedo is rich in pectin which tends to stabilize the emulsion, but it may impart a somewhat bitter flavor to the frozen juice. The pulp also contains a bitter constituent which may be released into the juice during storage or when the pulp is finely comminuted in a colloid mill or triturated with juice in a mortar. The pulp also contains much of the characteristic flavor of the orange.

In the commercial production of orange juice for freezing, the problem therefore consists in keeping those substances out of the juice which might tend to impair the quality of the frozen juice during storage. Flavedo and albedo must be largely eliminated from the juice and pulp, and orange oil must be kept so low as not to be objectionable.

In addition to the actual constituents of

the orange which might affect the quality of the frozen juice, certain treatments of the orange and extraction practices were investigated in their relation to the keeping quality. Thus no material difference was observed between green and ethylene-ripened fruits in regard to taste, flavor, or acidity of the frozen juice. Juices which were extracted in the dark, in diffused sunlight, in direct sunlight, and in electric light were of about equal keeping quality.

The extent to which oxygen can be removed from the juice or prevented from entering it during expression and freezing is an important factor in determining the keeping quality of frozen juice. In this connection it is of interest that, according to preliminary experiments, there are in the orange distinct zones where a reducing effect is prominent and other zones where an oxidizing effect prevails. In the freshly filtered juice the oxidation is absent. The reducing effect appears to be associated with the pigment. The extracted pigment itself has no reducing power, but, when dissolved in an aqueous acidified solution of monosaccharides, a strong reducing effect is produced, similar to that in orange juice.

Investigations at the plant laboratory of this company in Tampa, Fla., indicate that the dissolved gases in orange juice can be removed only by subjecting the juices to high vacua for considerable periods of time. Thus it was found necessary to subject the juice to a vacuum of 29.6 inches (75.2 cm.) for 36 minutes in order to remove a practical maximum of the dissolved gases. Under these conditions 39.8 and 51.5 cc. of gas were removed from liter samples of a freshly burred Valencia juice and from a pressed juice, respectively. In the case of the latter juice only 79 per cent of the total gas was removed on evacuating for 20 minutes. The gases removed from freshly expressed juice contain considerable quantities of carbon dioxide. As the exposure of the juice to air is increased, the carbon dioxide content decreases and the air content (oxygen and nitrogen) increases.

Conditions of freezing orange juice also affect its properties. Thus when orange juice is slowly frozen, there remains a viscous fraction called the "metacryotic" liquid. Its composition is fairly constant at 8 per cent acid and 64 per cent carbohydrates. It has no definite freezing point. At −20° C. it is liquid, at −28° C. it is gummy, and at −95° C. it is still plastic. By suitable quick-freezing methods, the amount of this metacryotic material can be reduced to negligible amounts. On freezing orange juice, the volume increases to the extent of about 7.5 per cent.

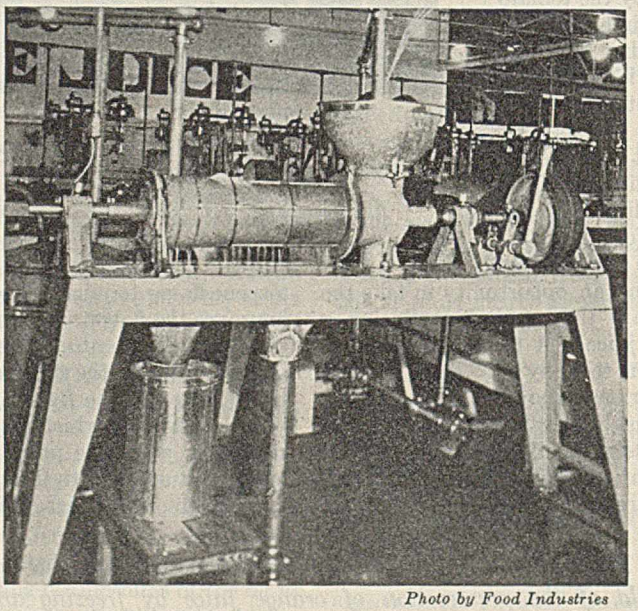


Photo by Food Industries

STRAINER FOR REMOVING EXCESS PULP FROM JUICE

MICROBIOLOGICAL CONDITIONS

That the danger of spreading disease through orange juice is negligible is generally known, but it was considered desirable to study the viability and growth of *Escherichia coli* in orange juice because this organism was the best index organism whose reactions would be a dependable guide as to what pathogenic bacteria would do. Cultures of *Lactobacillus acidophilus* and a member of the *Bacillus subtilis* group were also included. These three organisms were unable to multiply in orange juice at any temperature; the death rate of the three organisms was most rapid at 37° C., was slower at 25° C., and was still slower at −12° C. It was concluded that organisms of the *coli* type would fail to survive longer than 2 weeks in frozen orange juice but that spores would probably remain for a long time in frozen orange juice. There are strains of yeasts which will grow slowly at 0° F. (−17.8° C.) and will grow rapidly at 32° F. (0° C.). Experience in the commercial pack showed that, when frozen juice was stored at about 5° F. (−15° C.) the yeast, in general, died off to the extent that at the end of about 6 months the counts dropped from several thousand down to several hundred. Total mixed bacteria counts on standard media likewise decreased on 6-month storage at 5° F.

INDUSTRIAL METHODS OF OBTAINING JUICE

Although several different methods have been used to extract the juice from the orange, the one most generally used is that of burring with a rotating grooved extractor or burr, using a combination of pressing and tearing (7). This process does not require that the fruit be peeled. By regulating the pressure with which the halved orange is held against the burr, the amount of juice and the amount of orange oil can be regulated. Of course, this introduces a large amount of hand contact with the juice.

Another commercial method utilizes the Skinner plunger press which cuts the oranges in two and squeezes the juice from the halves, resulting in the introduction of a larger percentage of orange oils in the juice than by the so-called expeller method.

By this latter method the juice is expressed continuously by a horizontal rotating screw of the expeller type, allowing the juice to flow through screens in the bottom of the press and forcing the so-called residual rag out through an adjustable opening. In the Florida operations of this company the chilled fruit was first closely graded by size and then placed by hand on vertical Coons citrus peelers which removed most of the peel. The peeled fruit was distributed into Allegheny metal boxes from which it was picked up by hand and the remainder of the peel removed with Allegheny metal hand knives. The peeled fruit was then fed through Allegheny metal troughs into Enterprise expeller presses whose screws were made of monel metal and whose barrels were made of Allegheny metal. The operation was continuous and could be adjusted to vary the yields. The juice then passed through screens to remove such material as the coarse pulp and seeds. A later improvement consisted of an attachment on the discharge end which facilitated the delivery of a juice with only about one-tenth as much pulp, as well as to the delivery of a drier refuse, thereby greatly increasing the yield of juice.

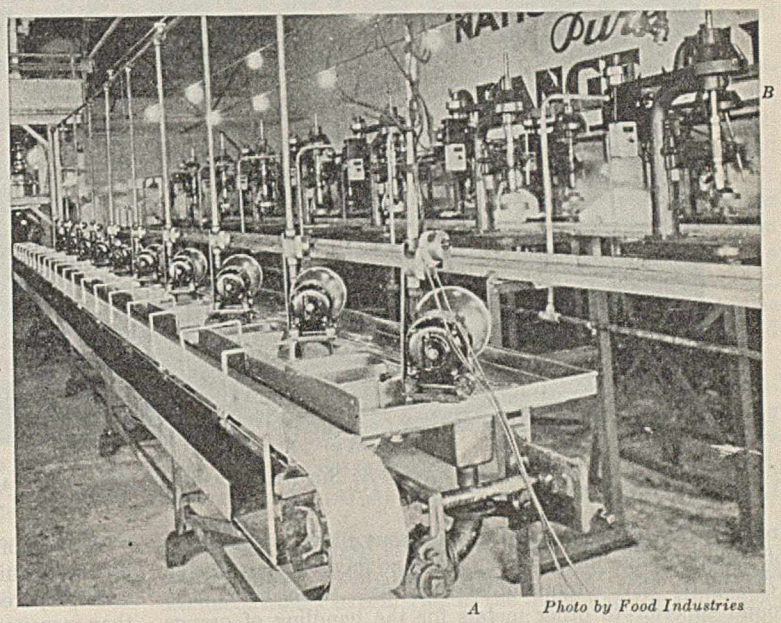
The juice was conducted through sanitary piping to Allegheny metal surge tanks where gas was removed from the juice by evacuation.

During the first half of the season, these were operated on only a 20-inch (50.8-cm.) vacuum, but during the remainder of the year their performance was stepped up to a regular operation of 27 inches (68.6 cm.).

Industrial Methods of Freezing Juice

Several methods have been used commercially to freeze the juice. In one of these the juice was frozen into large cakes which, immediately before delivery, were ground to a slush and packed as such. This procedure did not yield a very good product.

The methods which were most successfully used in Florida were the freezing of the packaged orange juice by submersion in a brine bath, and the freezing to a slush in an ice cream freezer and then packaging into final containers for subsequent hardening by cold air. These processes are well discussed and illustrated by Burton (*2*) and Joslyn (*7*). In the Tampa plant of this company the deaërated juice was dropped out of the evacuated surge tanks into evacuated, vertical, ice cream freezers. Here the juice was frozen to a slush and then forced out by positive nitrogen pressure into the fillers which discharged the slush into the cartons. The cartons were filled and closed, leaving scarcely any head space. They were then conveyed to a sharp freezer where they were subjected to temperatures of about −10° F. (−23.3° C.) and then stored at temperatures of about 0° to 10° F. (−17.8° to −23.3° C.).



A *Photo by Food Industries* *B*

Machine for Reaming Out the Orange Halves, *A*, and Paper-Container Cap Sealers, *B*

Factors Affecting Quality

Quality of Fruit. The Florida orange packing season covers the production of several varieties of oranges which ripen at successive periods. Chief among these are the Pineapples in the early part and the Valencias toward the end. Each of the varieties exhibits packing characteristics of its own. The chemical composition varied during the season as follows:

	Variation
Total solids, %	7.63–16.92
Reducing sugars, %	2.20–6.87
Nonreducing sugars, %	2.60–5.77
Total saccharides, %	5.92–11.37
Nitrogenous matters (calcd. as protein), %	0.35–0.73
Acid (about 0.5 per cent of total acid is volatile) as citric, %	0.53–1.61
Ash, %	0.32–0.55
Alkalinity of ash as CaO, %	16.67–45.00
P_2O_5 in ash, %	4.28–14.59
Specific gravity	1.0310–1.06
Pectin, %	0.001–0.1
Freezing point of juice, ° F. (° C.)	28–28.5–(−2.2–−1.9)

The nature and condition of the fruit exert dominant effects on the quality of the juice. During the operations the fruit was irregular in quality and often arrived at the plant sporadically, making it necessary occasionally to shut down. Such conditions make it essential to develop packing procedure to suit the variability of the stock. Therefore, the conditions under which the authors operated were not conducive to the production of uniform quality of juice. Joslyn (*7*) describes the quality of juice made from immature and overripe fruit as being stale and flat, respectively. Copeman (*6*) states that insecticide sprays markedly affect the composition of the orange. Nelson and Mottern (*11*) showed that trees sprayed with lead arsenate produced oranges with a lower vitamin C content than that from similar unsprayed trees. Fruit that is warm may be too soft to hold its form on the peelers, thus precluding clean peeling. Dirty fruit, of course, must be given either a special processing or be rejected. In the light of all of these cumulative factors which influence the quality of juice, it is clear that to obtain a reasonable constancy in quality, a method must be worked out to mix the fruit or to blend the juices. If only one variety of fruit is handled, then the packing facilities must be enormously expanded in order that the whole pack may be completed in the very short period that the given variety is available.

Cleanliness of Manufacture. Orange juice is particularly susceptible to spoilage by yeast fermentation and by bacterial growth of mixed flora. No pockets, dead ends, or other such places where juice can accumulate should exist anywhere in the plant. It was noticed that on rough places in the equipment, corners, covers, and other places where splash could accumulate or where there was no constant current, or where the juice moved slowly as in vertical piping, there was formed a hard, greenish yellow scale. This scale was so tenacious that, although the entire plant was frequently dismantled and the various units were soaked in alkali solution, scrubbed, and rinsed with hypochlorite solution, the scale was found to adhere even after this drastic procedure. It could be loosened by tapping the pipes with wooden mallets. The passage of grapefruit juice through the lines for about 16 hours removed any scale which had previously formed. The surface of the Allegheny equipment in contact with this scale became roughened. A determination of the metallic content of the scale indicated that it was associated with corrosion of the monel and Allegheny metals.

It is absolutely essential that all of the equipment be made of sanitary construction so that it can be dismantled and thoroughly scrubbed as carefully as any milk plant. There should certainly be two clean-ups every 24 hours. The neglect of such sanitary precautions leads to high microbiological content of the packaged juice with attendant early development of off-flavor.

Content of Pulp. When orange juice is filtered clear of suspended pulp, the flavor is fair. On the other hand, too much pulp is organoleptically distasteful. If the pulp becomes very finely comminuted so that the flavor constituents and the cell walls diffuse into the juice, a somewhat bitter or otherwise unpleasant flavor obtains.

Metal Contamination. Blount and Bailey (*1*) have reported that Duraloy (29.5 per cent chromium, 70.5 per cent

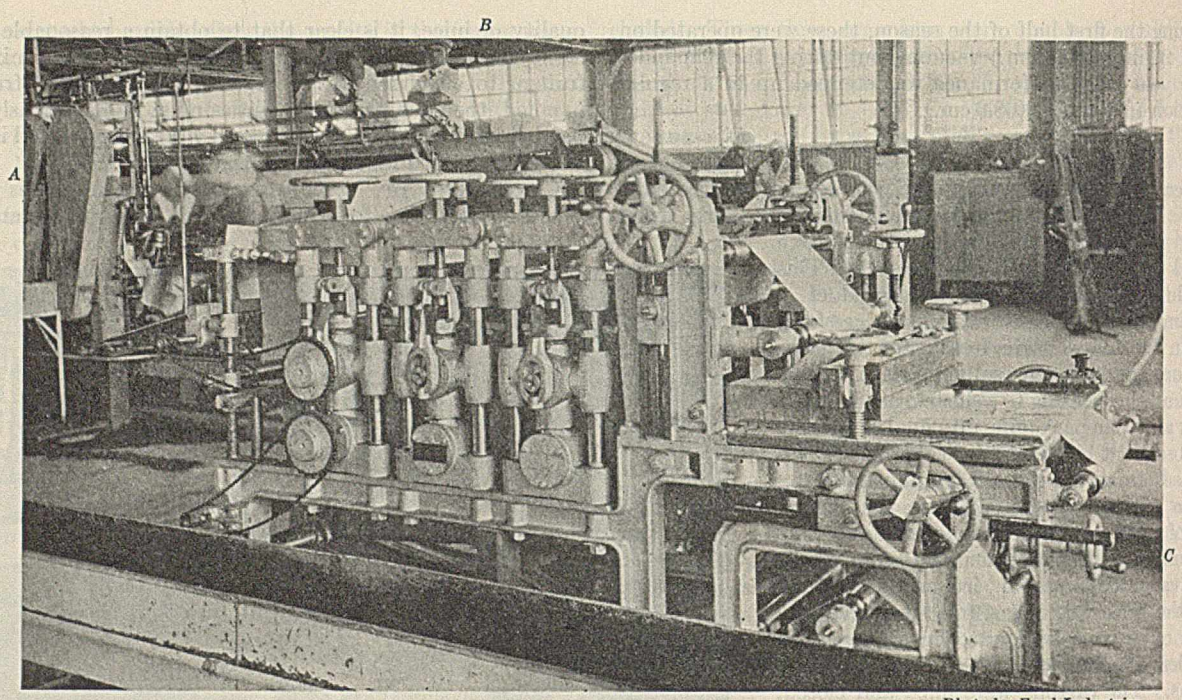


Photo by Food Industries

ORANGE OIL ROLLER PRESS, *A*; SIZER *B* FOR SEPARATING THE VARIOUS ORANGES GOING TO PEELERS *C*

iron) was the most resistant of numerous alloys to the action of boiling orange juice. They made no flavor tests. Joslyn (*7*) reports that aluminum and stainless steels have been found superior to other metals for the handling of orange juice, whereas copper and iron exert deleterious effects. The writers' own experiments confirm Joslyn's findings. They found that copper and iron imparted off-flavor when present to the extent of 5 p. p. m. Chromium spoiled the flavor at 30 p. p. m. Tin exerted uncertain effects over a range of 15 to 60 p. p. m. Aluminum and nickel did not impart any flavor. Piping troughs and tanks of Allegheny metal (8 per cent nickel, 18 per cent chromium, 74 per cent iron) were satisfactorily resistant to corrosion, although this metal was slightly roughened where scale formed.

DEGREE OF DEAËRATION. During the first half of the season, the vacuum system was only strong enough to impart a vacuum of not more than 20 inches but thereafter new equipment yielded regularly a 27-inch vacuum. Furthermore, the juice was exposed to this reduction of pressure for the relatively short periods of time required to fill the three 30-gallon (113-liter) Allegheny surge tanks which emptied in staggered rotation. According to Joslyn and Marsh (*8*) deaëration is not effected until a vacuum of at least 27 inches is reached. Therefore, the juice in the present experiments was not effectively evacuated. In these experimental packs, no adjusted degree of evacuation of juice or temperature of freezing was found to exert any beneficial effects on juice which was packed in cartons, whereas such treatment did make slight differences in juice which was frozen in cans. In the latter series, it was evident that deaërated juice kept better than juice which was not deaërated. Moreover, deaërated juice could be packed under atmospheres of carbon dioxide, nitrogen, hydrogen, oxygen, and helium with, substantially, equally good results. On the other hand, deaërated juice, charged by bubbling these gases through it, held up in the following order of excellence: hydrogen was best; then helium and nitrogen of equal quality; followed by carbon dioxide and oxygen. When different degrees of evacuation were applied to the freezers, no appreciable difference was noticed in the quality of the frozen juice.

In spite of the precautions taken to keep oxygen from the plant-run juice, certain experimental batches of juice which were prepared by bubbling oxygen through them were better than more carefully prepared juice, because, presumably, they contained some constituent which rendered them less susceptible to oxidation. Chace's finding (*4*) was confirmed that the charging of a juice before freezing, or the packing of it after freezing in an atmosphere of carbon dioxide, does not exert an appreciable influence to improve the product.

PACKAGES. Generally, packaging in cardboard cartons was found satisfactory for short-time storage, but during long storage the contents deteriorated markedly. Packaging in tin cans, plain or enamel, exhibited good quality even for as long as 3 years. Cans showed no signs of corrosion and were not even spangled.

QUALITY AS PRODUCED

VITAMIN C. In this laboratory, Conn and Johnson (*5*) showed that frozen orange juice, kept in storage for 5 months, does not lose any of its original vitamin C potency. Substantially all of this vitamin occurs in the filtered juice, and therefore the presence of pulp in juice adds nothing to the latter's vitamin C content. Nelson and Mottern (*12*), found that frozen orange juice packed with no precautions to exclude air maintains its original vitamin C content unimpaired for at least 10 months. Buskirk, Bacon, Tourtellotte, and Fine (*3*) report that frozen orange juice retains its full vitamin C potency when stored for 20 months.

In this connection it might be interesting to call attention to the work of Maslow, Shelling, and Kramer (*9*) who irradiated orange juice for 3 hours and imparted sufficient vitamin D potency for definite cure of rachitic rats. In a personal communication Shelling states that in the application of this work to children, they readily took the juice, and it was clinically effective. The work was not continued because of the development of viosterol. (They quote Zilva that irradiation of lemon juice for 8 hours did not impair its antiscorbutic potency.)

FLAVOR. In general, practically all the juice which was packed before April 15 possessed good flavor and has main-

tained it for 3 years in storage. On the other hand, almost all the juice packed after this date was of unsatisfactory quality and appreciably deteriorated in storage. The period of best juice coincided with the Pineapple season and the application of only 20 inches evacuation, whereas poorer quality of frozen juice was produced with Valencia oranges and the application of 27 inches evacuation. Juice which was good immediately after packing remained so during storage. No involved packing procedure has succeeded in making a poor juice into a good one.

Appearance. Frequently there is associated with spoilage an unsightly coagulation on the pulp. On defrosting, this settles out, leaving a perfectly clean supernatant solution. Sometimes this coagulation is accompanied with a browning of the color. Often it is accompanied with off-flavor.

Defrosting. Just as much care is necessary to defrost a frozen orange juice properly as was originally expended in preparing it for freezing. Attempts to hurry and defrosting by placing the carton in hot water, or otherwise by rapidly heating it, will hurt the flavor. Slow defrosting by allowing the juice to sit in a household refrigerator overnight yields the best product. An intermediate quality is obtained by allowing the package to defrost at room temperature, which may require several hours.

Refreezing. If a carton of frozen orange juice is slowly defrosted to the extent that there still remains a small amount of ice, the package may be returned to the sharp freezer and refrozen without deleteriously affecting the flavor. A repetition of this treatment definitely impairs the quality.

Such refreezing in an air blast is a relatively slow procedure. It results in the development of the so-called metacryotic fraction. This may ooze or leak out of the carton or cup and impart a sticky unsightly appearance to the package.

Marketing Experiences

Attendant upon the widespread acceptance of the teachings of the newer knowledge of nutrition, the demand for orange juice at breakfast became very great. Attempts to prepare a bottled juice preserved by chemicals or heat treatment had not met with success. None of these products tasted like fresh (or even near fresh) orange juice. Accordingly, several attempts were made to preserve the juice by freezing it and delivering it to the householder every day. The failure of such efforts was attributed to poor quality of product and faulty marketing procedure. Inasmuch as the diaryman had built up an extensive delivery system to handle highly perishable milk every morning, and since orange juice was properly considered as being complementary to milk in the diet and preponderantly used at breakfast, it was thought that the milk wagon would be the ideal means for delivering frozen orange juice.

Every morning the householder would find a package of frozen orange juice on his doorstep, along with his milk and cream. He would not have to go to the expense of buying oranges, half of which was wasted in pulp and peel and freight. He would not have to bother with the messy squeezing of the oranges. A simple defrosting would give him fresh orange juice quickly. It all sounded so plausible that numerous dairymen embarked on the enterprise.

It never had a chance to succeed. There were several causes for failure, any one of which was great enough it itself. In the first place, the economics of the plan was unsound. The country was suffering from the depression, the price of fresh oranges was low, and the alleged economies to the householder were not convincing. A falling market was no time to inaugurate the distribution of a new, relatively high-priced product.

Moreover, the housewife found that the proposition was not labor-saving or convenient. If the package of frozen juice was taken indoors soon after delivery, the problem was to melt it down for breakfast. To hurry matters, the package was heated, thereby impairing the flavor. If the juice was delivered too early on a hot morning, it was all melted when taken indoors. Some bought the juice one day and left the package in the refrigerator to defrost slowly for use the next day. This was the correct method. But, in general, it was found that customers cannot be educated overnight to the use of a new product which must change their buying and culinary habits.

Furthermore, high-pressure salesmen unloaded large quantities of the juice on delicatessen and other store dealers who did not have the facilities for keeping the juice in the proper condition. This brought an inevitable result of dissatisfaction and adverse criticism.

To meet the customer's complaint of not wanting to bother with the defrosting job, the frozen product was removed from cold storage 24 hours before delivery to allow it to thaw to a mushy condition at the time that it was put on the wagons. Accordingly, when the customer was ready to use it, the juice was in a liquid state but still cold. However, returns could not be sent out again.

Then too, the milk wagon drivers were not properly instructed or interested. Many reacted strongly against having to handle the orange juice in their deliveries. The drivers always had to take out more than they were expected to sell, with the result that the returned cartons were in all stages of defrosting.

Also, it was almost impossible to deliver a product of constant quality. From the discussion above, it is seen that the uncontrolled irregularity in the quality of the fruit operated to produce juice which varied markedly in its composition even from hour to hour. Of course, such a situation brought complaints. Uniformity of quality is a prime requisite for successful marketing.

Finally, the frozen orange juice was not equal in quality to that which is freshly extracted from the orange. Some batches have maintained an excellent quality in storage for 3 years whereas other batches soon became unsalable. Spoilage embraced molding, yeast growth, discoloration by browning, coagulation of pulp, loss of flavor, development of terpene flavor, etc. A juice must closely match the fresh product if it is to find favor in a large way.

However, in spite of the above difficulties, frozen orange juice is still being marketed by several firms who handle the product in bulk and sell it to institutions, schools, restaurants, manufacturers of orange juice soft drinks, and similar businesses. Many persons, especially children, like to eat it in the form of a slush something like the so-called snowball. As a matter of fact, present stocks of frozen orange juice yield better juices than much of the alleged fresh juice which is now served at good restaurants.

With regard to the future, it is clear that some of the foregoing difficulties are correctable. The depression will not last forever, and accordingly the question of prices will again become significant. The education of the salesman and consumer are matters of time and intelligent effort. Two difficulties remain, and they await the attention of further research effort. These are constancy in quality of product and an improvement in quality to equal more nearly that of freshly expressed juice. When these two problems are solved, the market for frozen orange juice will increase.

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Phase Equilibria in Hydrocarbon Systems

IV. Solubility of Propane in Two Different Oils[1]

B. H. SAGE, W. N. LACEY, AND J. G. SCHAAFSMA, California Institute of Technology, Pasadena, Calif.

THE composition of a hydrocarbon gas has a large influence upon the solubility of the gas in a hydrocarbon liquid. Previous experimenters (*1*, *3*, *4*, *8*) have presented results which indicate that variations of the composition of the gas may have a much larger effect than variations of the composition of the liquid upon the changes resulting when the two are brought to equilibrium with each other. In a study of the effect of gas composition on such equilibria, it seems desirable to make measurements using, in a pure state, each of the several constituents found in natural gas and thus lay a foundation for correlating and predicting the behavior of mixed gases. Such studies are being made as a part of the work carried on under Research Project 37 of the American Petroleum Institute. This article presents the results of measurements of the solubility and resulting changes of properties when pure propane gas is brought to equilibrium with each of two oils at various temperatures from 70° F.

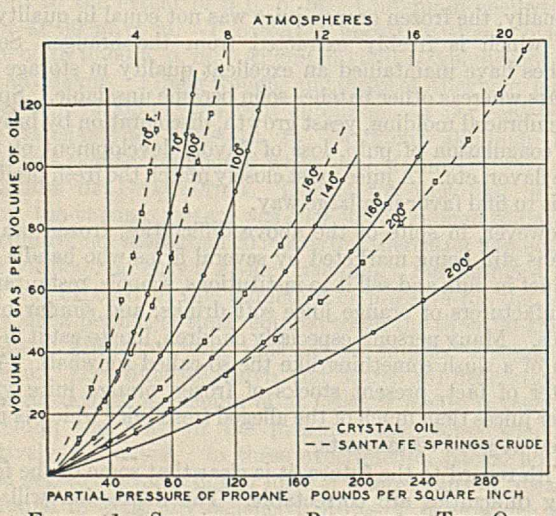

FIGURE 1. SOLUBILITY OF PROPANE IN TWO OILS

(21.1° C.) to 200° F. (93.3° C.) and at pressures up to approximately 70 per cent of the vapor pressure of propane at each temperature.

SOURCE OF MATERIALS AND METHODS OF PROCEDURE

The supply of C. P. propane for this work was obtained from the Philgas Company. Their careful analysis by special methods showed no appreciable amounts of other hydrocarbons to be present. The purity was also verified by excellent constancy of vapor pressure throughout complete isothermal condensation.

One of the oils used was a highly refined, water-white material known as crystal oil. It was chosen for this and other studies as a stable liquid of moderately high viscosity and relatively narrow range of composition and of boiling point, with practically no constituents likely to vaporize in the range of temperatures included in these studies. The other oil consisted of a blended sample taken from Santa Fe Springs Field, Calif. The properties of these two oil samples are as follows:

	CRYSTAL OIL	SANTA FE SPRINGS CRUDE OIL
Sp. gr. (100°/39.2° F.)	0.8665	0.8339
Gravity, ° A. P. I. (60° F.)	29.1	35.1
Viscosity at 200° F., millipoises	40.5	12.0
Mol. wt.	337.5	199.

Since all the temperatures involved in the work here presented lie below the critical temperature of propane, it will be seen that the maximum pressure at which a gas phase would exist would be the vapor pressure of propane at the particular temperature prevailing, when the oil itself has no appreciable vapor pressure, as in the case of the crystal oil. Where the solvent has an appreciable vapor pressure, as in the case of the Santa Fe Springs oil sample, this maximum total pressure would be greater than the vapor pressure of propane. In both the propane–crystal oil system and the propane–Santa Fe Springs crude oil system the temperature range studied was below the critical temperatures of both constituents involved, and so there would be no tendency for transfer of the solvent to the vapor phase, beyond that due to the vapor pressure at the existing temperature, as the

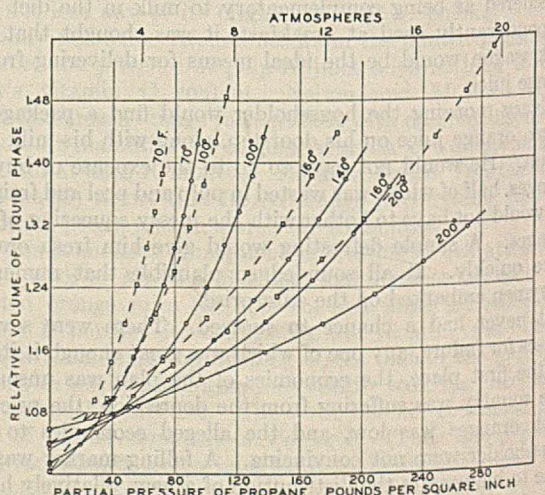

FIGURE 2. VOLUME OF SATURATED SOLUTIONS COMPARED TO VOLUME OF ORIGINAL OIL

[1] For Parts I, II, and III, see literature citations *10*, *11*, and *4*.

TABLE I. ORIGINAL DATA ON PROPANE–CRYSTAL OIL SYSTEM

(P = partial pressure of propane, pounds per square inch absolute; S = propane dissolved, cubic feet per pound of crystal oil; V_L = volume of liquid phase, cubic feet per pound of crystal oil)

At 70° F.			At 100° F.			At 140° F.			At 160° F.			At 200° F.		
P	S	V_L	P	S	V_L	P	S	V_L	P	S	V_L	P	S	V_L
0.0	0.0	0.01823	0.0	0.0	0.01845	0.0	0.0	0.01879	0.0	0.0	0.01891	0.0	0.0	0.01926
33.4	0.4002	0.01956	29.7	0.2223	0.01916	40.1	0.2043	0.01962	56.4	0.2502	0.01981	51.8	0.1557	0.01978
45.3	0.6135	0.02030	53.5	0.4652	0.02000	75.6	0.4464	0.02040	101.0	0.5131	0.02077	97.0	0.3225	0.02042
55.8	0.8441	0.02106	72.4	0.7022	0.02092	105.3	0.6918	0.02133	138.1	0.7789	0.02176	137.6	0.4914	0.02106
64.9	1.066	0.02180	87.2	0.9340	0.02169	130.7	0.9391	0.02225	168.2	1.039	0.02274	174.6	0.6645	0.02172
72.8	1.308	0.02258	100.4	1.175	0.02254	152.6	1.198	0.02320	194.7	1.312	0.02379	208.5	0.8388	0.02239
79.7	1.541	0.02343	111.6	1.419	0.02351	172.0	1.461	0.02415	217.8	1.592	0.02489	240.6	1.025	0.02314
85.2	1.766	0.02419	121.2	1.668	0.02429	189.4	1.733	0.02510	237.8	1.871	0.02571	270.5	1.214	0.02391
90.1	2.007	0.02502	129.5	1.906	0.02512									
94.4	2.241	0.02586	136.4	2.144	0.02604									

amount of propane and the pressure were increased. The effect of total pressures, such as those encountered in this work, upon the vapor pressure of the liquids used would be negligible. In these systems, therefore, the only process occurring when propane is added to the system in increasing amounts, with consequent increases in pressure, is a simple dissolving (*4*) of increasing amounts of propane in the liquid.

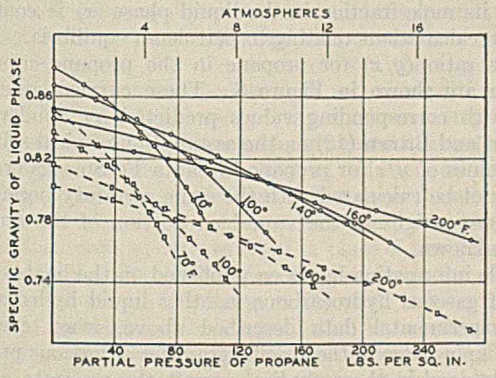

FIGURE 3. SPECIFIC GRAVITY OF SATURATED SOLUTIONS

It has been assumed, in the case of the propane–Santa Fe Springs crude oil system where the oil has appreciable vapor pressure, that Dalton's law of partial pressures was applicable and therefore that the partial pressure of propane in the system at any time could be obtained by subtracting the vapor pressure of the crude oil for the temperature existing from the total pressure as measured. Any uncertainty in the solubility values caused by this assumption would be small in this case since there would result only a small error in the amount of gas in the gas phase, which was in turn only a small fraction of the total gas added to the system, the rest being in solution in the oil.

The solubility measurements were made with the apparatus and by the methods described by Sage and Lacey (*10*). Air was removed from the solubility cell before addition of propane by cooling the cell and contents to the temperature of solid carbon dioxide, evacuating to remove the air, closing the valve, and then bringing the cell to the temperature at which the measurements were to be made. Cooling the liquid prevented any appreciable loss of the constituents of the oil during evacuation. The viscosity determinations were made by means of the apparatus described by Sage (*9*). The specific gravity of propane gas at 60° F. and 14.73 pounds per square inch absolute pressure was found by experimental measurements to be 0.001889 compared to that of liquid water at its maximum density as unity.

The method used consisted in expanding a carefully weighed amount of liquid propane from a special light-weight bomb into an accurately calibrated, mercury-filled pipet in a thermostat. The volumes used for each determination were approximately 300 cubic inches (5 liters), and the final conditions are mentioned above. The value thus obtained differs from that taken from the literature (*2*) for use in a previous article of this series (*11*).

RESULTS OF EXPERIMENTS

The experimental results obtained from the study of the propane–crystal oil system are shown in Table I. Corresponding tabulation has not been made for the propane–Santa Fe Springs oil system because of the belief that the results could be shown graphically to as great an accuracy as the reproducibility of the oil sample would justify. The values of solubility of propane are given in terms of volumes of propane dissolved in unit volume of original oil, both being measured at 60° F. and 14.73 pounds per square inch absolute pressure.

In Figure 1 is shown the variation of solubility as a function of the partial pressure (absolute) of propane for equilibrium at each of a series of different temperatures. The points shown were calculated directly from the experimental observations. The curves for both oils are shown on the same figure for purposes of comparison. To convert the solubility values to cubic feet of gas per barrel of original oil, multiply by the factor 5.615.

The relative volumes of the liquid phases as compared to those of the original oils (at 60° F.) are given as functions of the partial pressures of propane for saturation at several temperatures by the curves of Figure 2. The fact that the curves do not start at the origin is due to the thermal expansion of the oil on heating from 60° F. to the temperatures at which the determinations were made. Both the solubility curves of Figure 1 and the relative volume curves of Figure 2 would be expected to approach infinity as the partial pressure of the propane in each case approached the vapor pressure of pure propane at the temperature of the run.

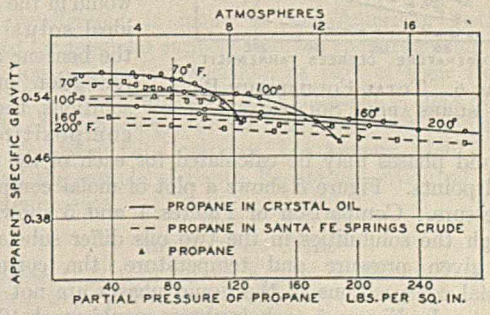

FIGURE 4. APPARENT SPECIFIC GRAVITY OF DISSOLVED PROPANE

Figure 3 presents the variations in the specific gravities of the liquid phases with changes in the partial pressures of propane at equilibrium. The specific gravities given in this paper are the ratios of the weights of unit volumes of the liquids to the weight of a unit volume of liquid water at its maximum density. Each curve of Figure 3 would end at a point corresponding to the vapor pressure and the specific gravity of pure liquid propane at the temperature to which the curve applies. The more rapid reduction of specific gravity of the liquid for the lower temperature is due to the greater solubility under these conditions.

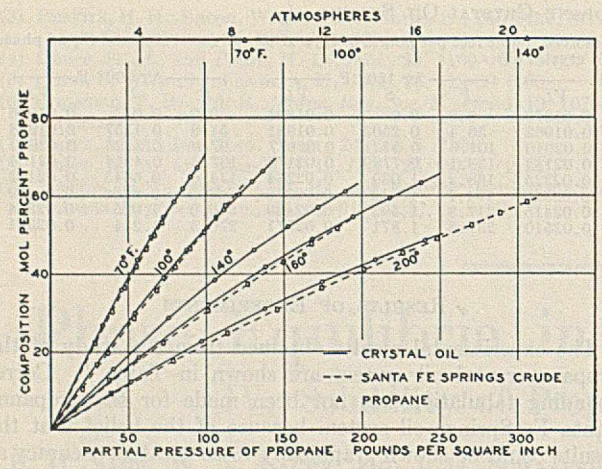

FIGURE 5. MOLAL COMPOSITIONS OF SATURATED SOLUTIONS

If the change in volume of the liquid phase, as propane dissolves, is assumed to represent the volume of the dissolved propane, the apparent specific gravity of the latter may be directly calculated from the experimental data. This would not be the same as the partial specific gravity (*5*) of propane since it takes into account the total change from zero pressure. Figure 4 shows the results of such calculations. The values are considerably higher than the corresponding specific gravities of pure liquid propane in equilibrium with propane gas. They would approach the latter values as the partial pressures approach the vapor pressures of propane.

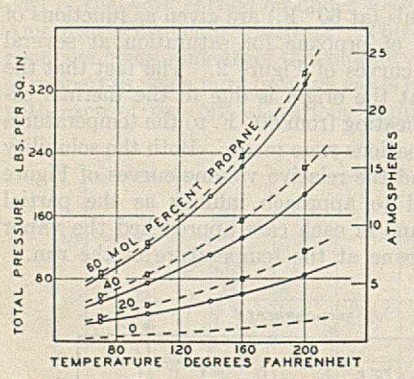

FIGURE 6. TOTAL EQUILIBRIUM PRESSURES ABOVE SOLUTIONS

The average molecular weights of the samples of oil were determined by measurement of the freezing point lowering of benzene. Assuming this method to furnish a correct measure of molecular weight, as it would in the case of ideal solutions in the benzene and no formation of solid solutions, the molal compositions of the liquid phases may be calculated for each of the experimental points. Figure 5 shows a plot of molal composition *vs.* pressure. Comparison of Figures 1 and 5 shows that, although the solubilities in the two oils differ substantially for a given pressure and temperature, the corresponding molal compositions of the liquid phases are not greatly different. In Figure 5 each iostherm would reach 100 mole per cent propane at the vapor pressure of pure propane at the given temperature. The divergence of these curves from the straight line predicted by Raoult's law is small. Since the molecular weight of the Santa Fe Springs oil is nearer that of propane, it would be expected that the divergence would be smaller in its curves, and this is found to be the case. It is surprising that the curves should cross the Raoult-law line and this may point to small errors due to the method used in determination of the molecular weights which would cause the curves to pivot slightly about the origin. Considering the wide difference in properties of the two oils used, the similarity of the curves for them indicates the possibility of satisfactory correlations of propane solubility data by means of this type of plot.

Total pressure curves for mixtures of fixed composition are shown in Figure 6. The points shown were taken directly from a graph similar to Figure 5 except that in this case the total pressure on the system was employed rather than the partial pressure of propane. The lowest dashed curve shows the variation with temperature of the pressure exerted by the Santa Fe Springs oil itself.

The effect of dissolved propane upon the viscosity of the liquid phase is shown in Figure 7. The more rapid decrease in the viscosity of the Santa Fe Springs crude at 140° F. results from a greater solubility for a given pressure at the lower temperature. Curves of similar appearance are obtained when viscosities are plotted against molal compositions of the liquid phases. Viscosity measurements at the lower temperatures were precluded by the requirement of large amounts of propane due to high solubility and the relatively large volume of the viscometer.

The ratio of the mole fraction of propane in the gas phase (y) to its mole fraction in the liquid phase (x) is commonly used in calculations relating to petroleum equilibria. Values of this ratio (y/x) for propane in the propane–crystal oil system are shown in Figure 8. These curves agree fairly well with corresponding values predicted by Souders, Selheimer, and Brown (*12*) on the assumption of ideal solutions. The values of y/x for propane in Santa Fe Springs crude oil could not be calculated with the same certainty because the molecular weight of the vaporized portion of the crude oil was unknown.

Little information has been published on the heats of solution of gaseous hydrocarbons in other liquid hydrocarbons. The experimental data described above, when combined with a knowledge of the specific gravities of gaseous propane, also obtained in these studies, permit the accurate calculation of the partial heat of solution of propane gas in liquid crystal oil for any temperature and pressure combination within the ranges studied. In this connection the partial heat of solution is considered to be numerically equal (but of opposite sign) to the heat required to vaporize one pound of propane from a solution in crystal oil under equilibrium

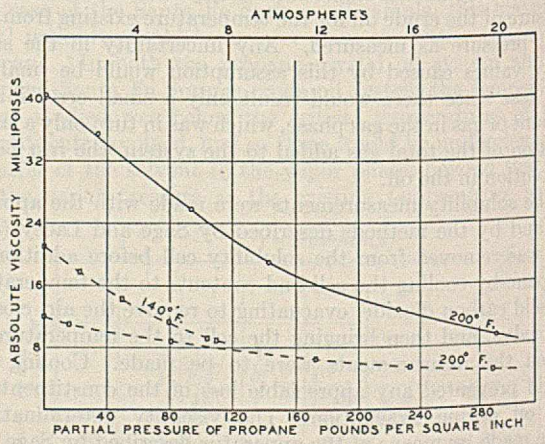

FIGURE 7. VISCOSITIES OF SATURATED PROPANE SOLUTIONS

conditions at a given composition of the solution. This process would be approached when the amount of the solution was large compared to the quantity of propane vaporized or when one considered conditions at a fixed point in a continuous process where the temperature and pressure remained constant with respect to time. The above definition is the same as that of the partial heat of solution given by Lewis and Randall (*6*).

The conditions specified make directly applicable the Clapeyron equation (*7*):

$$\left(\frac{\delta P}{\delta T}\right)_x = \frac{\Delta H}{T\Delta V}$$

ΔH in this case is the partial heat of solution of one pound of propane in a solution in crystal oil. The change in volume, ΔV, is the difference between the change in volume of the

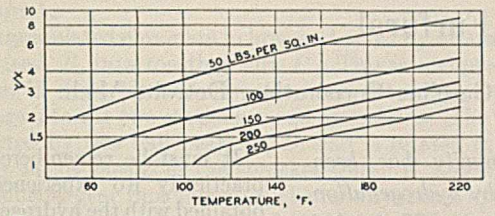

FIGURE 8. VALUES OF y/x FOR PROPANE IN THE PROPANE–CRYSTAL OIL SYSTEM

solution due to dissolving in it one pound of propane (i. e., the partial specific volume of propane) and the specific volume of gaseous propane at the specified temperature and pressure. ΔV was, therefore, directly obtained from the experimental data. Values of $(\delta P/\delta T)_x$ for each set of conditions were determined from the slopes of the constant composition–total pressure curves of Figure 6 by graphical interpolation.

The values of the partial heat of solution at constant pressures are shown as functions of the temperature in Figure 9. To avoid the plotting of negative values, they have been expressed in terms of heat evolved in place of heat absorbed. These values can be applied to a process where the pressure and temperature are changing, if the path is known. For isothermal conditions where equilibrium is maintained, the path may be predicted from the data corresponding to Figures 1 and 2. For these isothermal conditions the heat absorbed, when the equilibrium partial pressure of propane is increased from zero to some given final pressure, P, has been calculated in the following manner: The partial heat of solution in Figure 9 may be written $(\delta H/\delta W)_T$ where W is the weight of propane dissolved. The slope of the solubility curves may be written as $(\delta W/\delta P)_T$ per pound of crystal oil, proper con-

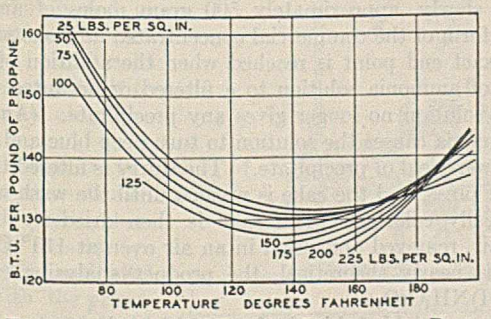

FIGURE 9. PARTIAL HEAT OF SOLUTION OF PROPANE IN CRYSTAL OIL

sideration being given to the conversion of the units of volume to units of weight. The product of these two quantities gives the rate of heat absorption as the partial pressure of propane is increased, expressed as B.t.u. per pound per square inch for one pound of crystal oil. It should be understood that the propane must be added to the system at the same pressure and temperature at which it is dissolved in the solution. Graphical integration of the quantity,

$$\int_0^P \left(\frac{\delta H}{\delta W}\right)_T \left(\frac{\delta W}{\delta P}\right)_T dP$$

for constant temperature gives the heat absorbed when one pound of crystal oil is saturated with propane at a given temperature by a reversible isothermal process of solution, in which the partial pressure of propane is gradually increased from 0 to P, each increment of propane dissolved being furnished at the then existing partial pressure.

The results of such calculations are shown in Figure 10. For convenience in avoiding negative quantities, these results are expressed as heat evolved rather than heat absorbed. As the vapor pressure of pure propane is approached, the heat evolved approaches infinity since an infinite amount of propane must be dissolved in the one pound of crystal oil in order that the equilibrium partial pressure shall reach the vapor pressure of pure propane.

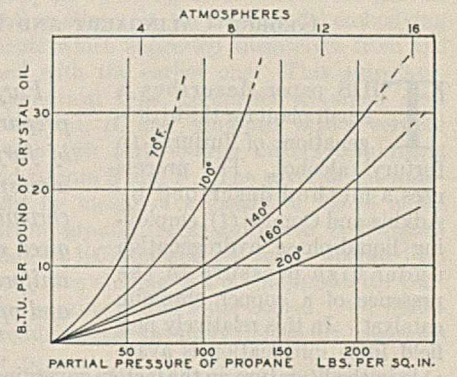

FIGURE 10. HEAT EVOLVED WHEN THE TOTAL AMOUNT OF PROPANE NECESSARY TO SATURATE ONE POUND OF CRYSTAL OIL AT A GIVEN PRESSURE IS DISSOLVED AT CONSTANT TEMPERATURE

CONCLUSIONS

The following conclusions regarding the behavior of mixtures of propane and two petroleum oils have been reached:

1. The solubility of propane in an oil increases rapidly as its partial pressure approaches the vapor pressure of pure propane.
2. The apparent specific gravity of the dissolved propane is greater than that of pure saturated propane liquid at the same temperature.
3. The molal composition of the liquid phase for a given temperature and given partial pressure of propane is almost the same for each of the solvents in the range investigated.
4. The laws of ideal solution appear to apply to propane rather closely when dissolved in crystal oil.
5. The heat of solution of propane in crystal oil is comparable to the heat of condensation of propane at the lower part of the temperature range investigated but is much larger than the heat of condensation as the critical temperature of propane is approached.

ACKNOWLEDGMENT

Acknowledgment is made to the American Petroleum Institute for financial support and for encouragement in the prosecution of this investigation, as part of their Research Project 37. Thanks are due R. G. Dickinson, of the California Institute of Technology, for his helpful criticism and suggestions. The Shell Oil Company, Los Angeles, Calif., kindly furnished the sample of Santa Fe Springs crude oil used in these experiments.

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Small-Plant-Scale Liquid-Phase Hydrogenation under High Pressure

Hydrogenation of Furfural

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Furfuryl alcohol of high purity has been prepared in a small-scale plant by hydrogenation of furfural around 175° C. under 50 to 100 atmospheres pressure in the presence of a copper chromite catalyst. A detailed description is given of the delicate preparation of a highly and uniformly active catalyst, as well as of the design and operation of the hydrogenation plant.

THIS paper describes a small plant for the hydrogenation of furfural to furfuryl alcohol. The process uses a method described by Adkins and Connor (*1*), employing liquid-phase hydrogenation under high pressure in the presence of a copper chromite catalyst. In this relatively new field little information is available in the literature on the factors governing successful operation on a manufacturing scale. The experiences acquired in this particular instance are reported here in the hope that they may be of some value to those interested in similar problems.

Laboratory experiments readily confirmed the report of Adkins and Connor but made it also apparent that the process could not be transferred to plant scale without certain modifications. Three main difficulties became apparent at once: (*a*) The decomposition of the complex copper chromate is exothermic and self-sustaining, yet the temperature must be kept below certain limits; otherwise the product formed shows only very slight, if any, activity. This can be done fairly readily on small batches in the laboratory, but the suggested procedure must be considerably modified if it is desired to produce regularly several kilograms a day of catalyst of a uniformly high activity. (*b*) The hydrogenation reaction is also exothermic, and both furfural and furfuryl alcohol are somewhat sensitive to high temperature, tending to polymerize. To obtain a product of high purity, it is necessary, therefore, to employ a catalyst of sufficient activity to induce a high rate of reaction at a moderate temperature, and to remove the heat of reaction rapidly enough to prevent a substantial rise in temperature during the hydrogenation. (*c*) Efficiency of stirring is an important factor in liquid-gas reactions, but the method of stirring used in the laboratory (rocking autoclave) was not very adaptable to plant-scale operation, and no data were available on the relative efficiencies of different methods of stirring. Other minor problems arose as the development work progressed, and various solutions were tried until a process was finally evolved which appeared satisfactory. This final process will be described here, only passing reference being made, when relevant, to procedures which were tried and later discarded. While the plant operated smoothly and economically, the authors have no doubt that further experimentation might result in further improvements and greater economy.

As explained below, the process proved to be even more attractive than was indicated by Adkins and Connor. Under the proper conditions a catalyst was prepared which would hydrogenate furfural in less than 30 minutes instead of 2 hours, as reported by these investigators. Another advantage is that the product obtained is of high purity, being light in color and remarkably free from tetrahydrofurfuryl alcohol, methyl furane, and pentanediols, which are usually present when a nickel catalyst is used.

It must be remembered that practically no experience was obtained with the hydrogenation of any substance other than furfural. Some of the details of operation were no doubt made necessary by the characteristics of the two materials involved—furfural and furfuryl alcohol. It seems likely, however, that in the main (and particularly in what relates to the preparation of the catalyst and the type of autoclave used) the experience reported here is substantially directly applicable to any similar hydrogenation process.

PREPARATION OF CATALYST

BASIC COPPER AMMONIUM CHROMATE. As indicated by the amounts of materials reacting, by the yield, and by the analysis of the product, the copper chromate intermediate is precipitated in accordance with the equation:

$$2CuSO_4 + Na_2Cr_2O_7 + 4NH_3 + 3H_2O = 2Cu(OH)NH_4CrO_4 + Na_2SO_4 + (NH_4)_2SO_4$$

In a 400-liter earthenware crock fitted with a monel stirrer, 250 gram moles of powdered commercial $CuSO_4 \cdot 5H_2O$ and 125 gram moles of commercial $Na_2Cr_2O_7 \cdot 2H_2O$ are dissolved in 300 liters of water. To this solution are then added slowly, approximately 500 gram moles of ammonia in the form of the commercial concentrated aqueous solution. The exact end point is reached when the addition of a few drops of ammonia solution to a filtered or decanted sample of the solution no longer gives any precipitate. (An excess of ammonia causes the solution to turn deep blue and results in a lower yield of precipitate.) The slurry is filtered through a filter press, and the cake is washed until the wash water is practically colorless. The cake is then dried by blowing with air, removed and dried in an air oven at 110° C. The yield is nearly theoretical, the product analyzing close to $Cu(OH)NH_4CrO_4$.

This material is fed in the form of friable lumps to a powder mixer in which it is mixed with enough water (about 10 per cent) to give a powder moist enough to cohere when squeezed in the hand without, however, becoming sticky. This is then fed to a granulator fitted with 12-mesh screen (about 5 mesh per cm.), and the granulated material is again dried in the oven. The final product contains about 80 per cent of granules and 20 per cent of fines. Material of this type is handled satisfactorily by the roaster described below, but, when the product contains enough fines to interfere with the operation of the roaster, these fines are sifted out and fed back to the powder mixer.

COPPER CHROMITE. As stated in the introduction, the decomposition of the complex chromate is induced by heat but is exothermic and self-sustaining. Assuming the formula given above to be correct, the reaction can be written:

$$2Cu(OH)NH_4CrO_4 \longrightarrow Cr_2O_3 \cdot 2CuO + N_2 + 5H_2O$$

The problem is, then, to raise the material to a temperature sufficient for the reaction to start and to keep it there while removing the heat as fast as it is evolved. The type of equipment finally adopted was a continuous rotary tube furnace, heated electrically, in which the chromate is fed from a hopper by means of a screw feed. This furnace is illustrated in Figure 1.

The granulated chromate in hopper *A* is fed by means of the screw feed, *B*, into roasting tube *C*. This is a copper tube 7.5 cm. in diameter and 1 meter long, fitted by means of bushings into the two stationary end assemblies. The tube is supported by two ball bearings, *D*, and is rotated at about 15 r. p. m. by means of the sprocket wheel, *E*, and a motor and reducing gear (not shown). The tube is heated by means of a resistance wire, *F*, wound around it on a thin coating of alundum cement, in two circuits with terminals at *G*, *H*, and *I*, connected to posts *J*, *K*, and *L*, to which the current is supplied by means of the rotating disk collector, *M*. Both circuits are controlled independently by means of suitable rheostats. In the first half of the tube the heating wire remains uncovered while the second half is lagged with asbestos tape *T*. The bearings are protected from heat radiation from the winding by the baffle plates, *N*. Short stem thermometers, *O*, of range 200° to 400° C. are inserted through seven holes along the tube in such manner that the bulbs come in contact with the granules passing through the tube. A strip of 12-mesh copper screen (5 mesh per cm.), about 1 meter long and 7.5 cm. wide, is held inside the tube by friction. This screen acts as a scoop and picks up and mixes the granules at each revolution of the tube. The progress of the granules through the tube is facilitated by the tilt of the tube. The roasted catalyst is discharged into header *P* and is received into a suitable container at *Q*. The back of the header remains open at *R* for inspection and sampling, and a hand-type vacuum cleaner is connected at *S*, drawing air through *R* and creating a slight suction inside the tube. This is essential to keep dust from seeping out through the joints and also to prevent the water formed in the reaction from condensing in the cold feed and causing it to cake and clog the tube.

The heat on the two coils is so controlled that the middle thermometer reads between 320° and 340° C. With the proper adjustment of heat and lagging, the temperature along the tube rises rapidly to 200° C. in the first 20 cm., then to 320–340° in the middle, and decreases slowly to 250–220° at the discharge end of the tube. Under normal operation a tube of this type will produce about 2 kg. per hour of roasted material. The product obtained is homogeneous in composition and uniform in quality as long as the temperature is controlled carefully. It has the appearance of black granules, somewhat velvety or lustrous like soot, and with a faint brownish cast. Underroasted material is decidedly brown, while overroasted granules are grayish or dull black with chrome-green specks.

The granulated material is pulverized by passing through an impact mill. The powdered catalyst is ready for use or may be stored in closed containers for several days without loss in activity. [Washing with acetic acid was found to remove some of the copper oxide without causing an increase in the activity of the material. Also, on sifting, 80 per cent of the product passed a 200-mesh screen (80 mesh per cm.), and the unsifted material was just as active as the portion which passed the screen.]

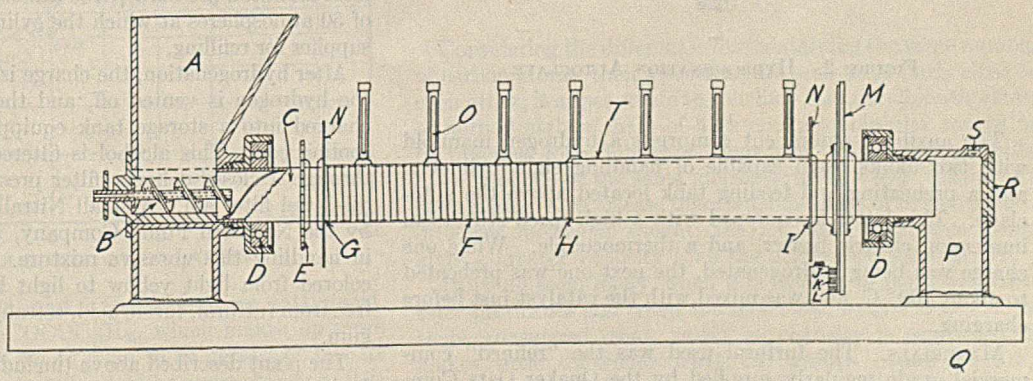

FIGURE 1. CATALYST ROASTING TUBE

HYDROGENATION

EQUIPMENT. The autoclave (Figure 2) was built by the Blaw-Knox Company of Pittsburgh. It follows the general design of a first and smaller unit, the later model embodying several improvements which suggested themselves from the experience obtained with the earlier one. This autoclave, of the vertical cylindrical type, comprises a forged steel shell, *A*, with bolted lid, *B*, and equipped with a vertical shaft, *C*, fitted with two turbine-type mixers comprising rotors *D* and *G* and stators *E* and *F*. The cover of the autoclave is made tight by means of a gasket of monel metal confined in a narrow groove. The autoclave is designed for normal operation at 100 atmospheres and is operated up to 120 atmospheres. The stuffing box is equipped with Garlock Chevron metal packing and is water-cooled. A 1 horsepower motor and reducing gear assembly (not shown) operates the stirrer at 325 r. p. m.

The autoclave body is approximately 40 cm. in diameter and 80 cm. deep, with a total capacity of 100 liters and a working capacity of 80 liters. The level of the top turbine is adjustable and is placed about 3 to 5 cm. below the liquid level. This creates a vortex which sucks hydrogen into the liquid and causes very efficient mixing. The cover of the autoclave is fitted with several openings: a gas outlet and a connection for the pressure gage (not shown), a liquid inlet, *H*, and a thermocouple tube, *J*. This latter is welded into the cover but is open and threaded at its bottom and is fitted with a cap. The thermocouple, similar to the one described by Dykstra and Calingaert (*2*), is immersed directly in the charge, thus avoiding any lag in reading the true temperature of the liquid. The hydrogen inlet, *K*, and the discharge opening, *L*, are at the bottom of the autoclave. All gas connections are fitted with Vogt high-pressure needle valves, and both liquid inlet and outlet with high-pressure Nordstrom Merco lubricated valves. In spite of the fact that the liquids handled always contained suspended solid matter, no difficulty was ever encountered in making the valves close tightly.

The autoclave is surrounded by a heating and cooling jacket, *M*, tested at 10 atmospheres hydrostatic pressure. The jacket contains a spiral baffle, *N*, welded onto the shell but without making a tight joint with the outer shell. The purpose of this baffle is to increase the efficiency of cooling by causing the cooling water to circulate at a high velocity in the spiral space. Suitable connections to the jacket permit

heating by means of steam at 7 atmospheres (175° C.) or cooling with water.

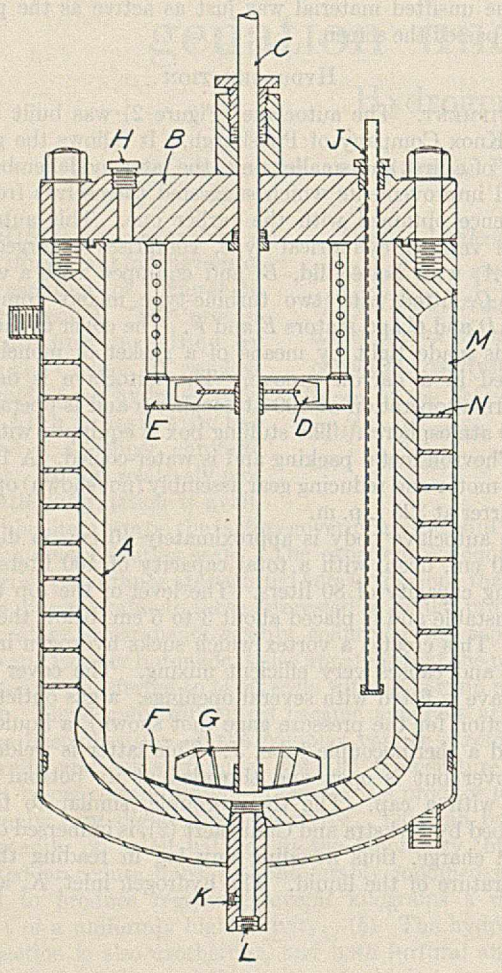

FIGURE 2. HYDROGENATION AUTOCLAVE

The auxiliary equipment comprises a hydrogen manifold with two banks, each capable of handling eight cylinders, and a preheating and feeding tank located above the autoclave. This latter is equipped with a high-speed stirrer, an immersion electric heater, and a thermocouple. While one charge was being hydrogenated, the next one was preheated to about 100° C. and was mixed with the catalyst just before charging.

MATERIALS. The furfural used was the "refined" commercial grade regularly supplied by the Quaker Oats Company. Later it was found that, if a material practically free from furoic acid is used, the result is a slightly higher rate of hydrogenation and a product which is only slightly colored. The hydrogen was electrolytic hydrogen received in standard 192-cubic-foot (5500-liter) cylinders, under 2000 pounds per square inch (137 atmospheres) pressure. The batch process used made it necessary to vent the residual hydrogen after each run so that there was no danger of accumulating oxygen if a trace of it should happen to be present in the hydrogen as received.

About 20 grams of dry slaked lime per liter of furfural were also added. F. N. Peters of the Quaker Oats Company recommended the use of magnesia to reduce acidity (*3*), but runs in the authors' laboratory showed the superiority of lime for that purpose. In the absence of a neutralizing agent, the rate of hydrogenation is decreased and the product is dark in color, probably because of a partial polymerization of the furfuryl alcohol.

PROCEDURE. The stirrer is started, and a charge of 80 liters of refined furfural containing 40 grams per liter of catalyst and 20 grams per liter of dry slaked lime, usually preheated to 100° C., is charged into the autoclave. The free space is flushed two or three times with hydrogen at 3 atmospheres, and the pressure is then raised to 100–120 atmospheres. Steam at 10 atmospheres is admitted into the jacket, and, when the temperature of the charge reaches 140° to 150° C., hydrogen absorption begins as evidenced by a drop in pressure. The steam is then shut off and the autoclave is maintained close to the specified operating temperature by regulating the hydrogen input and the cooling water. In 2 or 3 minutes the rate of reaction reaches a fairly constant figure, which maintains itself until the hydrogen absorbed corresponds to about 95 per cent of that calculated for the reaction. The rate then drops sharply, and the absorption stops, practically completed, with an accompanying drop in temperature, when 100 to 103 per cent of the theoretical hydrogen has been used.

The choice of a proper operating temperature is a matter of importance in this process. As mentioned before, both furfural and furfuryl alcohol are sensitive to heat, and time is an important factor in determining the maximum allowable temperature. Using a given amount of catalyst of a given activity, it was found advantageous to raise the temperature in order to decrease the time of reaction. Thus a better product (lighter in color and lower in gum) is obtained if hydrogenation is completed in 10 to 12 minutes at 180° to 190° C. than if it takes 30 to 40 minutes at 150° to 160° C. Operating around 175°, the time elapsed between the first drop in pressure and the temperature drop, which indicates completion of the reaction, varies from 11 to 30 minutes, depending on the purity of the furfural and on the activity of the catalyst, and averages usually around 18 to 22 minutes. During the run the hydrogen pressure used is lowered from an initial pressure of 100 atmospheres to a final pressure of 50 atmospheres at which the cylinders are returned to the supplier for refilling.

After hydrogenation, the charge is cooled down to 100° C., the hydrogen is vented off, and the furfuryl alcohol is discharged into a storage tank equipped with a stirrer and a cooling coil. This alcohol is filtered as soon as convenient through a closed-delivery filter press, using filter paper and Sil-O-Cel filter aid. A small Nitralloy pump, manufactured by the Northern Pump Company, was found very effective in handling this abrasive mixture. The filtered product is colored from light yellow to light brown and is practically free from furfural, furoic acid, tetrahydrofurfuryl alcohol, and gum.

The plant described above (including two catalyst roasting furnaces) was in operation for several months and functioned steadily without breakdowns, leaks, or major difficulties, turning out, whenever required, as many as eight to ten batches (a total of 800 to 1000 kg.) of hydrogenated product per 7-hour day.

ACKNOWLEDGMENT

The authors wish to acknowledge the important contributions made to the development of this process by their collaborators F. J. Dykstra, D. T. Flood, and R. K. Scales.

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RECEIVED May 19, 1934.

Viscosity of Esters of Saturated Aliphatic Acids

Relation to the Synthesis of Fine Lubricating Oils

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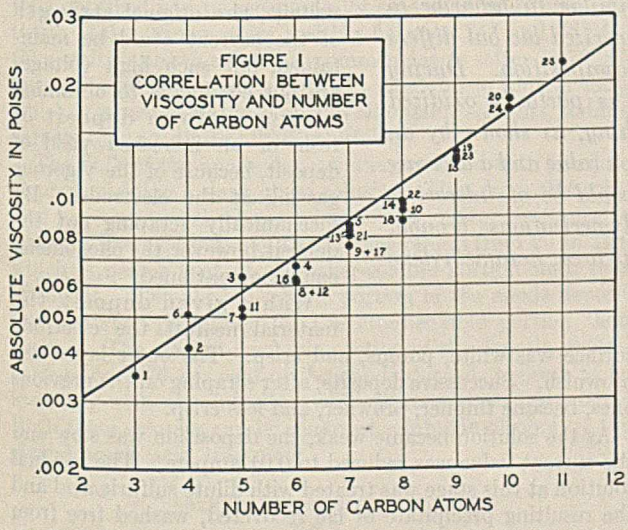
PORPOISE jaw oil has been used for about a hundred years for the oiling of the finest and most delicate machinery—i. e., timepieces. Its lack of change in air, low viscosity, and high lubricating power especially adapt it for this purpose. It is, however, expensive, costing at times $60.00 per gallon. A synthetic substitute is to be predicted. Gill and Tucker (*2*) found the oil to be composed of about 60 per cent isovalerin, 6 per cent tripalmitin, 4 per cent triolein, 3 per cent free isovaleric acid, and 27 per cent dodecyl isovalerate.

The synthesis of the glycerides would not be easy and the palmitin and the olein could well be omitted on account of the instability of the latter. The artificial preparation of the oil resolves itself practically into that of the liquid wax, dodecyl valerate. In fact, it is believed that a satisfactory substitute could be made solely with this latter compound, or one of an



equal molecular weight, and a saturated free fatty acid. Dodecyl valerate, $C_4H_9COOOC_{12}H_{25}$, which makes up more than a fourth of the oil, would seem to be necessary, but its synthesis from dodecyl alcohol would be expensive since it is a chemical curiosity. The question arose as to whether this valerate was actually necessary, or whether any similar ester of the same number of carbon atoms, e. g., $C_8H_{17}COOOC_8H_{17}$, or any other arrangement of $C_{16}H_{34}$ could replace it. In other words, is the viscosity of ACOOB practically the same as the viscosity of BCOOA? If this is the case, a synthetic substitute is nearer and less expensive.

The viscosities of the various esters from methyl acetate to amyl valerate were determined at 25° C. by the Ostwald viscometer. This was cleaned with chromic acid, washed with alcohol and ether, and standardized from 0° to 45° C. by water according to the procedure recommended by Bingham (*1*), taking the viscosity in centipoises from the International Critical Tables (*3*). The esters used were as pure as could be obtained from the Eastman Company, or were carefully prepared in the laboratory from the normal alcohols and acids. Their viscosities are shown in Table I, which values agree with many of those in the International Critical Tables. They are charted in the semi-logarithmic Figure 1.

TABLE I. VISCOSITY OF ESTERS

	Compound	Boiling Point ° C.	*N* Viscosity at 25° C. *Poises*
1.	Methyl acetate (C_3)	57.5	0.003503
2.	Ethyl acetate	77	0.004158
3.	Propyl acetate	101–102	0.006389
4.	Butyl acetate	125	0.006714
5.	Amyl acetate	148	0.008528
6.	Methyl propionate (C_3)	79	0.005082
7.	Ethyl propionate	99	0.005045[a]
8.	Propyl propionate	122.4	0.006104
9.	Butyl propionate	144	0.007618
10.	Amyl propionate	164	0.009355
11.	Methyl butyrate (C_4)	102	0.005259
12.	Ethyl butyrate	119.9	0.006127
13.	Propyl butyrate	143	0.008319
14.	Butyl butyrate	165	0.009766
15.	Amyl butyrate	176	0.012558
16.	Methyl valerate (C_5)	127.3	0.006227
17.	Ethyl valerate	144.5	0.007623
18.	Propyl valerate	167.5	0.008875
19.	Butyl valerate	186–187	0.013479
20.	Amyl valerate	204–207	0.018153
21.	Methyl caproate (C_6)	150	0.008096
22.	Ethyl caproate	166.6	0.009881
23.	Propyl caproate	185.5	0.012864
24.	Butyl caproate	204.3	0.017250
25.	Amyl caproate	224	0.022707

[a] Checked several times, probably impure.

Considering the different esters containing the same number of carbon atoms, their viscosities are seen to be fairly close to each other; it appears safe to conclude that, in aliphatic esters of normal carbon chain of high enough molecular weight to be practical for a lubricant, there will be interchangeability of compounds of the same molecular weight well within 0.05 centipoise. Also, in case there is a difference, or in compounds of lower molecular weight, the alcoholic methylene group gives a greater viscosity than the acidic methylene group.

It would seem likely, when it is feasible to make synthetic ester lubricants and when the molecular weight is the factor to be considered, that, as far as viscosity is concerned, it makes little difference what the groups concerned are;[1] comparisons must be made, however, with groups of the same constitution—that is, normal with normal esters, iso with iso-esters, and hydrocarbons with hydrocarbons. Substances of the same molecular weight do not necessarily have the same viscosity.

The subject is being still further studied.

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[1] The same seems to be true of the boiling points, which means that their flash and fire points would be nearly the same.

Electrodeposition of Shellac

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A solution of shellac in alkali carbonate has the properties of a true colloid, and the shellac micelles which are formed carry a negative charge and migrate toward the anode under the influence of a difference of potential. This suggested the possibility of electrodeposition of lac.

A current of 0.2 ampere at 6 volts will secure the deposition of lac at the anode. Addition of salts such as sodium chloride increases the rate of deposition but brings about other changes such as oxidation and polymerization.

The accelerated electrodeposit consists of an alcohol-soluble fraction, a large portion of which is also soluble in ether. It approximates in composition the ether-soluble portion of shellac. The alcohol-insoluble portion, consisting of about 70 per cent of the deposit, represents a polymerized modification of the "pure resin."

The electropolymer is similar in behavior to the hydrochloric acid–polymerized lac but differs from it as regards chemical composition. During electrodeposition the resin is partially oxidized and saturated as in bleaching, as shown by an increase in the saponification value and a decrease in the iodine value. It would be of interest to study the nature of polymerizations brought about by accelerators such as urea, hexamethylene tetramine, etc.

SHELLAC behaves anomalously toward solutions of alkali carbonates. Electrometric titrations carried out by Gardner and Whitmore (*1*) point to the conclusion that the acid components of shellac correspond in strength to weak organic acids such as benzoic, lauric, glutaric, and cinnamic. A clear aqueous solution of the alkali soap of shellac has been described by Gardner, Whitmore, and Harris (*2*) which can be made to pass completely through a membrane found to retain gold sol. The soap solution, therefore, does not possess true colloidal characteristics. Nagel and Körnchen (*5*) have observed that shellac can be easily esterified with methanol, and that an alcoholic solution of shellac acts upon metals such as copper, zinc, etc. On the other hand, Wolff (*10*) noted that shellac is insoluble in a solution of sodium bicarbonate and does not displace the theoretical quantity of carbon dioxide when it is dissolved in a solution of sodium carbonate. This led him to conclude that the main function of sodium carbonate was to peptize shellac.

Whatever be the nature of dilute solutions, there is little doubt that concentrated cuts of shellac exhibit marked characteristics of a true colloid. They show the properties of imbibition, syneresis, and setting similar to those of a typical hydrophilic colloid such as gelatin. The shellac solution can, in fact, be employed as "office glue" with advantage. Salts coagulate the alkaline solution of shellac, throwing out a jelly-like spongy mass which, on squeezing, yields a solid. This on treatment with distilled water can be repeptized, yielding the original colloidal solution.

While attempting to electrodialyze alkaline solutions of shellac, it was observed that shellac was deposited on the parchment membrane nearest the anode. Shellac micelles, therefore, carry a negative charge similar to that carried by an aqueous suspension of shellac in the experiments of Picton and Linder (*7*). This suggested the possibility of electrodeposition of shellac from its alkaline solutions, and the present communication deals with a study of the conditions of deposition and the nature of the deposit.

Experimental Procedure

Preliminary trials showed that nickel, copper, and lead anodes were unsuitable since they were attacked; with an aluminum anode, no deposition took place (possibly because of the formation of a thin insulating oxide film as in the case of the aluminum electrolytic rectifier). A platinum anode has been used throughout as being the most suitable since this investigation involved a study of the chemical composition of the deposit. A nickel cathode was employed in all the experiments.

A 10 per cent cut of Palas (*Butea frondosa*) seed lac in 1 per cent sodium carbonate solution (free from wax) was placed in a platinum basin which served as the anode, and a rod of nickel dipping into the solution acted as the cathode. Electrodeposition was allowed to proceed at 6 volts, a current of 0.2 ampere (0.0052 ampere per sq. cm.) flowing in the initial stages. As the deposit grew thicker, the current decreased to a value as low as 0.03 ampere (0.0008 ampere per sq. cm.). By progressively increasing the voltage, the original strength of the current could be maintained, but such high voltages are not conducive to obtaining either a uniform deposit of resin or an increased yield of deposit, because of the vigorous gassing at the electrodes. By mechanically scraping out the deposit, however, the phenomena could be continued.

With a given deposit, the material nearest the electrode surface was white, porous, and crisp. The outer layer was brownish. Successive deposits, after scraping off the previous ones, became thinner, browner, and less crisp.

As the solution became weak, the deposition was slow and the current value was reduced to 0.01 ampere. The residual solution at this stage was treated with dilute sulfuric acid and the resulting precipitate of lac recovered, washed free from acid, and dried. The sample on analysis showed that its properties were very similar to those of the original lac. Deposition of shellac on the abode was obtained from other alkaline solutions such as ammonia, sodium silicate, etc.

Influence of Electrolytes on Deposition. For a study of the nature of the deposit, genuine kusum shellac and "pure resin" (the ether-insoluble portion) were used. In both cases a thin, transparent, insulating film was obtained which offered resistance to a further flow of the current a few minutes after the start of the experiment. By frequent removal of the film, however, further deposition could be secured, and a sufficient quantity of the substance was thus obtained to establish its identity with the original resins.

In the case of shellac and "pure resin" solutions, the resistance offered to the flow of current was very high as compared with seed lac solution, which is presumably associated with electrolytes, including laccaic acid. The ash content of seed lac, in fact, is higher than that of shellac. It was of interest therefore to determine if additions of electrolytes to shellac solutions would improve the deposition.

Electrodeposition experiments were carried out with solutions of shellac and "pure resin" in the presence of sodium chloride. It was found that the rate of deposition far exceeds that obtained with seed lac solutions, and continues for a longer time. In the presence of high concentration of sodium chloride, the size of the shellac micelle is found to increase, giving a bluish opalescence. With still higher concentrations actual precipitation of shellac takes place. Thus, it is probable that the increased size of the ionic micelles is partly responsible for the increased rate of deposition in the presence of salt. The more easily noticeable effect of the addition of salt is the increase in conductivity of the shellac solution and the porosity of the deposit which, unlike the tough insulating deposit, helps in maintaining the current. Other salts such as sodium sulfate, sodium nitrate, sodium acetate, and ammonium sulfate were employed. Sodium chloride was found to be the best from the point of view of the rate of deposition. With sodium acetate, however, the deposit was dark, slimy, and gelatinous. Shellac deposition in the presence of electrolytes occurs with such great ease that a simple voltaic couple of copper and zinc is sufficient; the deposition takes place on the zinc surface.

Physical and Chemical Examination of the Deposit. The deposits obtained from solutions of seed lac, shellac, and "pure resin," after washing with distilled water, were subjected to electrodialysis to insure a more complete removal of the electrolytic impurities. The material was then dried *in vacuo* in a desiccator over sulfuric acid. Each sample thus obtained can be mechanically separated into three portions: (*a*) a brown mass melting between 74° and 78° C.; (*b*) a whitish brown substance commencing to soften at 70° C. but not melting even at 110° C.; and (*c*) a whitish mass which is infusible and insoluble in all organic solvents, sodium carbonate, and dilute alkali solutions.

The bulk of the anode deposit was extracted with absolute alcohol, yielding a dark green solution; films from this solution have a greenish tinge and possess a greater resistance to water. The acid value of the extract ranges from 99 to 119, which is nearer that of the ether-soluble portion than that of shellac. The alcohol-soluble portion of the anode deposit has a higher percentage of the ether-soluble portion than shellac. The alcohol-insoluble portion of the deposit, constituting about 70 per cent of the anode deposit, appears to be identical with the infusible whitish mass described above. Both these samples can be rendered soluble in alcohol by the glacial acetic acid treatment.

Table I. Analysis of Samples

Sample	Shellac	HCl–Polymerized Shellac	Pure Resin	Electropolymerized Lac A	Electropolymerized Lac B	Bleached Lac
Iodine value	15.8	16.1	9.7	7.7	6.8	8.0
Acid value	72.4	...	59.2	...	...	94.0
Saponification value:						
0.5 hr.	211.0	209.0	232.0	247.0	258.0	253.0
2.5 hr.	217.0	212.0	237.0	255.0	261.0	258.0

One of the main effects of the chlorine ion on the deposit appears to be to polymerize or harden the "pure resin" fraction of shellac during electrodeposition. The polymerization is favored by the nascent chlorine liberated at the anode. It was of interest to study the nature of this change with a view of determining how far the phenomenon corresponded or differed from the polymerization brought about by heat, on the one hand, and by hydrochloric acid on the other.

A comparative analytical study of the samples, with reference to their acid, saponification, and iodine values, was undertaken and the results are given in Table I. Iodine values were determined by the Wijs method, the procedure being the same as that described by Langmuir (*4*) except for the fact that a small trace of hydrochloric acid was added to facilitate the solution of polymerized lac. Saponification values were determined by a procedure described by Whitmore and Weinberger (*9*). Acid values were determined electrometrically with a quinhydrone electrode as described by Narasimhamurty (*6*).

Discussion of Results

When shellac is heated at 150° C., the molten mass gradually turns viscous and in about 70 minutes is converted into a rubber-like mass which soon hardens into a brittle, dark brown resin. This change is accompanied by the release of water and vapors of an acid character which render the mass porous. This heat-hardened shellac is soluble in alcohol only to the extent of 25 per cent, and the acid value of the extracted fraction (113) corresponds to that (114) of the ether-soluble portion of shellac. The insoluble residue is only partially soluble in acetic acid, unlike that of electropolymerized or hydrochloric acid–polymerized shellac.

The polymerizations brought about through the agency of heat differ from those brought about by hydrochloric acid. Nagel and Körnchen (*5*) have shown that during heat polymerization water is split off. This is probably due to the formation of lactides, the hydroxyl and carboxyl groups of the aleuritic and shellolic acids participating in the reaction. This involves a decrease or a disappearance of the hydroxyl and carboxyl groups, rendering the product insoluble in polar solvents such as ethyl alcohol. The hydrochloric acid polymerization is mainly a process of aggregation of molecules into a more complex one, effecting a more or less complete saturation of the residual valences. This aggregation, characteristic of the shellac resin, is favored probably by the presence of lactones, acid anhydrides, or hydroxyl groups (*8*).

Harries and Nagel (*3*) have observed that hydrochloric acid–polymerized shellac or "pure resin" is more difficult to saponify than the corresponding untreated substances. Nagel and Körnchen (*5*) extended their observation to shellac which had become insoluble on aging, and found that it exhibits a decreased rate of hydrolysis. Heat polymerization of shellac or "pure resin," however, does not alter its rate of saponification. The above conclusions regarding hydrolyzability have been drawn from the yields of potassium aleuritate obtained by the hydrolysis of the samples with 5 *N* caustic potash. It was of interest to find out how the saponification value and rate as determined by standard methods differ in the case of electropolymerized and of hydrochloric acid–polymerized samples of shellac. Table I shows that the rate of hydrolysis of the polymerized samples is not very different from that of the untreated control samples. The saponification value of the hydrochloric acid polymer is practically the same as that of the control. In the case of the electropolymer there is a distinct increase in the saponification value as compared with the value for the untreated "pure resin." This points to the conclusion that electropolymerization is accompanied by an oxidation of the resin, resulting in an increase of carboxyl groups, the oxidation being brought about by the nascent oxygen or chlorine evolved during the deposition. Such a type of oxidation occurs during the bleaching of lac whose saponification value should therefore be expected to be high. Analysis confirms this suspicion. An independent confirmation of the oxidation theory has been obtained by a determination of the iodine value of the samples. Table I shows that, while there is a lowering of the iodine value both in the case of the electropolymerized and bleached lac, the iodine value of the hydrochloric acid polymer is not altered.

The insoluble portion of the electrodeposited lac consists entirely of the modified "pure resin" and has been found to be rendered soluble by glacial acetic acid treatment. The resulting product, while being soluble in ethyl alcohol, is completely insoluble in ether. It is curious that both the

electropolymer and the well-washed hydrochloric acid polymer of lac require for their solution in acetic acid a trace of hydrochloric acid.

Electrodeposition of shellac has possibilities of wide application. Experiments are in progress for obtaining insulating coatings on metal surfaces by simultaneous electrodeposition of rubber and shellac from a mixture of their alkaline solutions. The possibility of recovering shellac from waste products will also be investigated.

Acknowledgment

The work embodied in this communication was undertaken by the authors in March, 1930, in the Department of Biochemistry, Indian Institute of Science, and their grateful thanks are due V. Subrahmanyan for the interest he has taken in the work.

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Chemical Laboratory Paris, 1760

Through the courtesy of Percy C. Kingsbury we are enabled to bring as No. 44 in the Berolzheimer series of Alchemical and Historical Reproductions, an engraving from Diderot's Encyclopédie ou Dictionnaire Raisonné des Sciences.

This plate shows a chemical laboratory in Paris in 1760, with the instruments, furnaces, vessels, and other laboratory utensils.

The key below the plate serves to identify the various objects by the names they bore in 1766 when the dictionary was published.

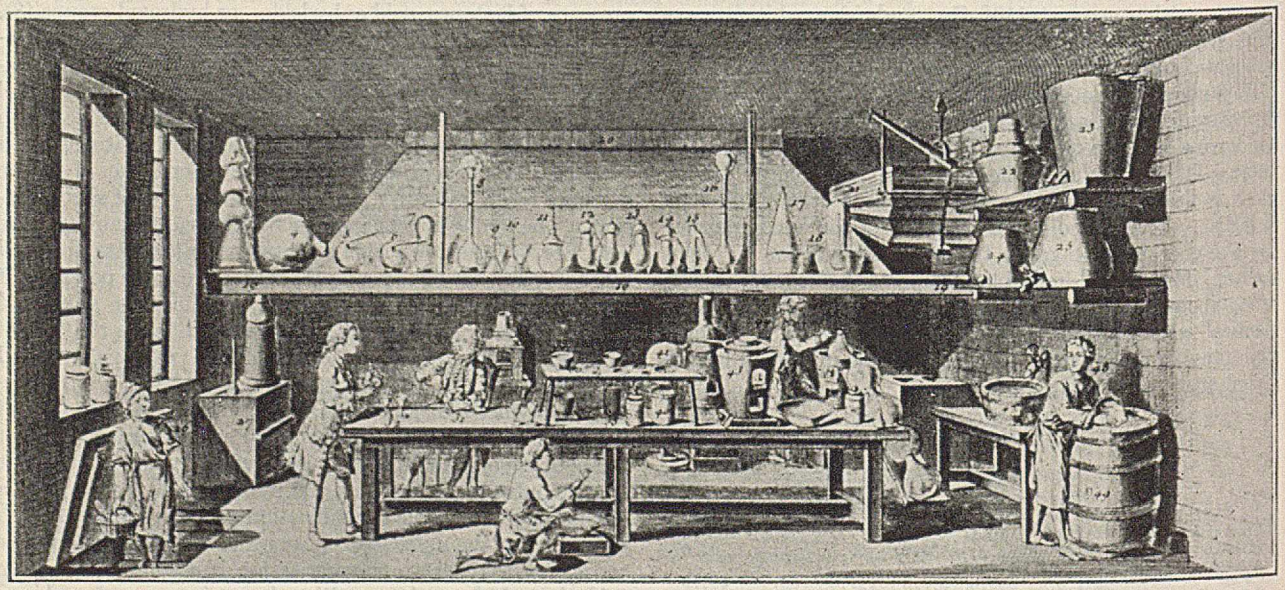

Fig. 1. Poudrier.
2. Flacon à goulot renverſé, avec ſon bouchon de verre.
3. Aludels pour tirer l'eſprit de ſouffre, ſelon la méthode de Stahl.
4. Balon ou récipient.
5, 6. Cornues.
7. Cucurbites de rencontre.
8. Matras avec ſa tête de maure.
9, 10. Entonnoir.
11. Enfer de Boyle.
12. Jumeaux.
13. Pélican.
14. Alambic avec ſa cucurbite.
15. Vaiſſeau à retirer les huiles eſſentielles peſantes, de M. Venel.
16. Matras de rencontre.
17. Vaiſſeau pour la ſublimation des fleurs de Benjoin.
18. Appareil pour meſurer la quantité d'air qui s'échappe des corps en fermentation.
19, 19, 19, 20. Manteau de la cheminée.
21. Soufflet de forge.
22. Bain-marie pour une cucurbite de verre.
23. Serpentin double dans la cuvette.
24. Cucurbite d'un alambic de cuivre.
25. Son chapiteau.
26. Garçon de laboratoire, portant du charbon.
27. Athanor.
28. Matras en digeſtion dans l'athanor.
29. Tour de l'athanor.
30. Phyſicien conférant avec un Chimiſte ſur la diſſolution.
31. Table du laboratoire.
32. Verres où ſe font des diſſolutions métalliques.
33. Chimiſte.
34. Fourneau d'eſſai.
35. Entonnoirs à filtrer des liqueurs.
36. Table percée pour recevoir pluſieurs entonnoirs.
37. Récipient placé au-deſſous d'un entonnoir.
38. Bocal placé au-deſſous d'un entonnoir.
39. Flacon bouché.
40. Bocal couvert de papier.
41. 42. Récipient adapté à une cornue placée dans le fourneau 42.
43. Fourneau à capſules.
44. Chimiſte faiſant des projections pour les cliſſus.
45. Appareil des cliſſus.
46. Forge.
47. Baquet au-deſſous d'une fontaine.
48. Garçon de laboratoire lavant les vaiſſeaux.
49. Tonneau plein d'eau.
50. Autre garçon de laboratoire.

Mechanism of Gum Formation in Cracked Gasoline

Formation of Peroxide, Aldehyde, and Acid in Storage

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Universal Oil Products Company, Chicago, Ill.

Earlier work has shown that peroxide, aldehyde, and acid can be detected in cracked gasoline as it deteriorates and forms gum. In this study the rate of formation of substances of these four classes has been followed in gasolines of several origins. Some were unrefined, some refined, and some contained inhibitors. The deterioration has been studied during storage for a year.

Peroxide can be detected early in the storage period when no aldehyde or acid and practically no gum is present. The rate of peroxide formation accelerates with time. Aldehyde begins to appear somewhat later and increases more gradually than peroxide. Acid formation begins still later, and acid concentration increases more slowly than that of either aldehyde or peroxide.

Gum begins to appear in rather large amount as soon as considerable peroxide has formed and before any large development of aldehyde or acid. The curve of gum content vs. time is similar in shape to the peroxide curve, and the conclusion seems justifiable that gum formation is closely related to the concentration of peroxide, and that aldehyde and acid are products of secondary reactions rather than intermediates in gum formation.

THE reactions which occur when cracked gasoline is stored in contact with air are complex. The first evidence of change that has been detected is the formation of peroxidic products. From a commercial standpoint, at least, the final step in deterioration is the formation of gum. Besides these two products, aldehydic and acidic products have been reported. No one has conclusively shown what relationships exist between the peroxides, aldehydes, and acids formed and what part they play in the gum-forming process.

Smith and Cook (*9*) obtained evidence of aldehydes in aged cracked gasolines, and considered them primarily responsible for the formation of gum. Story, Provine, and Bennett (*10*) detected peroxides, acids, and aldehydes in gasoline which was being evaporated in a copper dish and in gasoline exposed to sunlight. They came to the conclusion that "the products of the oxidation appear to be principally peroxides, with acids as the chief end product, making up the gum." Yule and Wilson (*12*) showed that the peroxide method which Story, Provine, and Bennett used determined only a small part of the total peroxides in the gasoline. Brooks (*1*) stated that peroxides, aldehydes, alcohols, and ketones "could easily be detected in samples of cracked gasoline which have become slightly oxidized." He reported the identification of formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde in old gasoline. The aldehydes formed, he believed, by the reaction of peroxides with olefins (Prileshajew's reaction, *7*) and opposed the conclusion of Smith and Cook that aldehydes are intermediate in gum formation, as he found that addition of aldehydes to gasoline being evaporated did not increase the amount of gum formed. Brooks considered that gum was largely a mixture of peroxides, although the gum formed after a long period of storage contained acidic substances.

Wagner and Hyman (*11*) also reported aldehydes, acids, and peroxides in old gasoline, and, while they confirmed the finding of Brooks that addition of simple aliphatic aldehydes to gasoline did not increase its tendency to form gum, they found that crotonaldehyde did accelerate gumming. They also reported the odor of acrolein in gasoline oxidized under pressure. They postulated reactions giving rise to peracids, which they considered the essential catalysts in gum formation. Yule and Wilson (*12*) questioned this mechanism, pointing out that a sample of gummy gasoline which had been washed with sodium carbonate and therefore would not contain peracids, has just as great an effect in accelerating gum formation in freshly cracked gasoline as if it had not been washed.

Mardles and Moss (*6*) stated that "the process of gumming appears to be initiated by the primary formation of organic peroxides. . . . and the products of oxidation other than peroxides—namely, aldehydes, ketones, acids, etc.—were found to have no accelerating effect on the gum rate."

Hoffert and Claxton (*5*) have reported that aged benzols containing unsaturated hydrocarbons show the presence of peroxides, aldehydes, and acids.

These earlier studies were largely qualitative in nature. In the present investigation, the rates of formation of peroxide, aldehyde, acid, and gum have been determined quantitatively in a considerable number of samples of gasoline in storage. From these rates some idea of the mechanism by which gasoline deteriorates and gum forms may be obtained.

Methods of Analysis

Peroxides were determined by the thiocyanate method of Yule and Wilson (*12*). In considering the values reported, it should be borne in mind that, if determined by a method using potassium iodide, the peroxide concentrations would have been considerably higher. This was shown in the work of Yule and Wilson, and has been confirmed in this laboratory.

Aldehydes were determined by the amount of color imparted to a special Schiff reagent. The usual Schiff reagent, a water solution of rosaniline hydrochloride decolorized with sulfur dioxide, emulsifies badly if shaken with gasoline. Emulsification was avoided by adding alcohol to the reagent. The concentration of sulfur dioxide was varied until the desired sensitivity was obtained. The solution adopted had the following composition:

Rosaniline hydrochloride, 0.10 gram
Aldehyde-free ethyl alcohol (formula 30 containing 10% methanol), 200 cc.
Sulfur dioxide, 1.5 grams
Water to 500 cc.

The rosaniline is made up following Schibsted (*8*) in 2 per cent solution in aldehyde-free absolute alcohol, and the solution is filtered after standing for a few days and kept away from light to avoid decomposition. Sulfur dioxide is added in a solution of accurately known concentration. The completed reagent must stand about 12 hours to decolorize and is then usable for a number of weeks if sulfur dioxide is not allowed to escape. The reagent should be straw color; if it remains pink, slightly more sulfur dioxide may be added.

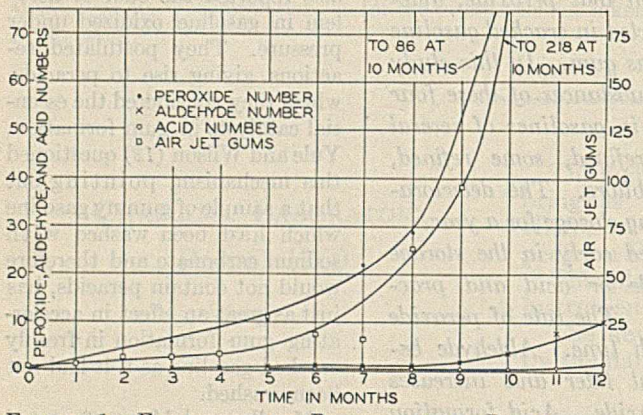

FIGURE 1. FORMATION OF DETERIORATION PRODUCTS IN MIDCONTINENT UNREFINED CRACKED GASOLINE

While several of the lower aliphatic aldehydes have been isolated from cracked gasoline, when a stored sample is being studied it is not known just what aldehydes are present and in what proportion they occur. For this reason the determination has been made arbitrarily by comparing the color given to the Schiff reagent by gasoline to the color given by a standard solution of butyraldehyde. The test is made as follows:

To 10 cc. of the Schiff reagent in a 125-cc. glass-stoppered Erlenmeyer flask are added 10 cc. of gasoline or of a solution of a known aldehyde in aldehyde-free straight-run gasoline. The mixture is shaken for 2 minutes and allowed to stand quietly for 8 minutes for development of maximum color (*3*). If the aqueous lower layer is not clear, it is pipetted out and filtered before testing. Comparisons of colors are made in Nessler tubes, using 2- to 5-cc. samples, which must not be diluted or allowed to stand more than one hour.

Comparisons were made of the colors produced by formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, heptaldehyde, crotonaldehyde, and benzaldehyde. Standard solutions of these aldehydes were made up in aldehyde-free straight-run gasoline.

Portions of each of these solutions were shaken with the reagent under the outlined conditions. All of the aldehydes gave what appeared to be the same shade of color with the reagent. Color intensities were compared by finding the amount of a solution of potassium permanganate containing 0.1 gram per liter (which to the eye has the same color as that produced in the aldehyde test) needed to give the same depth of color in a Nessler tube as given by the aldehydes with the special reagent. The following table shows the volume of the Schiff solution taken after 10 cc. of the solution had been shaken with 10 cc. of an aldehyde solution of the normality indicated, and the volume of permanganate solution needed to give the same color intensity:

ALDEHYDE	NORMALITY	SCHIFF SOLN.	PERMANGANATE SOLN.
		Cc.	*Cc.*
Formaldehyde	0.001	2	8.0
Acetaldehyde	0.001	2	6.0
Propionaldehyde	0.001	2	9.0
Butyraldehyde	0.001	2	8.5
Heptaldehyde	0.0025	2	7.0
Crotonaldehyde	0.001	1	8.0
Benzaldehyde	0.01	2	5.5

The first four aliphatic aldehydes give nearly the same color intensity, heptaldehyde somewhat less color, crotonaldehyde more color, and benzaldehyde very little color.

Butyraldehyde gives about a mean value for the lower aldehydes. It was therefore adopted and the results are expressed in terms of aldehyde number as butyraldehyde. Aldehyde number is defined as the number of gram molecular weights of aldehyde in 1000 liters. This unit was selected to correspond to the peroxide number, defined by Yule and Wilson as the gram equivalents of active oxygen per 1000 liters. A gasoline sample giving the same color intensity as 0.001 molar butyraldehyde has, therefore, an aldehyde number of 1. The reagent gives a distinct coloration with 0.00005 *M* butyraldehyde. Even lower concentrations can be detected if comparison is made between the sample in question and a blank sample made up by shaking the reagent with aldehyde-free straight-run gasoline. Tests can readily be made up to a concentration of 0.002 *M* aldehyde. Gasolines higher in aldehyde than this should be diluted with aldehyde-free straight-run gasoline before testing. Comparison is most accurate when made between an unknown gasoline and a standard butyraldehyde solution giving about the same color intensity; between two samples of considerably different aldehyde concentration, of which quite different volumes must be compared, there is a slight difference in shade owing to the residual color of the reagent.

ACID DETERMINATION

The following procedure was used in the determination of acid in gasoline:

To 10 cc. of freshly boiled water in a 25-cc. glass-stoppered graduate, a few drops of alcohol solution of bromothymol blue (or phenolphthalein) are added, and a drop of 0.01 *N* carbonate-free sodium hydroxide, giving a bright blue color (two drops may be added if necessary, but if more than this is needed the water is not free from carbon dioxide). Gasoline (10 cc.) is added and the graduate shaken. If acid is present, the blue color changes to green or yellow. Sufficient alkali is then added to bring back the blue color and cause it to remain during vigorous shaking for one-half minute. Acid concentration is reported in

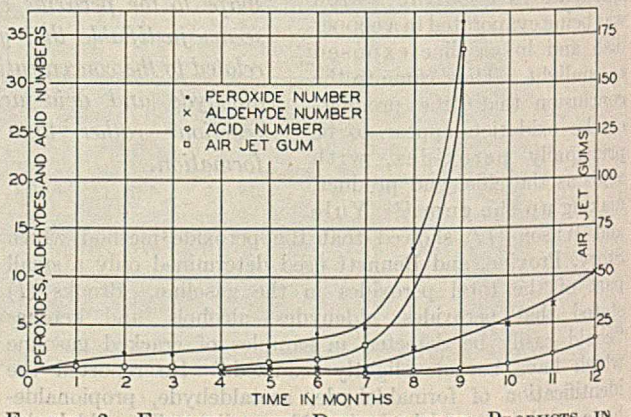

FIGURE 2. FORMATION OF DETERIORATION PRODUCTS IN PENNSYLVANIA REFINED CRACKED GASOLINE

this paper as acid number, which is here defined as gram atoms of hydrogen ion per 1000 liters, in order to make the figures for peroxides, aldehydes, and acids comparable. For this study such a unit is more useful than the conventional expression of acid number in terms of milligram of alkali per unit volume, which is used in fat and oil analysis. The method of titration is essentially that devised by Hall (*4*) for ether. It gives exact results when hydrochloric acid or acetic acid is added to gasoline but does not give results in accord with the theory for high-molecular-weight acids, such as oleic.

STUDY OF STORED SAMPLES

The determinations of peroxide, aldehyde, acid, and gum were made each month on samples of five cracked gasolines

which were stored for one year. The gasolines had been produced from representative charging stocks. Some of them had been refined, and some were untreated. A number of the samples contained antioxidants, which were selected to include compounds of varied degrees of effectiveness (*2*). All of the samples were stored in gallon (3.8-liter) bottles of brown glass, fitted with corks through which 0.25-mm. capillary tubes passed, to allow access of air but to avoid excessive loss of gasoline by evaporation. The storage room had an average temperature of about 25° C. (77° F.) which was the temperature of the atmosphere in summer and that of warmed air in winter. The properties of the original gasolines are given in Table I.

TABLE I. PROPERTIES OF GASOLINES

	Midcontinent				Pennsylvania				West Texas	
	Refined[a]		Unrefined		Refined[b]		Unrefined		Reformed[c]	
Sp. gr.	0.7511		0.7715		0.7470		0.7208		0.7358	
Gravity, ° A. P. I.	56.9		51.9		57.9		64.8		60.8	
A. S. T. M. 100-cc. distn.:	° C.	° F.	° C.	° F.	° C.	° F.	° C.	° F.	° C.	° F.
Initial b. p.	41	106	37	99	43	110	36	96	30	86
% distilled over:										
10	65	149	94	201	68	154	51	123	58	136
50	129	265	150	302	121	249	106	222	119	247
90	201	393	192	378	195	383	176	349	192	360
End point	217	422	209	408	230	446	178	353	206	403

[a] Treated with sulfuric acid.
[b] Treated with fuller's earth in the vapor phase.
[c] Made by pyrolysis of straight-run gasoline.

The storage data on these gasolines, uninhibited, is given in Table II. The formation of deterioration products is shown graphically in Figure 1 for the Midcontinent unrefined and in Figure 2 for the Pennsylvania refined gasoline.

These gasolines deteriorated at quite different rates. The rates, in all but the Midcontinent gasoline, corresponded to the initial induction periods of the gasoline. If the formation of 10-mg. air-jet gum is taken as the limit of serviceability of gasoline, the gasolines would be usable as follows:

Gasoline	Induction Period	Storage Life
	Minutes	*Months*
Midcontinent refined	205	11
Pennsylvania refined	185	6
Pennsylvania unrefined	60	2
West Texas reformed	40	Less than 1
Midcontinent unrefined	245	4

The unrefined Midcontinent gasoline had a high copper-dish-gum value of 95 mg. which appears significant as an indication of low storage stability. All the others had very low gum by this method.

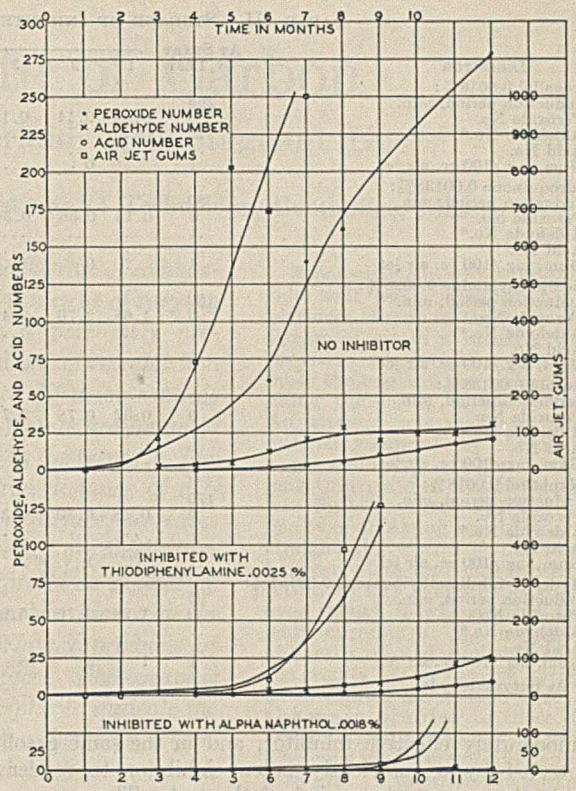

FIGURE 3. DEVELOPMENT OF DETERIORATION PRODUCTS IN INHIBITED AND UNINHIBITED PENNSYLVANIA GASOLINE

The data on inhibited samples of the Pennsylvania unrefined gasoline are shown in Table III. Comparison of Tables II and III shows that an inhibitor appears to produce no great change in the character of the deterioration process. Its effect is to slow down all the changes occurring. Formation of peroxides, aldehydes, acid, and gum are all retarded, and after a time, probably when the inhibitor is used up, the formation of these products goes on as it would have at the beginning had no inhibitor been present. The extent to which the reactions are slowed down is shown in Figure 3 in which, on the same scale, is shown the development of peroxide, aldehyde, acid, and gum in the untreated Pennsylvania gasoline, in the same gasoline protected by

TABLE II. STORAGE OF CRACKED GASOLINES

Gasoline	At Start of Test	Months in Storage 1	2	3	4	5	6	7	8	9	10	11	12
Midcontinent refined:													
Induction period, min.	205												
Peroxide No.	0.13	0.60	1.01	1.10	1.39	1.67	2.10	2.30	2.61	2.80	3.10	3.75	4.00
Aldehyde No.[a]	..	..	..	0	0	0	Trace	0.10	0.28	0.05	0.15	0.2	0.2
Acid No.	..	..	..	0	0	0	0	0	0	0	0	0	0
Gum, mg./100 cc. air jet	1	1	0	2	1	4	2	4	5	1	7	6	12
Midcontinent unrefined:													
Induction period, min.	245												
Peroxide No.	0.11	2.29	5.50	6.10	8.90	10.60	21.0	22.0	29.0	57.0	86.0	140.0	202.0
Aldehyde No.[a]	..	..	..	0.35	0.40	0.6	1	1	1	1.6	2.66	7.5	10.0
Acid No.	..	..	..	0	0	Trace	Trace	0.13	0	0.19	0.25	0.51	1.03
Gum, mg./100 cc. air jet	1	3	6	6	8	30	20	18	62	96	218	326	..
Pennsylvania refined:													
Induction period, min.	185												
Peroxide No.	0.04	1.05	2.09	1.91	2.58	3.10	4.00	4.88	12.7	36.5	37.5	61.0	86.0
Aldehyde No.[a]	..	..	..	..	0.30	0.67	0.4	0.45	2.5	4.5	5.0	7.0	10.0
Acid No.	..	..	..	..	0	0	0	0	0.13	0.38	0.64	1.55	3.11
Gum, mg./100 cc. air jet	0	3	4	4	3	6	8	14	11	168.0	198.0	..	..
Pennsylvania unrefined:													
Induction period, min.	60												
Peroxide No.	0	1.48	4.70	14.40	29.50	49.50	64.0	142	162	206	232.0	246.0	280.0
Aldehyde No.[a]	..	..	..	1.5	4	5	14	20	28.6	20	25.0	25.0	33.0
Acid No.	..	..	..	0.25	0.45	1.04	2.46	4.27	6.73	10.39	14.51	18.01	20.47
Gum, mg./100 cc. air jet	1	0	7	86	292	810	696	1002	520	426	610	..	..
West Texas reformed unrefined:													
Induction period, min.	40												
Peroxide No.	0	1.69	5.50	9.70	6.00	5.40	6.40	10.9	18.0	17.5	14.0	12.3	
Aldehyde No.[a]	..	..	..	..	1.25	1.00	0.80	0.80	3.5	2.1	1.25	1.2	
Acid No.	..	..	..	..	1.16	1.75	1.95	2.59	4.66	6.86	7.12	6.99	
Gum, mg./100 cc. air jet	0	19	52	136	138	216	224	286	366	..	..	..	

[a] As butyraldehyde.

TABLE III. STORAGE OF INHIBITED GASOLINES (PENNSYLVANIA UNREFINED)

INHIBITOR	AT START OF TEST	MONTHS IN STORAGE 1	2	3	4	5	6	7	8	9	10	11	12
Pyrogallol 0.0016%:													
Induction period, min.	265												
Peroxide No.	0	0.08	0.14	0.15	0.17	0.19	0.42	0.20	0.35	0.21	0.21	0.26	0.26
Aldehyde No.[a]	..	..	..	...	0	0.08	0.13	0	0.20	0.12	Trace	Trace	0.14
Acid No.	..	..	..	...	0	0	0	0	0	0	0	0	0
Gum, mg./100 cc. air jet	1	..	0	...	...	0	..	..	..	3	..	7	..
Hydroquinone 0.00138%:													
Induction period, min.	80												
Peroxide No.	0	0.14	0.36	0.34	0.69	2.50	6.8	34.0	72.0	122.0	163.0	174.0	176.0
Aldehyde No.[a]	..	..	..	...	Trace	0.31	1.1	4.0	6.0	20.0	17.0	20.8	20.0
Acid No.	..	..	..	...	0.06	0.45	0.03	0.19	0.45	1.55	3.75	5.44	7.90
Gum, mg./100 cc. air jet	1	..	0	...	3	2	31	..	576	928	..	..	..
Thiodiphenylamine 0.0025%:													
Induction period, min.	150												
Peroxide No.	0	1.68	2.70	2.40	2.87	5.00	20.2	34.0	65.0	114.0	158.0	178.0	192.0
Aldehyde No.[a]	..	..	..	...	0.31	0.40	2.5	5.0	6.4	9.0	14.1	22.2	25.0
Acid No.	..	..	..	...	0.13	0.45	1.13	0.26	0.64	1.94	4.53	7.38	10.23
Gum, mg./100 cc. air jet	0	1	2	...	10	116	52	..	392	508	..	..	..
Catechol 0.00138%:													
Induction period, min.	130												
Peroxide No.	0	0.32	0.78	2.77	9.0	35.0	44.0	102	114.0	152.0	..	..	..
Aldehyde No.[a]	..	..	..	...	1.5	4.2	7.5	12.0	16.0	33.0	..	..	..
Acid No.	..	..	..	...	0.06	0.26	0.65	1.81	3.75	7.12	..	..	..
Gum, mg./100 cc. air jet	1	..	1	6	34	462	424	..	326	304	..	..	..
α-Naphthol 0.0018%:													
Induction period, min.	170												
Peroxide No.	0	0.18	0.30	0.30	0.39	0.59	0.68	0.88	1.1	3.1	9.10	58.5	222.0
Aldehyde No.[a]	..	..	..	...	Trace	0.06	0.14	0	0	0.38	1.40	3.34	..
Acid No.	..	..	..	...	0	0.13	0	0	0	0	0	0.19	1.77
Gum, mg./100 cc. air jet	1	..	1	2	...	8	3	..	5	16	76	416	..
2-Hydroxy-1,3-dimethylbenzene 0.00154%:													
Induction period, min.	95												
Peroxide No.	0	1.28	2.70	5.90	13.8	35.6	46.0	118.0	142.0	..	..	..	..
Aldehyde No.[a]	..	..	..	...	6.0	8.4	10.0	11.0	15.0	..	..	..	..
Acid No.	..	..	..	...	0.13	0.71	0.86	2.33	4.66	..	..	..	..
Gum, mg./100 cc. air jet	1	1	2	18	74	608	256	..	258	..	..	..	..

[a] As butyraldehyde.

a moderately effective inhibitor, and in the same gasoline protected by a sufficiently potent inhibitor to render it stable throughout the period of the test. These tests are representative of a large number which have been made.

As in the uninhibited gasolines, the induction periods have been found to be an indication of the length of storage life, except in the case of hydroquinone which protects stored gasoline longer than would be expected from the induction period. It was noted in an earlier paper (*2*) that the inhibitive value of hydroquinone cannot be satisfactorily evaluated by the accelerated oxidation test, and this has been attributed to direct oxidation of the hydroquinone at the elevated temperature of the bomb test.

Because of the similarity of the results on uninhibited and inhibited gasolines, they may be discussed together. Apparently whether an inhibitor is present or not, the reactions which occur are much the same. The effect of the inhibitor is simply to retard the entire deterioration process. The data confirm the often repeated statement that the formation of peroxides is the first step in gasoline deterioration. Peroxides were present in considerable amount in these samples before there was any detectable formation of aldehyde and acid, or more than a few milligrams of gum. The rate of peroxide formation increased slowly at first, but, after about a 5 number was reached, it accelerated greatly. At about this same point rapid gum formation began, although there was slow gum formation from the beginning.

Aldehyde could usually be first detected when the peroxide number was 0.5 to 1.0. The aldehyde concentration then increased slowly, with a marked rise in the rate at about the point where peroxide and gum formation show marked acceleration. The rate of aldehyde formation did not at any time, however, show the great increase that is manifested by peroxide and gum. Acid was still slower to develop and did not form in more than minute amount until peroxide, gum, and aldehyde had all reached a considerable figure. The rate of acid formation increased with time but, like the aldehyde, did not show the marked acceleration noted in the curves for peroxide and gum.

The behavior of the West Texas gasoline differed somewhat from that of the others. The peroxide number corresponding to a given gum content was much lower than in the other samples. Peroxide and aldehyde increased very slowly in this gasoline and dropped off toward the end of the storage period, while in all the other gasolines the concentrations increased throughout the test.

From the curves, particularly for gum and peroxide, the conclusion appears justified that peroxides are primarily concerned in gum formation. The peroxides are the only deterioration products found which are present in any considerable amount at the time gum formation begins. The sharp acceleration in rate of formation of gum practically coincides with the point of marked increase in the formation of peroxide. This implies a relationship between the two, especially as there is no corresponding acceleration in the formation of aldehyde and acid. Aldehydes and acids probably have a minor part, if any, in gum formation. Substances of both of these types are most likely secondary products formed from peroxides, as they appear late in the deterioration process. The fact that the inhibitors check the formation of all these products simultaneously is evidence that they have a common origin. Were they formed independently, it is unlikely that they would all be retarded together by a single inhibitor.

These conclusions cannot be considered as fully proved but are indicated by the data, and attempts will be made to substantiate them further.

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Combustion Rate of Carbon

Combustion at a Surface Overlaid with Stagnant Gas[1]

H. Davis[2] and H. C. Hottel, Massachusetts Institute of Technology, Cambridge, Mass.

Data have been obtained for the rate of combustion of several types of carbon in cups of varying depths, and compared with a previously presented quantitative formulation of combustion rate under conditions in which diffusion controls the rate. The experimental results are found to lie within the limits imposed by the theory. The rate of combustion, for a given distance of diffusion of oxygen to the carbon surface, decreases with an increase in the degree of graphitization of the carbon. This is interpreted as indicating a decrease in the ratio of carbon monoxide to carbon dioxide formed as primary products of combustion at the carbon surface. Photographic studies of the combustion of spheres indicate the existence of a zone about the spheres in which counterdiffusing oxygen and carbon monoxide burn.

IN A PREVIOUS paper[1] the authors and C. M. Tu have presented data for the rate of combustion of 1-inch (2.5-cm.) spheres of brush carbon in oxygen-nitrogen mixtures. These data were examined in the light of a theory based on the concept of a stagnant film of gas about the carbon, through which the oxygen must diffuse to and the products of combustion away from the carbon surface. Although the experimental results obtained lay within the limits imposed by the theory presented, those limits were broad, partly on account of the necessity for depending on the questionable Reynolds analogy to obtain an estimate of the film thickness. It becomes highly desirable, therefore, to devise a type of experimentation in which the distance through which diffusion must take place can be precisely controlled and in which diffusion can be made positively the controlling factor.

Experimental Method

An experiment conforming to the above requirements is one in which a disk of carbon is allowed to burn in the bottom of a straight-sided cup under conditions permitting the concentration of oxygen to be maintained uniform and constant at the plane of the cup mouth, with no eddy currents in the cup. These conditions might possibly be met by inserting a small deep cup in the side of a large stream-lined body over which the combustion medium is passed, with the mouth of the cup flush with the surface of the body; but such an arrangement would probably necessitate the determination of carbon combustion rate by analysis of the gas because of the difficulty in measuring a small change in weight of so massive a system.

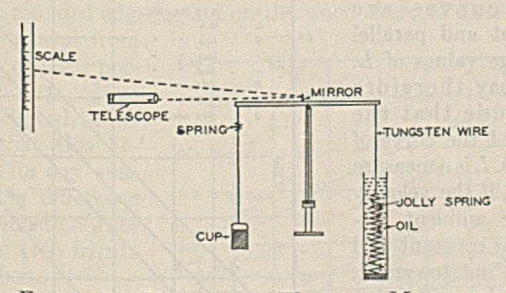

Figure 1. Diagram of Weighing Mechanism

In the present work a simpler procedure was adopted, dictated in part by adaptability to the equipment used in studying the combustion of carbon spheres:

A porcelain cup with cylindrical side wall was suspended by a platinum stirrup in the path of a stream of air in a furnace, with provision for weighing continuously the cup and the carbon disk lining the inside of its bottom. An attempt was made to minimize eddy currents by the use of a porcelain cup integral with a long thin plate in which the cup was flush-mounted, but the difficulty of obtaining a satisfactorily straight plate and good bond between plate and cup caused a return to the simpler system, even though it was realized that eddy currents at the mouth of the cup would probably affect the results. The furnace system and weighing mechanism were, in the main, similar to those described in a previous paper.[1] The cups used were of sillimanite, 1.15 cm. in internal diameter, 2 cm. deep, and 0.25 cm. thick, with interiors ground with a fine lapping compound to produce smooth walls and a truly circular shape. The balance used in the previous work was replaced by one of higher sensitivity, from one arm of which the cup was suspended in the furnace by a wire containing a spring to minimize the transmission of vibrations from the cup to the balance (Figure 1). A 12-inch (30.5-cm.) helical copper Jolly spring, totally submerged in a dampening bath of straw oil, was attached to the other arm of the balance by a 0.0003-inch (0.00076-cm.) tungsten wire running below the level of the oil. Provision of this fine wire was found necessary to minimize the variation in surface tension exerted on a larger wire as it moved up and down through the liquid surface. The photographic weight-recording mechanism used in the preceding work was replaced by a telescope and illuminated scale, the latter at 7 feet (2.1 meters) from the small mirror fastened on the balance arm. Calibration of the unit was made by direct addition of known weights to one side of the system under full load. Although disturbances produced a normal oscillation equivalent in amplitude to 0.7 mg., a permanent change in weight of 0.15 mg. could be detected.

The carbon employed was (*a*) brush carbon of grade identical to that used in the study of spheres, and (*b*) wood charcoal of a grade used in blow pipe analysis, cut with its burning face normal to the grain of the wood. These were turned on the lathe into cylinders fitting snugly into the crucibles, and then cut into disks of various thicknesses. Each disk was subjected to one burning and then discarded. Because of the difference of expansion between the samples and crucible a tight fit was

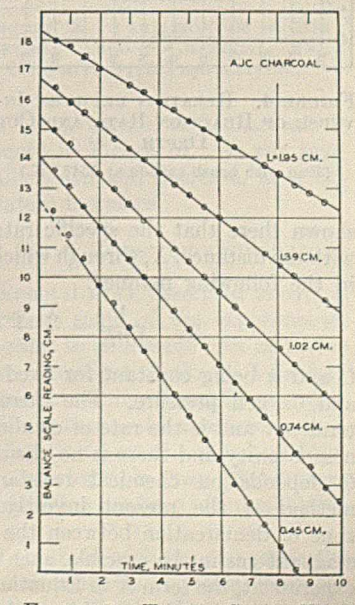

Figure 2. Typical Set of Time-Weight Records

[1] The first of this series of articles appeared in Ind. Eng. Chem., **26**, 749 (1934).

[2] Present address, The Foster-Wheeler Corporation, Carteret, N. J.

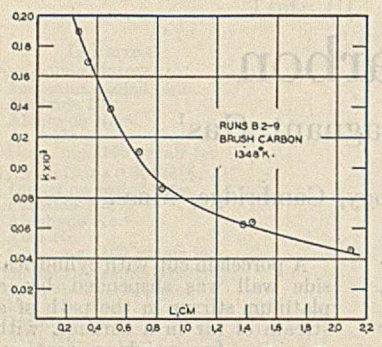

FIGURE 3. EFFECT OF CUP DEPTH ON COMBUSTION RATE

not possible at furnace temperatures, and a slight amount of burning occurred along the sides of the disks; this was judged to be negligible. Since the charcoal at times showed a tendency to burn somewhat preferentially on selected spots of the surface, shorter burning times were used to insure minimum departure from a plane surface.

Prior to a burning, the crucible and contents were brought to a constant temperature, measured by an optical pyrometer sighted on the crucible exterior, by heating in oxygen-free nitrogen. Air was then admitted, and after a 2-minute flushing period readings were taken at 30-second intervals. Burning times of 7 to 12 minutes were employed, depending on the rate of combustion. The normal air velocity employed was 5.32 cm. per second at 0° C. and 1 atmosphere pressure, after a study of this factor.

Thermocouples were located as in the preceding experimentation on spheres.[1] The temperature recorded as pertinent to the experiment was an average of the average thermocouple readings and an optical pyrometer reading, obtained by sighting on the wall of the crucible. The very low rates of combustion encountered guaranteed the maintenance of a temperature at the carbon surface differing little from that of the outside of the crucible.

DISCUSSION OF RESULTS

Results of a typical set of runs are presented in Figure 2 for the combustion of charcoal in air at 1260° K. and an air velocity of 5.32 cm. per second. The slopes of the lines, multiplied by the calibration factor on the balance, represent the specific rates of combustion, K, corresponding to the different depths of crucible. Values of K obtained in this manner are plotted against crucible depth L in Figure 3. Indication of how further to interpret these results will be given by a consideration of the nature of the relation presented in the first paper of this series.[1] It was shown there that the specific rate of combustion, K, varies with the distance, X, through which diffusion must take place, in the following manner:

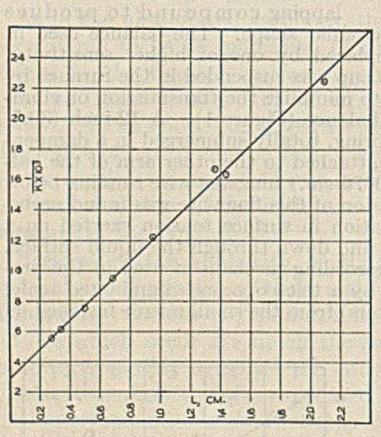

FIGURE 4. RELATION BETWEEN INVERSE OF REACTION RATE AND CUP DEPTH

(Run with brush carbon at 1348° K.)

$$\frac{1}{10^3 K} = \frac{X + C}{\alpha} \qquad (1)$$

C and α being constant for fixed conditions of temperature and oxygen pressure. The quantity α measures diffusion tendency and is the rate of combustion when the film thickness is unity and there is no chemical resistance. The term C depends on chemical resistance. If the experimental method of the present investigation established a sharp zone of demarcation between the ambient medium and the stagnant gas in the crucible, such as is described in the ideal experiment, the term X in Equation 1 would be identical with the depth, L, of the crucible, and a plot of $1/K$ vs. L would give a straight line with slope equal to $1/\alpha$, measuring diffusional resistance, and an intercept on the L axis equal to $-C$, measuring chemical resistance. However, the actual experimental method introduces the certainty that no such sharp zone exists. The surface at which the oxygen concentration in the gas begins to depart from that in the ambient medium may lie well outside the mouth of the crucible or may extend down into it, depending on such factors as gas velocity, crucible depth L, conditions upstream from the crucible, and temperature as affecting viscosity. In addition, a zone may exist near the mouth of the crucible in which oxygen is transported by eddy currents rather than by diffusion. These considerations indicate that the interpretation of Equation 1, as applied to the present experimentation, must be modified; either that X may be pictured as replaceable by the term $(L + l)$, in which l is the "effective" end correction of such artificial thickness as to obey the same transport law as L (the crucible depth), or that the term C may be pictured as including the sum of two resistances, one chemical, the other semi- or pseudodiffusional. So long as experimental conditions are such that this end correction or pseudodiffusional resistance should remain constant, the slope of the curve of $1/K$ vs. L should truly equal the term $1/\alpha$ of Equation 1. It becomes desirable, therefore, to investigate the conditions under which this end correction does remain constant. The effect of L at a fixed low velocity and constant temperature was first studied. From data such as are presented in Figure 3, $1/K$ was plotted against L to give results such as those of Figure 4. The straightness of the line, even down to quite small values of crucible depth L, indicates that at the low gas velocity used, the end correction is substantially independent of L over a wide range, and that the slope of the line is therefore equal to the term, $1/\alpha$, of Equation 1. Figure 5 presents similar results, for different velocities of the air past the crucible. As before, the lines are straight over the full range of variation of L, when the air velocity is low; but at high velocities a curvature is found as L becomes small, indicating that the end correction or amount of oxygen transport by eddy currents begins to be affected by the depth of the crucible as the depth becomes small. The curves are straight and parallel at large values of L. One may therefore conclude that the slope of the curve of $1/K$ vs. L is a measure of $1/\alpha$ if the velocity of the ambient medium is constant and if L is not too small, that the restriction on variation in L is minimized by the use of low gas velocities, that therefore the optimum condition for the further experimentation is the use of a low air velocity, constant during any set of runs. Accordingly, all subsequent runs were made at the constant velocity of 5.32 cm. per second measured at standard conditions.

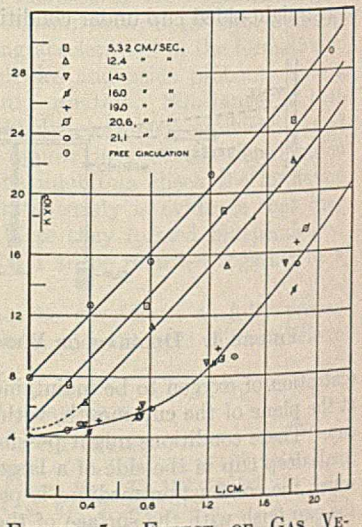

FIGURE 5. EFFECT OF GAS VELOCITY ON REACTION RATE AT 1045° C. WITH BRUSH CARBON

It is impractical to present here the complete original data on nearly four hundred runs. From each run a slope was obtained, measuring K. For a series of runs at a fixed temperature and gas velocity, $1/K$ was plotted against L, as in Figure 4, and a straight line was put through the data by

the method of least squares. Similar plots were made at other temperatures. From these straight lines, values of K for four different fixed values of L were read and plotted against temperature in Figures 6 and 7, for brush carbon and wood charcoal, respectively. From lines put through these data, $1/K$ was plotted against L for different temperatures, to give a family of straight lines. The slopes, $1/\alpha$, were measured and their reciprocals, α, were plotted against temperature in Figure 8. The term α is given in grams per square cm. per second per cm. thickness (times 10^4). Since it is a measure of diffusion tendency, expressed in terms of carbon consumption, a possible reason for its having lower values for brush carbon than for wood charcoal is that different amounts of oxygen are required to gasify the same amount of carbon in the two forms, owing to a smaller proportion of carbon monoxide to carbon dioxide formed at the brush-carbon than at the wood-charcoal surface. The maximum possible variation in α capable of explanation on these grounds is twofold; the experimental values of α for brush carbon and wood charcoal differ by a maximum factor of 1.7. However, α was determined at 1280° K. for a third type of carbon, graphite, and found to have a value of 0.64, which differs by a factor of 2.3 from that for wood charcoal. Another possible explanation of part of the difference in the values of α obtained for the different kinds of carbon lies in the possibility that the amount of carbon surface exposed to combustion was greater in the case of the wood charcoal, as evidenced by the rounded edges found on the wood charcoal disks after their removal from the base of the porcelain cup. It is not believed, however, that this accounts for any considerable difference in combustion rate for the two kinds of carbon.

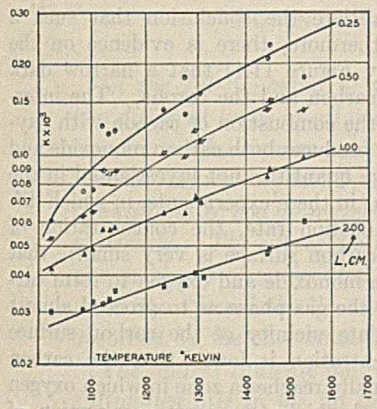

FIGURE 6. EFFECT OF TEMPERATURE ON REACTION RATE OF BRUSH CARBON AT VARIOUS CUP DEPTHS

For comparison with experiment, the term α may be obtained from Equation 1 in conjunction with Equations 7 and 11 of the authors' preceding paper:[1]

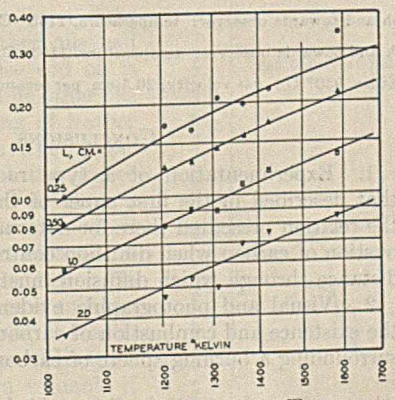

FIGURE 7. EFFECT OF TEMPERATURE ON REACTION RATE OF WOOD CHARCOAL AT VARIOUS CUP DEPTHS

$$\alpha = \frac{12\Phi 10^3 p_{og}\pi D}{p_i RT} = \frac{12\Phi 10^3 p_{og}\pi D_o T^{n-1}}{p_i R\ 273^n} \qquad (2)$$

As mentioned before, n may be expected to vary between 1.6 and 1.9, and Φ may lie between 1 and 2. Putting these limiting values into Equation 2, one obtains the dashed or dotted lines in Figure 8, establishing the absolute magnitude of α, for all carbons, within a factor of about 3. On the same plot are presented the experimental curves of α for brush carbon and wood charcoal and a single point obtained from data at 1280° K. on graphite. The experimental results are seen to lie within the zone established by theory.

When the specific combustion rate, K, has been determined in other investigations in which diffusion controls the combustion rate, the value of α from the present investigation may be used for determining effective film thickness. This has been done with Tu's data on carbon spheres[1] in the range in which diffusion determines the combustion rate; and the results have been compared to the film thicknesses predicted by Reynolds' analogy:

$$d/X = \frac{\Psi}{8}\left(\frac{du\rho}{\mu}\right)\left(\frac{c\mu}{k}\right)$$

where d = diameter of the sphere
Ψ = drag coefficient for spheres
u = linear velocity of gas past the sphere
ρ, μ, c, k = density, viscosity, specific heat, and thermal conductivity, respectively, of the gas

It has been pointed out[1] in effect that, where d/X is small and diffusional resistance is controlling, the specific combustion rate is given by the equation:

$$\frac{1}{10^3 K} = \frac{d/2}{(1 + d/2X)\alpha} \qquad (3)$$

The comparison has been made for combustion data on spheres at 1400° K. and at various velocities, using for α the value 0.109 found in the work with cups described in this paper. The results are shown in Figure 9, both coördinates of which are logarithmic. The effective film thickness determined by combining the results of the present experimental study with those of Tu is greater than the film thickness calculated from the Reynolds analogy. This difference is in the expected direction, since Reynolds' analogy has been found to predict too low a film thickness when applied to flow past wires.

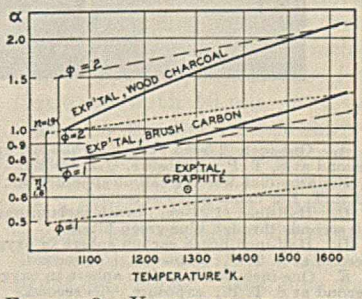

FIGURE 8. VARIATION OF α FOR BRUSH CARBON, CHARCOAL, AND GRAPHITE WITH TEMPERATURE

Although the term C of Equation 1 is not capable of close interpretation because it includes both chemical resistance and resistance in the eddy layer above the cup mouth, the variation of C/α with temperature, for both brush carbon and charcoal, is presented as a matter of record in Figure 10. At any temperature these are practically equal and decrease, at a decreasing rate, as the temperature increases.

PHOTOGRAPHIC STUDIES OF FLAME ZONE AROUND SPHERES

Preliminary to the experimental work described above, it was thought desirable to repeat some of the experimental work of Tu on spheres,[1] in order to gain some idea as to the reproducibility of his results. Excellent checks on Tu's data were obtained; in the course of obtaining them, the presence of a blue-green zone about the sphere and a spasmodic emission of sparks from the surface were noted. Consequently, arrangements were made to photograph these phenomena. The work done so far in this direction has been of a qualitative nature.

Photographs were at first obtained with the camera in the axis of the horizontal furnace tube, downstream from the sphere of carbon, looking in through the discharge nozzle. Subsequently the camera was placed above the furnace tube,

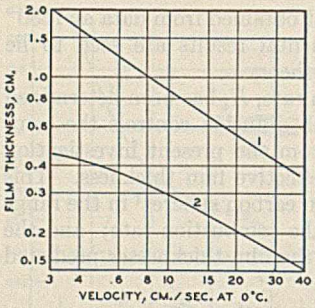

FIGURE 9. COMPARISON OF FILM THICKNESS FOR 1-INCH (2.5-CM.) SPHERES AT 1400° K.

1. Calculated from combustion data of Tu on spheres and of Davis on cups
2. Calculated from Reynolds analogy

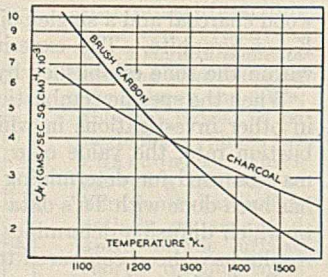

FIGURE 10. VARIATION OF C/α WITH TEMPERATURE

in the top wall of which was placed an optical flat of quartz in a special refractory shape. The sphere of carbon, for the latter photographs, was supported from below by a refractory pedestal and nickel pin. Various types of photographic film were tried, Eastman Ortho-Press being found most satisfactory.

Visual observation had shown the presence of sparks around the sphere to such an extent that some doubt was felt as to whether the simple picture of diffusion through a stagnant film to the surface of the sphere, outlined in the first paper of this series,[1] could fit the phenomena observed. The successive photographing of a burning specimen, with exposure times of $^1/_{100}$ to $^1/_{250}$ second, showed, however, that the emission of a spark, in the course of combustion in air, is a relatively infrequent occurrence of very short duration, the visual appearance of several simultaneous spark traces being an optical illusion due to persistence of vision. Out of nearly one hundred photographs of combustion in air, there was no positive evidence of the presence of a single spark trace. The average value of the total area at which combustion occurs differs almost negligibly, therefore, from that of the sphere itself. Figures 11*A*, *B*, and *C* are typical photographs of combustion in air. The corona around the spheres is plainly visible.

The photographing of the spheres in a direction normal to the direction of gas flow was undertaken to determine the degree of uniformity of thickness of the corona. Figures 11*C* and *F* show the corona to be considerably more intense on the upstream side of the sphere. These photographs were taken through a blue filter to suppress the red background relative to the blue flame.

Figures 11*D*, *E*, and *F* show the effect of the much more violent combustion attending the use of oxygen instead of air. A considerable portion of the total combustion obviously occurs at other surfaces than that of the main sphere because of frittering of the carbon at high combustion rates.

Visual observation of combustion under any conditions of temperature and gas velocity used in Tu's experimental work indicated plainly the presence of a corona of the same blue color that characterizes the combustion of carbon monoxide. The photographs substantiate the conclusion that such a corona is present. Furthermore, there is evidence on the photographs (particularly Figure 11*A*) that a narrow dark zone exists between the carbon and the corona. The interpretation offered is that the combustion of carbon with oxygen at the carbon surface produces both carbon monoxide and carbon dioxide, in relative quantities not investigated in the present experiments; that in these experiments, in which diffusion controls the combustion rate, the concentration of oxygen adjacent to the carbon surface is very small; that the combustion of carbon monoxide and oxygen to form carbon dioxide is so slow in the gas phase as to proceed almost negligibly in the immediate vicinity of the carbon surface where the oxygen concentration is low; that the carbon monoxide diffusing out finally reaches a zone in which oxygen concentration is sufficiently high to permit combustion of carbon monoxide to carbon dioxide to proceed at a rate which is indicated qualitatively by the thickness of the corona observed.

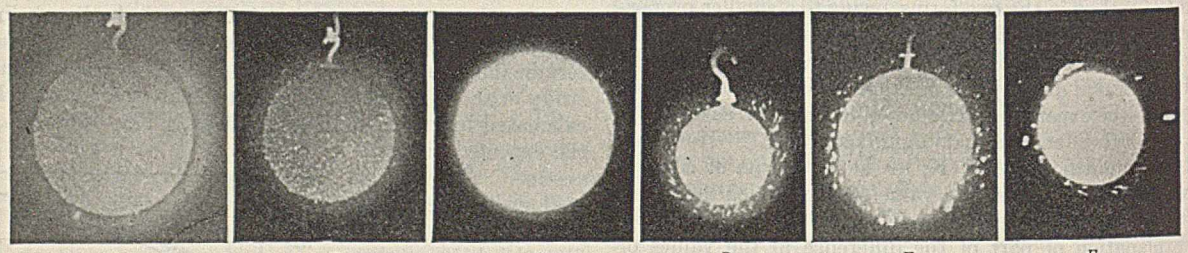

FIGURE 11. FLAME ZONES AROUND SPHERES

A. One-inch (2.5-cm.) brush carbon sphere in air; gas flow, normal to photograph and towards observer; temperature, 1215° C.; gas velocity, 25.3 cm. per second at S. T. P.; exposure, $^1/_{150}$ second.
B. One-inch welding carbon sphere in air; gas flow, normal to photograph and towards observer; temperature, 1215° C.; gas velocity, 25.3 cm. per second at S. T. P.; exposure, $^1/_{150}$ second.
C. Half-inch (1.27-cm.) brush carbon sphere in air; gas flow, left to right; temperature, 930° C.; gas velocity, 25.3 cm. per second at S. T. P.; exposure 10 seconds through blue-green filters.
D. Half-inch brush carbon sphere in oxygen; gas flow, normal to photograph and towards observer; temperature, 1155° C.; gas velocity, 11.9 cm. per second at S. T. P.; exposure, $^1/_{100}$ second.
E. One-inch brush carbon sphere in oxygen; gas flow, normal to photograph and towards observer; temperature, 1193° C.; gas velocity, 11.4 cm. per second at S. T. P.; exposure, $^1/_{100}$ second.
F. Half-inch brush carbon sphere in oxygen; gas flow, left to right; temperature, 930° C.; gas velocity, 20.5 cm. per second at S. T. P.; exposure, $^1/_{100}$ second.

CONCLUSIONS

1. Experimentation of a type radically different from that described in the first paper of this series substantiates the relation presented there for determining the rate of combustion of carbon when diffusion controls the reaction, if the distance through which diffusion must take place is known.
2. Visual and photographic evidence are presented for the existence and combustion of carbon monoxide in the film surrounding a burning sphere of carbon.

RECEIVED November 12, 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.

CORRECTION. Through an inadvertence, the main title of the article by Brewer and Ryerson [IND. ENG. CHEM., 26, 734–40 (1934)] was wrongly given as "Production of High-Hydrogen Water Gas from Younger Coke Coals;" this should have read "Production of High-Hydrogen Water Gas from Younger Coal Cokes." The percentage of ash in electrode carbon, Table II, page 736, should read 0.761.

Distribution of Free and Combined Oil in Chrome Leather Layers[1]

EDWIN R. THEIS AND J. M. GRAHAM, Lehigh University, Bethlehem, Pa.

In the fat-liquoring of chrome-tanned calfskin two different types of oil are used. Many calfskin tanners use fat liquors made up of sulfonated neat's-foot oil, raw neat's-foot oil, soap, and egg yolk, others use sulfonated cod oil mixed with moellons and other materials. The curves given show the effect of various mixtures of sulfonated and raw neat's-foot oil upon the "free," the "combined," and the total oil absorbed by the chrome-tanned leather.

The figures indicate that with low percentages of sulfonated oils in the fat liquors the oil prefers the grain, but as the percentage of sulfonated oil increases, the oil appears to be absorbed more and more by the flesh side. This fact is borne out in practice—raw oil mixtures tend to give a greasy surface. The work given here indicates that low percentages of sulfonated oil (neat's-foot 10, and cod oil 20 per cent) give the greatest total oil content, while larger percentages of sulfonated oil give the greatest combined oil value and correspondingly low values of free oil. This fact should be of value in the making of nondegreased patent leather, where a low free-oil content and a high combined-oil content are wanted. This work shows that every mixture of a sulfonated oil with another oil gives an entirely different type of fat-liquoring, if the distribution of free and combined oil plays any role in the characteristics of the finished leather.

VARIOUS workers have shown the penetration of oils into chrome-tanned leather. Wilson, Merrill, and Daub (*3*) studied the penetration of sulfonated neat's-foot oil and egg yolk mixtures, and showed that egg yolk caused the oil to be taken up preferentially by the flesh side. These workers also studied the effect of time, concentration, and hydrogen-ion concentration upon the penetration of the oil into the leather. In a recent paper, Henry (*1*) discusses factors affecting distribution of fat in leather, but he used only cod oil of three different sulfonations. The work would have been more valuable if various other oils had been employed because cod oil is highly unsaturated, while other oils used in the fat-liquoring of leather are more of the saturated type, Henry points out that the degree of sulfonation of cod oil plays a role in the amount of combined oil but not in the amount of total oil taken up by the leather. He shows that, as the degree of sulfonation of the oil increases, the combined oil also increases. His work would have been more valuable if the fat-liquored leather had been allowed to "mellow" for at least 2 weeks before analysis. Theis and Graham (*2*) have shown that, as leather mellows, more oil actually combines either with the skin fiber or with the chromium nucleus. Using sulfonated cod oil, the combination is steadily taking place over a 2-week interval.

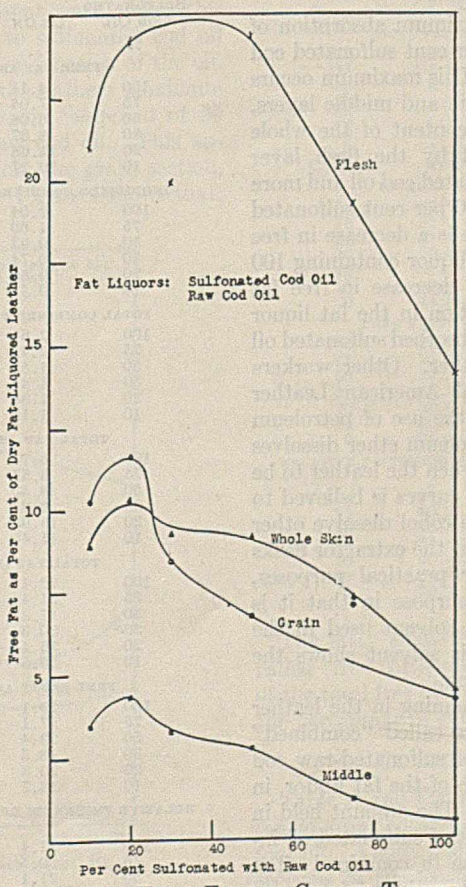

FIGURE 1. FREE FAT IN CHROME-TANNED SKIN USING COD OIL

EXPERIMENTAL PROCEDURE

Chrome-tanned steer hide was used for the fat-liquoring experiments included here. Samples weighing 100 grams (wet) and approximately 2 × 6 inches (5.1 × 15.2 cm.) in size were fat-liquored with 10 per cent oil (based on the wet leather shaved weight), using 600 per cent water at 130° F. (54.4° C.) by shaking for 1 hour. The fat-liquored samples were carefully dried and 2 weeks later cut into 0.25-inch (0.635-cm.) cubes; each cube was sliced into three layers: (*a*) grain, (*b*) middle section, and (*c*) flesh section. The middle sections were two to two and a half times the thickness of the grain and flesh sections.

The samples were dried overnight at 60° C., weighed, and extracted for 4 hours with low-boiling petroleum ether in order to determine the free oil present. The extracted samples were then hydrolyzed for 6 to 8 hours in boiling 20 per cent hydrochloric acid, and, after cooling, the combined unoxidized oil was extracted from the acid solution with carbon tetrachloride. The remaining acid solution was filtered and the combined oxidized oil obtained by washing the residue with hot 95 per cent alcohol.

The oils used were sulfonated and raw cod mixtures and sul-

[1] This is the fourth of a series on "Fat-Liquoring of Chrome Leather." Parts I and II appeared in IND. ENG. CHEM., 23, 50 (1931), and 24, 799 (1932). For the third article, see literature citation *2*.

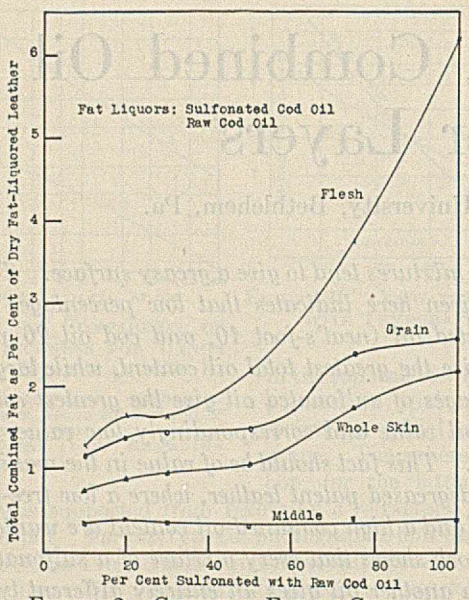

FIGURE 2. COMBINED FAT IN CHROME-TANNED SKIN USING COD OIL

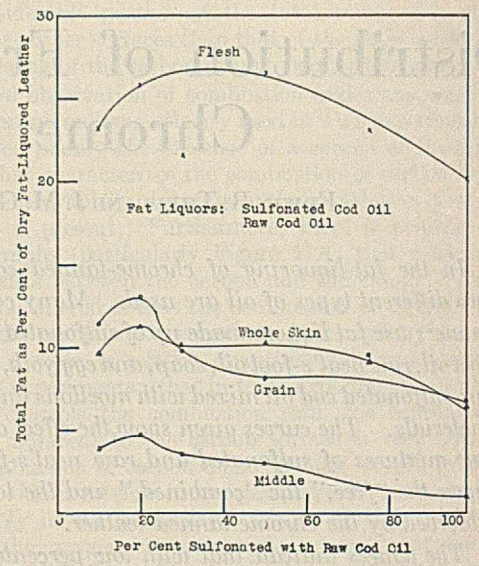

FIGURE 3. TOTAL FAT IN CHROME-TANNED SKIN USING COD OIL

fonated and raw neat's-foot oil mixtures as follows (per cent):

SULFONATED OIL	RAW OIL	SULFONATED OIL	RAW OIL
100	..	30	70
75	25	20	80
50	50	10	90

EXPERIMENTS WITH COD OIL

In Table I and Figures 1 to 4, a maximum absorption of free oil for a fat liquor mixture of 20 per cent sulfonated cod and 80 per cent raw cod oil is noted. This maximum occurs in the curves representing both the grain and middle layers, and in the curve representing the oil content of the whole leather (Figure 1). The oil absorbed by the flesh layer reaches a maximum at 20 per cent sulfonated cod oil and more or less maintains this maximum until 50 per cent sulfonated oil is reached. In all the sections there is a decrease in free fat as we approach more nearly the fat liquor containing 100 per cent sulfonated oil. Some of this decrease in free fat with increase of the sulfonated oil fraction in the fat liquor may be due to the fact that some of the absorbed sulfonated oil was not extracted by the petroleum ether. Other workers have pointed this out but the official American Leather Chemists Association method calls for the use of petroleum ether as the extractive. However, petroleum ether dissolves considerable of the sulfonated fraction when the leather to be extracted is dry; thus the trend of the curves is believed to be correct. Chloroform, acetone, and alcohol dissolve other compounds than free oil, as can be seen if the extractor flasks are carefully examined. However, for practical purposes, petroleum ether serves an additional purpose in that it is closely allied with naphtha and safety solvent used in the commercial degreasing of leather. This solvent shows the amount of oil extracted during degreasing.

Figure 2 gives the amount of oil remaining in the leather after petroleum ether extraction and is called "combined" oil. Figure 2 shows that in the case of sulfonated-raw cod oil mixtures the flesh layer retains much of the fat liquor, in all cases more than any other section. The amount held in the flesh section increases as the amount of sulfonated oil increases in the fat liquor. This increase in combined oil is very marked in the flesh layer when the original fat liquor contains more than 50 per cent sulfonated cod oil. The grain layer shows little difference in combined oil until a value of 50 per cent sulfonated oil is reached. For values of sulfonated oil better than 50 per cent, there is an increase in combined oil but it is not nearly as marked as was the case for the flesh layer. Further, the amount of combined oil (grain layer) reaches almost an equilibrium at 75 per cent sulfonated cod

TABLE I. COD OIL IN VARIOUS LAYERS OF DRY FAT-LIQUORED LEATHER

SULFONATED COD OIL %	GRAIN	CENTER	FLESH	TOTAL
FREE FAT AS % OF DRY FAT-LIQUORED LEATHER				
100	4.14	0.57	14.0	4.35
75	7.04	1.22	19.3	7.31
50	6.96	2.80	24.4	9.33
30	8.37	3.23	19.95	9.24
20	11.68	4.35	24.2	10.33
10	10.27	3.55	21.0	8.96
UNOXIDIZED COMBINED FAT AS % OF DRY FAT-LIQUORED LEATHER				
100	2.04	0.20	4.60	1.59
75	1.69	0.20	2.00	0.99
50	0.93	0.15	0.95	0.52
30	0.74	0.05	0.28	0.26
20	0.66	0.05	0.39	0.26
10	0.31	0.03	0.15	0.12
TOTAL COMBINED FAT AS % OF DRY FAT-LIQUORED LEATHER				
100	2.61	0.43	6.20	2.20
75	2.42	0.43	3.78	1.75
50	1.55	0.32	2.19	1.07
30	1.45	0.35	1.63	0.96
20	1.38	0.41	1.65	0.90
10	1.15	0.36	1.30	0.75
TOTAL FAT AS % OF DRY FAT-LIQUORED LEATHER				
100	6.74	1.00	20.2	6.53
75	9.57	1.65	23.1	9.17
50	8.50	3.05	26.5	10.40
30	9.82	3.69	21.6	10.20
20	13.03	4.76	25.8	11.22
10	11.40	3.91	22.2	9.69
TOTAL FAT IN EACH LAYER AS % OF TOTAL FAT				
100	22.1	8.60	69.5	...
75	21.4	9.54	69.1	...
50	17.3	15.8	66.9	...
30	20.3	17.4	62.3	...
20	26.1	23.6	50.4	...
10	26.5	22.3	51.2	...
FREE FATTY ACIDS IN FREE FAT AS % OF FREE FAT				
100	29.1	27.8	38.8	...
75	27.1	26.1	27.3	...
50	23.4	22.7	24.8	...
30	18.5	17.3	19.9	...
20	20.3	16.8	19.7	...
10	18.7	16.5	15.2	...
RELATIVE THICKNESS OF SECTIONS AS % OF TOTAL DISTANCE THROUGH LEATHER				
100	21.4	56.1	22.5	...
75	20.5	52.4	27.1	...
50	21.1	52.6	26.2	...
30	21.0	49.5	29.5	...
20	22.5	55.6	21.9	...
10	22.5	55.2	22.3	...

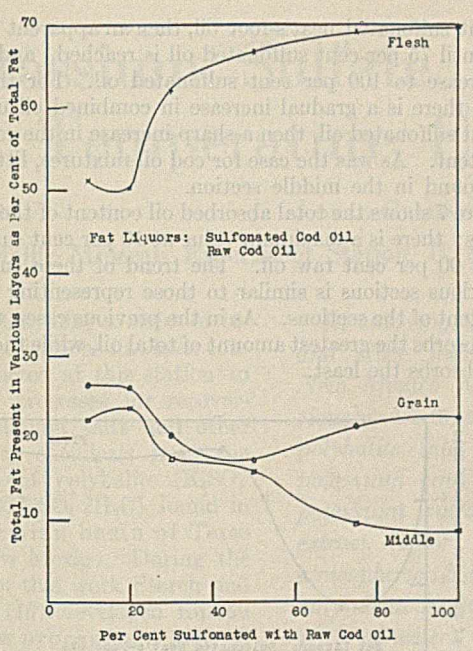

FIGURE 4. FAT DISTRIBUTION BETWEEN LAYERS IN CHROME-TANNED SKIN USING COD OIL

oil and increases only slightly thereafter. It would appear that the petroleum ether was extracting most of the free oil within the leather. This figure shows that very little oil combines with the middle section and is practically constant for any concentration of sulfonated cod oil. Henry showed that combination with the leather increased with increasing degree of sulfonation for cod oil, and the present work shows this same effect since the addition of raw to sulfonated cod oil might be judged to lower the degree of sulfonation of the oil. Figure 3 shows the total oil taken up by the leather; maximum total absorption occurs using a fat liquor composed of 20 per cent sulfonated and 80 per cent raw cod oil. This appears to be the case for the flesh section, the grain section, middle section, and for the entire skin. Figure 4 shows that,

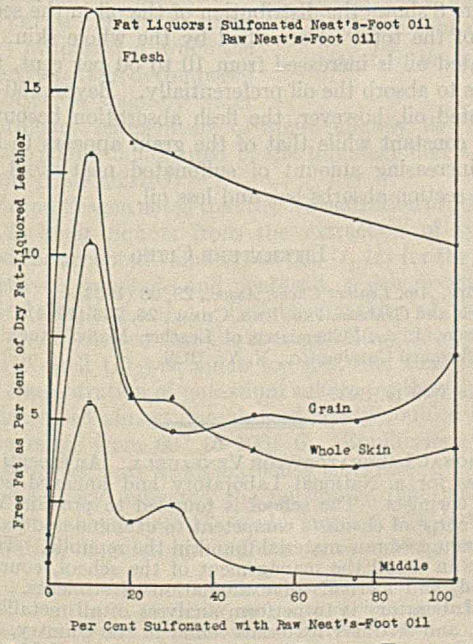

FIGURE 5. FREE FAT IN CHROME-TANNED SKIN USING NEAT'S-FOOT OIL

using 20 per cent sulfonated cod oil, the flesh had absorbed (free and combined oil) some 50 per cent of the total oil absorbed, the grain some 26 per cent, and the middle 24 per cent. As the percentage of sulfonated oil increased in the fat liquor, the flesh absorbed increasing amounts of the oil, reaching a value for 100 per cent sulfonated oil of 70 per cent of the total oil absorbed by the skin. The grain layer showed a decreased value for absorbed oil over this range and the middle layer a distinct and marked decrease in oil content. This is a practical observation, since it shows that, as the sulfonated cod oil increases in a given fat liquor mixture, it causes a preferential take-up of oil by the flesh side in preference to that of the grain layer.

TABLE II. NEAT'S-FOOT OIL IN VARIOUS LAYERS OF DRY FAT-LIQUORED LEATHER

Sulfonated Neat's-Foot Oil %	Grain	Center	Flesh	Total
	FREE FAT AS % OF DRY FAT-LIQUORED LEATHER			
100	6.91	0.11	10.22	4.19
75	4.91	0.17	11.04	3.63
50	5.16	0.45	11.94	4.09
30	4.68	2.45	13.06	5.65
20	5.73	1.94	13.43	5.69
10	13.08	5.52	17.41	10.35
0	1.44	0.68	2.93	1.15
Control	1.40	0.09	0.66	0.55
	UNOXIDIZED COMBINED FAT AS % OF DRY FAT-LIQUORED LEATHER			
100	3.46	0.00	4.36	...
75	0.94	0.00	2.99	...
50	0.64	0.00	2.80	...
20	...	...	...	...
10	0.01	0.00	0.16	...
0	0.00	0.00	0.00	...
Control	0.80	0.15	0.20	...
100	3.46	0.00	4.46	1.90
75	0.98	0.00	2.99	0.84
50	0.74	0.00	2.89	0.78
30	0.11	0.08	1.15	0.34
20	...	...	...	...
10	0.04	0.03	0.21	0.09
0	0.00	0.05	0.00	0.00
Control	1.07	0.26	0.34	0.47
	TOTAL FAT AS % OF DRY FAT-LIQUORED LEATHER			
100	10.37	0.11	14.68	6.09
75	5.89	0.17	14.03	4.47
50	5.90	0.45	14.83	4.87
30	4.79	2.51	14.21	5.99
20	...	...	...	...
10	13.12	5.55	17.62	10.44
0	1.31	0.77	2.93	1.12
Control	2.47	0.35	1.00	1.02
	TOTAL FAT IN EACH LAYER AS % OF TOTAL FAT			
100	43.0	3.2	53.8	...
75	32.0	4.7	63.3	...
50	27.5	7.1	65.4	...
30	20.5	21.8	57.7	...
20	...	...	...	...
10	33.4	26.1	40.5	...
0	34.3	32.3	33.5	...
	FREE FATTY ACIDS IN FREE FAT AS % OF FREE FAT			
100	26.0	24.3	29.7	...
75	26.3	20.2	...	...
50	22.1	21.9	24.8	...
30	19.8	22.0	21.6	...
20	20.0	17.2	19.4	...
10	20.5	17.1	16.8	...
0	21.3	11.4	16.0	...
	RELATIVE THICKNESS OF SECTIONS AS % OF TOTAL DISTANCE THROUGH LEATHER			
100	23.8	51.8	24.4	...
75	20.9	55.9	23.2	...
50	19.4	56.3	24.3	...
30	19.8	53.6	26.6	...
20	20.4	53.2	26.4	...
10	24.6	50.5	24.9	...
0	20.1	16.6	18.3	...

The fatty acids removed during the extraction of the so-called "free" oil showed values ranging from 15 to 31 per cent of the total free oil extracted. These fatty acids increased as the percentage of sulfonated oil increased in the fat liquor.

EXPERIMENTS WITH NEAT'S-FOOT OIL

Table II and Figures 5, 6, and 7 show the data obtained for fat-liquoring containing mixtures of raw and sulfonated neat's-foot oil. Figure 5 shows the free oil contained in the various sections of the leather and indicates clearly that there is a maximum value for free oil at a concentration of 10 per cent

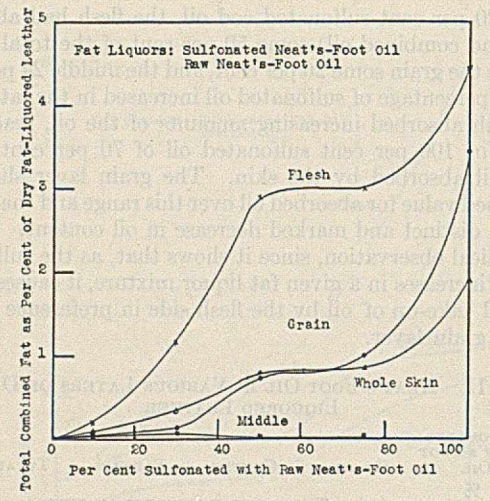

FIGURE 6. COMBINED FAT IN CHROME-TANNED SKIN USING NEAT'S-FOOT OIL

sulfonated and 90 per cent raw neat's-foot oil. This is evidenced by all sections. Beyond values of 10 per cent sulfonated oil, the free oil in the sections decreases to minimum values. As was the case for the cod oil mixtures, the flesh section shows the greatest values for free oil. In this case again it must be indicated that the decrease noted for free oil with the large increase in sulfonated neat's-foot oil used shows that the petroleum ether extraction is at least removing much of the sulfonated oil absorbed by the leather; otherwise a more drastic decrease in free oil should have resulted with large increases of sulfonated oil in the original fat liquor. Certainly the sharp decrease in free oil between 10 and 20 per cent sulfonated oil is not due to insolubility of the sulfonated fraction in petroleum ether, since beyond the value of 20 per cent sulfonated oil, drastic decreases in free oil do not occur. This fact should be noted for all sections.

Figure 6 shows the combined oil in the various sections. It is to be especially noted that in the case of the flesh section there is a large increase in the combined oil between 0 and 50 per cent sulfonated neat's-foot oil, then an apparent equilibrium until 75 per cent sulfonated oil is reached, and finally an increase to 100 per cent sulfonated oil. For the grain section there is a gradual increase in combined oil up to 75 per cent sulfonated oil, then a sharp increase in the combined oil content. As was the case for cod oil mixtures, little or no oil is found in the middle section.

Figure 7 shows the total absorbed oil content of the various sections; there is a maximum value at 10 per cent sulfonated oil and 90 per cent raw oil. The trend of these curves for the various sections is similar to those representing the free oil content of the sections. As in the previous cases, the flesh layer absorbs the greatest amount of total oil, while the middle layer absorbs the least.

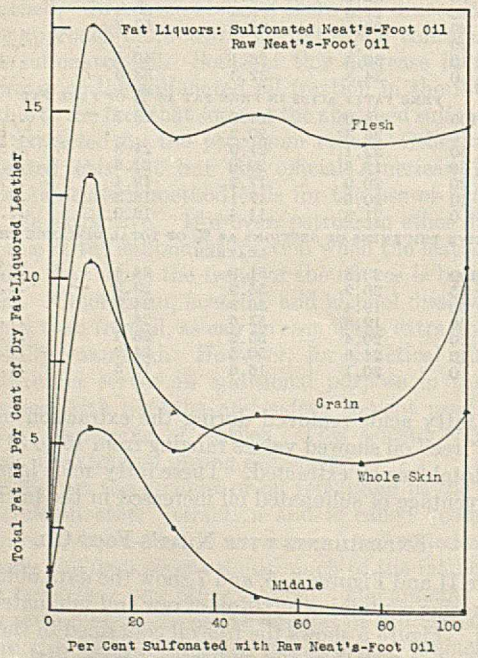

FIGURE 7. TOTAL FAT IN CHROME-TANNED SKIN USING NEAT'S-FOOT OIL

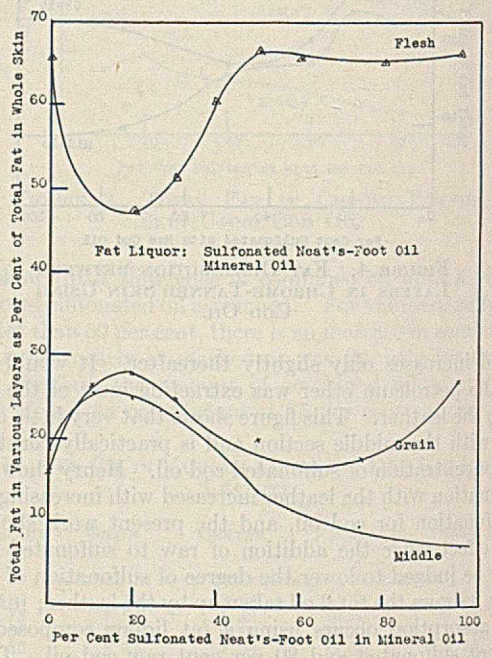

FIGURE 8. FAT DISTRIBUTION BETWEEN LAYERS OF CHROME-TANNED SKIN USING NEAT'S-FOOT OIL

Figure 8 shows the distribution of the oil in the sections in terms of the total oil absorbed by the whole skin. As the sulfonated oil is increased from 10 to 50 per cent, the flesh appears to absorb the oil preferentially. Beyond 50 per cent sulfonated oil, however, the flesh absorption becomes more or less constant while that of the grain appears to increase. With increasing amount of sulfonated neat's-foot oil, the middle section absorbs less and less oil.

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RECEIVED April 16, 1934.

NATIONAL LABORATORY FOR VENEZUELA. An executive decree provides for a National Laboratory and annexed school for expert chemists. The school is founded to provide Venezuela with a corps of chemists competent to examine and pass on the vast amount of raw material found in the republic. The decree outlines in detail the management of the school, courses to be followed, and methods of examination of students. The National Laboratory is to perform analyses of all metallic, hydrocarbon, and fertilizer materials found in the country, and is to actively coöperate with the Technical Section of Mines of the Ministry of Fomento.

Potassium Sulfate from Syngenite by High-Temperature Extraction with Water[1]

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In studying the recovery of potassium sulfate and other industrial chemicals from Texas–New Mexico polyhalite, this station has previously developed processes for converting the polyhalite into syngenite, a double sulfate of potassium and calcium, and then extracting potassium sulfate from this substance. The extract liquor obtained by operation at the atmospheric boiling point contained, however, only about 10 parts of potassium sulfate per 100 parts of water. An improved method for decomposing syngenite has now been worked out. This comprises a two-stage extraction with water at approximately 200° C. which yields a top liquor 2.5 times as concentrated with respect to potassium sulfate as could be obtained previously.

This paper describes the preliminary equilibrium measurements which indicated the possibilities of the process, as well as actual two-stage extraction tests in a small gas-fired autoclave, which yielded recoveries of 95 to 99 per cent of the potassium sulfate in the syngenite. A process outline is suggested which will produce a concentrated solution of magnesium sulfate, a residue of solid calcium sulfate, and a technically pure potassium sulfate, with a recovery of 87 per cent of the potassium sulfate initially present in the polyhalite.

SINCE 1928 a series of investigations has been conducted at this station to develop processes for recovering potassium salts and other industrial chemicals from the deposits of polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$) found in the Permian basin of Texas and New Mexico. During the course of this work Storch and Fragen (*16*) developed Bureau of Mines processes 4 and 4B for the production of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) from polyhalite, and process 4A for the recovery of potassium sulfate from the syngenite so obtained.

Process 4A comprises a two-stage extraction of syngenite with water. In the top stage the syngenite is decomposed by a hot dilute potassium sulfate liquor obtained in the bottom stage, forming potassium pentacalcium sulfate ($K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$) which will subsequently be referred to as pentasalt, and a liquor containing 9 to 10 grams of potassium sulfate per 100 grams of water. A potassium sulfate product is recovered from this top liquor by evaporation, while the solid pentasalt is decomposed in the bottom stage by water at an ordinary temperature of approximately 25° C., producing the dilute liquor used in the top stage and a residue of gypsum ($CaSO_4 \cdot 2H_2O$).

Storch and Fragen noted that the concentration of potassium sulfate in their liquors from the extraction of syngenite exceeded the accepted value at 100° C. (*1, 12*) for the equilibrium between syngenite and pentasalt, which would be the theoretical limiting value. Redeterminations of this equilibrium (*8, 11*) showed that the average value given by Anderson and Nestell (*1*) was much too low, and that the equilibrium concentration of potassium sulfate for these two solid phases increased almost linearly and nearly doubled in value over the range from 60° to 100° C. Equilibrium was attained, however, only at an extremely slow rate.

This discovery indicated the possibility that increase in temperature above 100° C. would increase still farther the concentration of potassium sulfate corresponding to the coexistence of syngenite and pentasalt. It also seemed probable that the rate of approach to equilibrium at the higher temperatures might be much more rapid than at 100° C. This paper presents some approximate equilibrium measurements in the range from 100° to 200° C., followed by the results of two-stage extractions of syngenite and the outline of an improved process for the recovery of potassium sulfate from polyhalite by way of this double salt.

Equilibrium Measurements in the System Potassium Sulfate–Calcium Sulfate–Water above 100° C.

The equilibrium measurements were made in a steel autoclave 76 cm. (30 inches) long and 10 cm. (4 inches) inside diameter, constructed from the design of Peters and Stanger (*14*). This was supported horizontally in an electrically heated furnace mounted on a cradle rocked by an electrically driven eccentric at 9 r. p. m. A calibrated chromel-alumel couple, placed in a horizontal thermometer well, actuated a Leeds & Northrup potentiometric recording and controlling instrument. By independent measurement of the electromotive force of the couple with a Leeds & Northrup Type K potentiometer, the regulation during a typical experiment was found to be within 1° C. of the mean temperature.

Most of the experiments were conducted by adding definite amounts of gypsum, potassium sulfate, and water to the cold autoclave, which was then brought to and maintained at the desired temperature. Samples of solution and solids were withdrawn from time to time for analysis. In order to approach equilibrium from the opposite direction, in some experiments the autoclave was first maintained at a temperature higher than that desired for a time sufficient to insure a rise in the potassium sulfate concentration above the value for the equilibrium to be studied.

Solid and liquid samples were obtained by use of a bronze sampling device, the construction of which is shown in Figure 1. The whole apparatus was heated in an electric oven to within a few degrees of the autoclave temperature and then connected to the sample line of the autoclave and evacuated through valve *A*, with valve *B* open. Valve *A* was then closed and the valve in the sample line was opened; 0.5 to 1.5 minutes were allowed for the sample to pass through filter *C*, after which the valve in the sample line and valve *B* were again closed. After the sampling device was removed from the autoclave, the solid collected on filter *C* was dried by suction. The chamber containing the solution sample was disconnected and weighed, and the sample removed for analysis.

Some uncertainty was introduced in several experiments by leakage of steam through the packing glands of the valves during

[1] This is the fifth article in a series on the Extraction of Potash from Polyhalite. For Parts I, II, and IV, see literature citations *14*, *15*, and *10*, respectively; for Part III, IND. ENG. CHEM., **25**, 1002–9 (1933).

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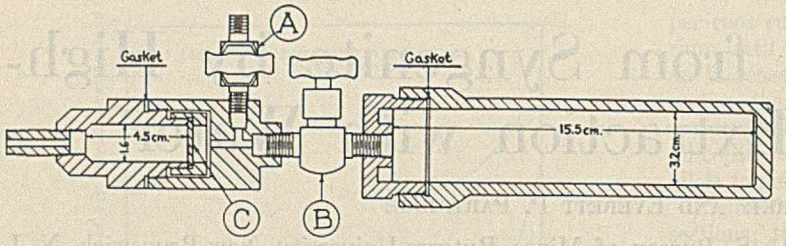


FIGURE 1. DEVICE FOR OBTAINING SIMULTANEOUS SAMPLES OF SOLUTION AND SOLID PHASE FROM AUTOCLAVE

sampling, through the seat of valve *B* after sampling, or through the various screwed joints or gaskets. With proper care it was possible, however, to obtain satisfactory results, as attested by a blank experiment in which only calcined gypsum and a sodium chloride solution of known concentration were placed in the autoclave. Chloride analyses for a series of samples were mutually consistent and agreed with the known initial composition of the solution.

TABLE I. EQUILIBRIUM DETERMINATIONS IN SYSTEM POTASSIUM SULFATE–CALCIUM SULFATE–WATER ABOVE 100° C.

Expt.	Sample	Temp. °C.	Time at Temp. Hours	Solution Composition K_2SO_4 Grams/100 grams	$CaSO_4$ Grams/100 grams
			SYNGENITE-PENTASALT		
1	a	137.5	4	16.4	0.078
	b	137.5	10	16.6	0.077
	c	137.5	25	16.7	0.077
	d	137.5	49	17.1[a]	0.078
2	a	140	24	19.6	0.069
	b	140	121	19.7	0.071
	c	140	196	18.6	0.069
3	a	135	2	16.4	0.073
	b	135	52	16.8	0.070
	c	135	145	17.5	0.067
	d	135	150	17.5	0.063
4	a	160	18	21.2	0.075
	b	136.5	28	18.1	0.070
	c	136.5	146	18.1	0.068
5	a	168	68	23.0	...
	b	168	167	24.0	0.061
	c	168	237	24.0	0.091
6		169	25	24.7	0.075
7	a	169	25	27.4	0.084
	b	169	49	27.3	0.082
	c	169	101	26.9[b]	0.084
8	a	200	27.5	32.8	0.101
	b	200	52	32.0	0.103
9		200	45	32.7	0.109
10		200	46.5	32.3	0.107
			POTASSIUM SULFATE–SYNGENITE		
11	a	151	21	29.4	0.040
	b	151	28	29.5	0.040
12	a	200	19.5	33.7	...
	b	200	25	33.6	0.098
			POTASSIUM SULFATE		
13		250	17	37.5	0
			PENTASALT-ANHYDRITE		
14		200	20	13.2	...
15	a	200	46	13.2	0.049
	b	200	68	14.0[c]	0.053
	c	200	92	13.6	0.052

[a] Equilibrium approached from below, final sample probably below equilibrium K_2SO_4 concentration.
[b] Equilibrium approached from above, final sample probably above equilibrium K_2SO_4 concentration.
[c] Concentration may be high, owing to leakage observed during sampling.

DISCUSSION OF EQUILIBRIUM DATA. Experiments 1 to 10 in Table I were attempts to realize the equilibrium between syngenite and pentasalt at various temperatures from 135° to 200° C. At the lower end of this range, experiments 1 and 3 represent approaches from temperatures, and hence from potassium sulfate concentrations, lower than the final state, while 2 and 4 represent approaches from initially higher temperatures and concentrations, as indicated specifically in sample 4a. The position of the syngenite-pentasalt boundary in the range from 135° to 140° C. is fixed with good accuracy by the final values of these experiments.

At the higher temperatures, experiments 5 to 10, inclusive, on the syngenite-pentasalt equilibrium require additional supporting data to establish their precise quantitative significance, although they are of great qualitative value since they indicate that the potassium sulfate concentration continues to increase with temperature up to at least 200° C. and probably higher. The concentration at 200° C., corresponding to the coexistence of syngenite, pentasalt, and solution, must be at least 32 grams of potassium sulfate per 100 grams of water, more than 2.5 times the corresponding value at 100° C.

The two determinations of experiments 11 and 12 help to define the equilibrium between potassium sulfate and syngenite, which forms the upper boundary of the region in which syngenite is stable. These are supplemented by a measurement of the solubility of potassium sulfate at 250° C.

An approximation of the equilibrium between pentasalt and anhydrite at 200° C. was attempted in experiments 13 and 14. Apparently the solution corresponding to this equilibrium must contain at least 13 grams of potassium sulfate per 100 grams of water.

No evidence of the formation of any double salt other than syngenite or pentasalt was given by petrographic examinations. This agrees with the results of d'Ans and Schreiner (*3*) who prepared double salts containing two moles of calcium sulfate to one of rubidium, ammonium, or sodium sulfate but were unable to produce potassium dicalcium sulfate from solution, even at temperatures as high as 170° C.

The concentrations of potassium sulfate corresponding to various equilibria at temperatures from 0° to 200° C. are

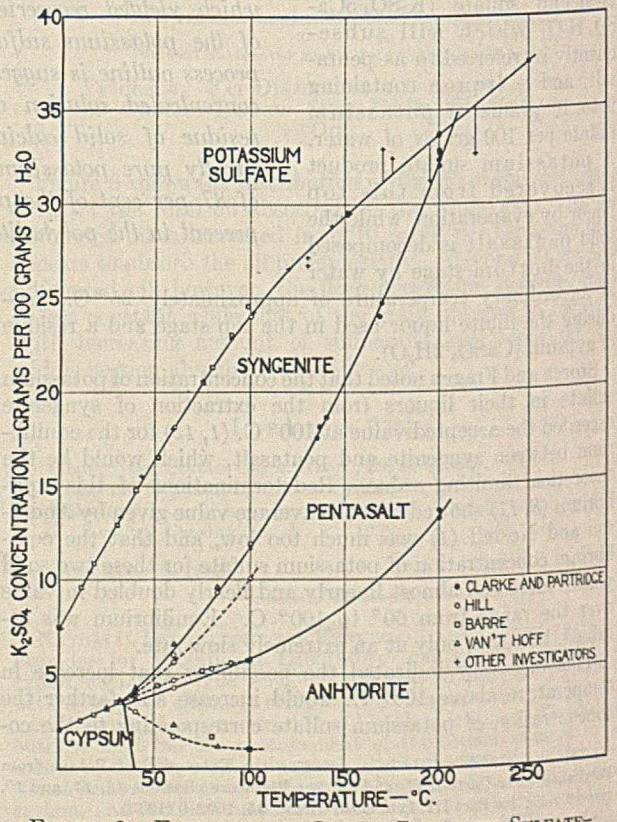


FIGURE 2. EQUILIBRIA IN SYSTEM POTASSIUM SULFATE–CALCIUM SULFATE–WATER FROM 0° TO 200° C.

TABLE II. RESULTS FROM SINGLE-STAGE AND TWO-STAGE EXTRACTIONS OF SYNGENITE BELOW 200° C.

Expt.	Stage	Temp.	Extraction Time	K_2SO_4 Concentration — Extract: After flash evaporation	K_2SO_4 Concentration — Extract: In autoclave	K_2SO_4 Concentration — Wash	K_2SO_4 Content of Dry Filter Cake	K_2SO_4 Loss in Handling	Extn. of K_2SO_4
		° C.	Hours	Grams/100 grams			%	%	%
22	1	131	2	13.2	12.2	10.3	24.1	3.2	71
24	1	166	2	15.6	14.4	10.2	22.3	3.0	74
25	1	165	1	14.5	13.2	9.2	24.3	4.0	69
33	1	165	2	15.0	13.2	7.2	23.8	...	71
	2	165	2	1.77	..	1.4	16.8	7.6[a]	83
40	1	165	2	15.4	13.2	7.7	..	...	69
	2	165	4.2	1.67	..	1.0	18.6	6.7[a]	80
36	1	165	2	16.3	14.3	7.9	..	...	..
	2	196	4	4.3	..	1.8	0.76	...	99
38	1	165	2	14.3	13.5	8.3	..	...	60
	2	196	1	4.0	..	1.4	2.03	6.9[a]	98

[a] Total for both stages.

shown in Figure 2, in which previously available data (*1*, *2*, *3*, *4*, *6*, *12*, *18*) are combined with those of Conley (*8*), Hill (*11*), and the authors. Because of the low concentrations of calcium sulfate involved, the potassium sulfate concentration for equilibrium between solid potassium sulfate and syngenite is almost the same as the solubility of potassium sulfate in water. The particularly precise values of the latter given by Berkeley (*5*) for temperatures from 0° to 101° C. and the values of Tilden and Shenstone (*17*) and of Étard (*9*) at higher temperatures are therefore included in Figure 2.

The solid lines in Figure 2 represent stable equilibria, the broken lines metastable or unstable equilibria. This diagram has many interesting features, but a full discussion would scarcely be relevant to the purpose of this paper. A glance at the upward trend of both the syngenite-pentasalt and pentasalt-anhydrite curves is sufficient to show that increase in temperature increases the concentrations of potassium sulfate theoretically attainable in each stage of the two-stage decomposition of syngenite previously developed at 100° C. (*16*).

More complete equilibrium data would ordinarily have been sought at the higher temperatures. Such measurements would, however, have been of little value to the chemical engineer in the present case because of the extremely slow rate of approach to the final state. Attention therefore was directed to the problem of developing a two-stage procedure for the extraction of syngenite which would combine the desirable features of high recovery and high concentration of potassium sulfate in the top liquor with a short operating cycle.

Extraction Tests

The extraction of potassium sulfate from syngenite and from pentasalt was tested at several temperatures between 100° and 200° C. in the equipment illustrated in Figure 3. The stirrer in the 1-gallon (3.8-liter) gas-fired autoclave was driven at 100 r. p. m. by a hollow shaft which was equipped with a valve and a flexible ball joint to allow the contents of the autoclave to be discharged to a small three-plate filter press. The autoclave was equipped with thermometer well, pressure gage, and piped inlets for wash water and compressed air. During the earlier experiments of Table II, temperatures were measured by a mercury thermometer and controlled within ±2° C. by manual regulation of the gas flow. In the later experiments of Table III the temperatures were measured by a calibrated chromel-alumel couple and recorded and automatically controlled by a Leeds & Northrup Micromax instrument operating a solenoid valve in the gas-supply line.

At the start of each test the extracting solution and the syngenite or pentasalt to be extracted were placed in the clean autoclave. After the head was bolted on and the agitator started, the temperature was brought up to the desired operating level as rapidly as possible and maintained at this level for a definite time. The contents of the autoclave were then discharged directly to the filter press, except that, when the temperature was above 170° C., the autoclave was first cooled to approximately this temperature to reduce the pressure to the safe limit of the press. As soon as filtration was complete, wash water was forced into the hot autoclave. After agitation for a few minutes, this was discharged by air pressure to the filter press, the wash liquor being collected separately from the original filtrate. This procedure effected a nearly quantitative removal of material from the autoclave.

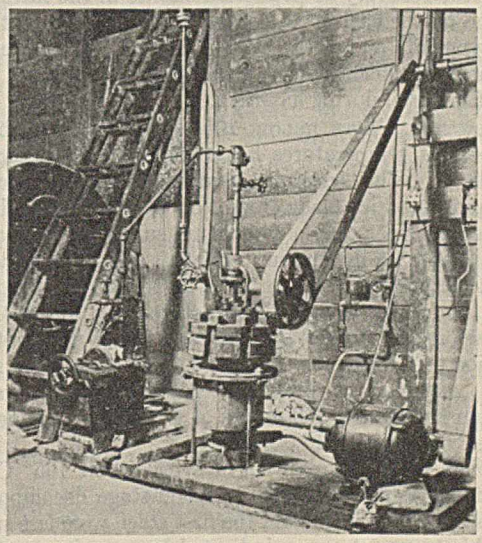


FIGURE 3. AUTOCLAVE AND FILTER PRESS FOR TWO-STAGE EXTRACTION OF SYNGENITE

INTERPRETATION OF EXTRACTION DATA. During each extraction test, water was lost from the system both by steam leakage through the packing gland of the autoclave and by flashing of steam from the filtrate as it left the filter press. The total loss of water, as estimated by material balances, ranged from 7 to 17.5 per cent of the water charged, with an average of 11.7 per cent for seventeen tests. While the leakage through the packing gland probably varied from test to test, the water lost in this manner generally must have been small compared to that flashed off during filtration. The flashing also caused some loss of potassium sulfate in a fine spray of liquor blown outside of the filter trough.

The performance of the extractions was measured in terms of both the concentration attained in the extract liquor and the degree of extraction from the solid phase. A conservative value for the concentration of potassium sulfate in the liquor in the autoclave before discharging was calculated by using the weight of potassium sulfate actually recovered in the filtrate and wash and the weight of water initially added to the autoclave. This value must be less than the actual concentration, owing to loss of water by leakage, loss of

TABLE III. RESULTS FROM TWO-STAGE EXTRACTIONS OF SYNGENITE AT 201° C.

EXPT.	STAGE	EXTN. TIME	K_2SO_4 CONCN. IN EXTRACT: After flash evaporation	K_2SO_4 CONCN. IN EXTRACT: In autoclave	K_2SO_4 CONTENT OF DRY CAKE	K_2SO_4 LOSS IN HANDLING	EXTN. OF K_2SO_4: I[a]	EXTN. OF K_2SO_4: II[b]
		Hour	*Grams/100 grams H_2O*		%	%	%	%
68	1	1	21.6	18.7	...	...	59	...
	2	1	7.7	6.9	1.95	5.0	93	98.0
70	1	1	22.1	18.2	...	...	62	...
	2	1	7.5	6.3	1.20	1.6	96	98.8
73	1	1	30.6	...	...	...	..	...
	2	1	7.5	6.3	1.93	...	..	98.0
75	1	1	25.1	23.9	...	...	41	...
	2	1	11.3	10.7	12.4	3.4	82	87.5[c]
77	1	1	27.6	24.0	...	...	52	...
	2	1	10.2	9.8	0.80	1.5	97	99.0
80	1	0.5	27.8	25.6	...	...	61	...
	2	0.5	8.4	8.1	0.86	2.8	95	99.2
82	1	0.5	29.6	27.0	...	...	62	...
	2	0.5	9.1	8.4	1.98	1.0	97	98.1
84	1	0.5	25.7	23.7	...	...	49	...
	2	0.5	8.8	8.2	8.82	5.7	83	90.0[d]
87	1	0.5	26.2	25.4	...	...	56	...
	2	0.5	10.2	9.9	4.15	3.4	92	95.9
93	1	0.5	21.1	18.8	...	...	52	...
	2	0.5	8.1	7.2	3.08	2.6	91	95.8

[a] Basis, total K_2SO_4 recovered in extract and wash solutions.
[b] Basis, K_2SO_4 contents of syngenite entering process and dry filter cake leaving process.
[c] Poor extraction due to use of insufficient water and poor temperature control in first stage.
[d] Poor extraction due to use of syngenite containing 4.1 per cent $MgSO_4$.

final products in handling, and incomplete displacement of adhering liquor from the solid during washing.

The degree of extraction has been calculated both on the basis of the recovery of potassium sulfate in the filtrate and wash and on the basis of the potassium sulfate content of the initial syngenite and of the final filter cake. The latter basis is the more significant of the two since it is less affected by the losses of material during handling.

EXTRACTION TESTS BELOW 200° C. The data obtained from tests at temperatures below 200° C. are summarized in Table II. The syngenite used was a finely crystalline, nearly pure product made from New Mexico polyhalite. It contained 52.4 per cent of potassium sulfate and only negligible amounts of magnesium sulfate, sodium chloride, and insoluble impurities. When this was treated for 2 hours at 165° C., concentrations in the autoclave of 13.2 to 14.4 grams of potassium sulfate per 100 grams of water were obtained. Reduction of the time to one hour at 165° C. yielded similar results. A somewhat lower concentration of 12.2 grams of potassium sulfate per 100 grams of water was obtained in a 2-hour extraction at 131° C.

Although the decomposition of syngenite at 165° C. gave satisfactory results, attempted second-stage decompositions of the pentasalt residue from the first stage were less successful at this temperature, as indicated by experiments 33 and 40 in Table II. The concentration obtainable after 4 hours was apparently below 2 grams of potassium sulfate per 100 grams of water. When the second stage was conducted at 196° C., however, the extraction was substantially complete at the end of 4 hours in experiment 36, and almost as complete after only 1 hour in experiment 38.

EXTRACTION TESTS AT 201° C. The improved results from the second-stage extractions at 196° C., combined with the trend of the syngenite-pentasalt boundary in Figure 1 toward higher concentrations with increasing temperature, led to a series of two-stage extraction tests with a temperature of approximately 201° C. in each stage, using syngenite of the composition indicated in Table IV. The successful attainment of high concentrations and high recoveries is attested by the results shown in Table III. Experiments 75 and 77 indicated that autoclave concentrations of 24 and 10 grams of potassium sulfate per 100 grams of water were possible after a treatment of 1 hour in the first and second stage, respectively. The comparatively poor extraction achieved in experiment 75 was due to the use of too little water and to faulty temperature regulation during the first stage. Experiment 73, run under the same conditions as experiment 77, showed a high extraction by analysis of the final filter cake. Unfortunately the first-stage extract liquor was lost by breakage of a bottle.

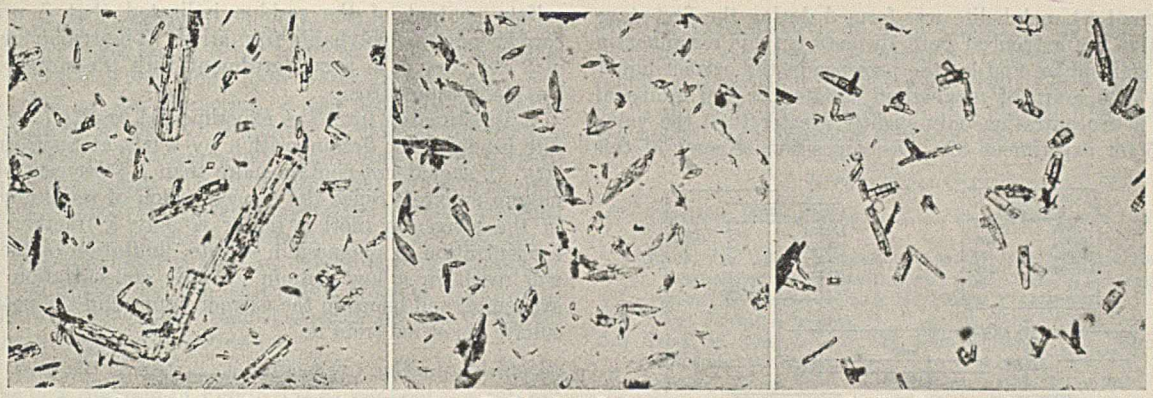
On cutting the time in each stage to 0.5 hour and increasing slightly the ratio of syngenite to water, equally good extractions combined with slightly higher concentrations were attained in experiments 80 and 82. At 201° C. the decomposition of syngenite to form pentasalt obviously proceeds very rapidly even at high concentrations of potassium sulfate.

In an industrial extraction process the solid residue of calcium sulfate leaving the second stage would probably be washed with the water about to enter this stage. Similarly, the pentasalt residue on its way from the first to the second stage would be washed with the less concentrated second-stage extract about to enter the first stage. While complete adherence to this plan would have been difficult in the extraction experiments, an effort was made to control conditions so that the potassium sulfate used in the initial liquor in the first stage would be equivalent to that obtained in the second-stage extract and the two washes. This objective was successfully approximated in several tests, and especially well in experiment 82, the material balance of which is given in Table IV.

The size and appearance of the initial syngenite, of the intermediate solid consisting essentially of pentasalt, and of the final residue of anhydrite are indicated in Figure 4, which represents the solid materials of experiment 82.

EFFECT OF MOISTURE IN SYNGENITE. The preceding tests were based on dry syngenite entering the first stage. However, it would be desirable to send the wet syngenite product obtained from polyhalite by a solution process (*16*) directly to the high-temperature extraction, since this would eliminate intermediate drying. The use of syngenite containing 23 per cent of free water on the wet basis[3] was simulated in experiment 87 by using more water in the first stage than in the second. As noted in Table III, autoclave concentrations of 24.5 and 9.9 grams of potassium sulfate per 100 grams of water were obtained in the first and second stages, respectively, combined with a high recovery. While further work will be necessary to determine how low a moisture content is obtainable in the filtration of syngenite and how high a moisture content can be tolerated in the high-temperature extraction, it seems possible that intermediate drying may be unnecessary.

[3] Syngenite produced in small-scale industrial equipment at this station, and filtered and washed continuously on a 1 × 1 foot rotary vacuum filter, contained approximately 40 per cent moisture on the wet basis. It is probable that the moisture content could be reduced considerably by proper compacting of the washed cake by means of a roller.



Syngenite entering first stage | Residue from first stage (pentasalt) | Residue from second stage (anhydrite)

FIGURE 4. PHOTOMICROGRAPHIC COMPARISON OF SOLIDS AT DIFFERENT POINTS DURING TWO-STAGE EXTRACTION OF SYNGENITE AT 200° C. (× 170)

EFFECT OF IMPURITIES IN SYNGENITE. Syngenite produced from polyhalite will contain some anhydrite ($CaSO_4$), together with perhaps 3 per cent of inert materials such as magnesite, clay, and iron oxide. In addition, there will be small amounts of sodium chloride and magnesium sulfate derived from retained mother liquor, as well as any magnesium sulfate combined in particles of incompletely decomposed polyhalite.

Although anhydrite is relatively inert in many process steps for the treatment of polyhalite, in the first stage of the high-temperature extraction it, as well as gypsum, is converted almost quantitatively into pentasalt, thereby tending to reduce the percentage extraction in the first stage and to increase the burden on the second stage. However, owing to the fact that pentasalt contains only 1 part by weight of potassium sulfate to 3.9 parts of calcium sulfate, this effect of anhydrite has proved relatively unimportant in the extraction of syngenite containing up to 5 per cent of anhydrite.

The effect of a large amount of excess calcium sulfate in the syngenite, either as anhydrite originally present in the polyhalite or as gypsum resulting from the use of insufficient potassium sulfate in the syngenite-formation step, may be deduced from the results of experiment 93, in which a wet syngenite-gypsum mixture containing 24.6 per cent of potassium sulfate, 1 per cent of magnesium sulfate, and 36 per cent of free moisture on the wet basis was put through the two-stage extraction at 201° C. In spite of the adverse effect of the moisture content and of calcium sulfate present in approximately 80 per cent excess over the amount corresponding to pure syngenite, it was possible to obtain good recovery combined with a concentration of 18.8 grams of potassium sulfate per 100 grams of water in the autoclave in the first stage. A higher concentration would probably have been attainable if either the moisture content or the excess of calcium sulfate had been lower.

The mineral impurities other than anhydrite are so inert and are present in the syngenite in such small amounts that they have no noticeable effect on the high-temperature extraction. On the other hand, the magnesium sulfate content of the syngenite must be limited to a low value to prevent the formation of polyhalite in the first stage. The material balance for experiment 82 in Table IV shows that 1.2 per cent of magnesium sulfate in the syngenite did not cause any appreciable formation of polyhalite. When the magnesium sulfate content was increased to 4.1 per cent in

TABLE IV. ANALYTICAL DATA AND MATERIAL BALANCE FOR TWO-STAGE EXTRACTION OF SYNGENITE AT 201° C.

(Experiment 82)

	Material	Composition				Material Balance				
		K_2SO_4 %	$MgSO_4$ %	NaCl %	H_2O %	Total Grams	K_2SO_4 Grams	$MgSO_4$ Grams	NaCl Grams	H_2O Grams
					FIRST STAGE					
In	Syngenite	48.5	1.20	0.60	5.0	1000	485	12	6	50
	Make-up soln.	..	..	..	...	2130	230	0	0	1900
	Wash water	..	..	..	...	500	0	0	0	500
	Total in	..	..	..	...	3630	715	12	6	2450
Out	Extract	22.7	0.34	0.24	...	2091	475	7.1	5.0	1604
	Wash	12.4	0.21	0.11	...	435	54	0.9	0.5	380
	Filter cake	..	..	..	...	756	..	..	...	120
	Total out	..	..	..	...	3282	..	..	...	2104
	Loss	..	..	..	...	348	..	..	...	346
	% Loss	..	..	..	...	..	..	..	...	14.2
					SECOND STAGE					
In	Filter cake	..	..	..	...	756	..	..	...	120
	Extn. water	..	..	..	...	1900	0	0	0	1900
	Wash water	..	..	..	...	500	0	0	0	500
	Total in	..	..	..	...	3156	..	..	...	2520
Out	Extract	8.32	0.13	0.02	...	1850	154	2.4	0.4	1693
	Wash	4.13	..	..	...	390	16.1	..	...	374
	Filter cake	1.98[a]	..	..	...	628	8.6	..	...	193
	Total out	..	..	..	...	2868	178.7	..	...	2260
	Loss	..	..	..	...	288	..	..	...	260
	% Loss H_2O	..	..	..	...	..	..	..	...	10.3
					OVER-ALL BALANCE					
In		..	..	..	...	..	715	12.0	6.0	..
Out		..	..	..	...	..	708	10.4	5.9	..
Unaccounted for		..	..	..	...	..	7	1.6	0.1	..

[a] Dry basis (wet cake contained 44 per cent H_2O on dry basis, or 31 per cent on wet basis).

experiment 84, polyhalite was formed during the first-stage extraction, as evidenced both by petrographic examination of the solid phase and by the presence in the extract liquor of but 0.49 gram of magnesium sulfate per 100 grams of water, a concentration only slightly greater than the value of 0.45 for experiment 82. Decomposition of some of this

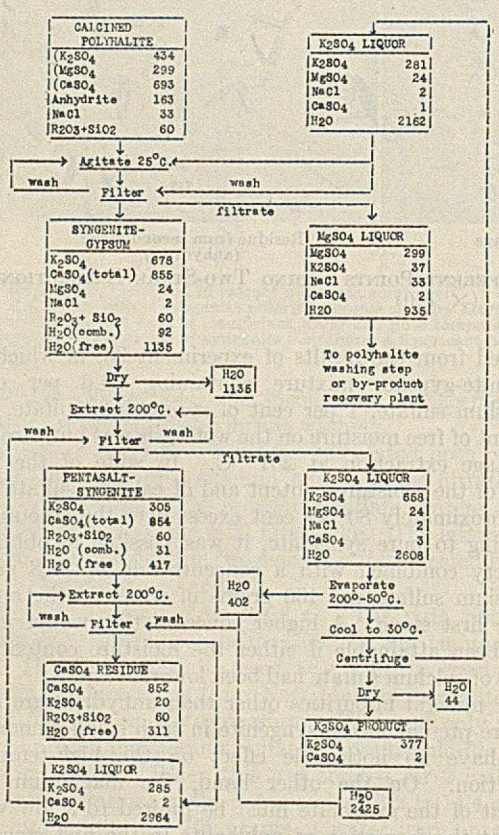


FIGURE 5. FLOW DIAGRAM FOR PROCESS 5A

polyhalite in the second stage is indicated by the higher concentration of magnesium sulfate in the second-stage extraction, as shown in Table V; but, since in continuous operation this extract would be returned to the first stage, the system would simply tend to approach a steady state in which a certain fraction of the magnesium sulfate entering the first stage would be discharged as polyhalite with the calcium sulfate residue from the second stage.

TABLE V. EFFECT OF MAGNESIUM SULFATE IN SYNGENITE UPON EFFICIENCY OF EXTRACTION OF POTASSIUM SULFATE AT 201° C.

Expt.	Stage	$MgSO_4$ in Syngenite	$MgSO_4$ Concn. Extract[a]	$MgSO_4$ Concn. Wash	Compn. of Dry Filter Cake $MgSO_4$	Compn. of Dry Filter Cake K_2SO_4	Extn. of K_2SO_4
		%	*Grams/100 grams H_2O*		%	%	%
82	1	1.2	0.44	0.24			
	2		0.14	..	0.37[b]	1.98	98.1
84	1	4.1	0.49	0.70			
	2		0.67	0.74	4.17	8.82	90.0

[a] After flash-evaporation.
[b] Estimated on assumption that all $MgSO_4$ unaccounted for in material balance of Table IV was present in filter cake.

The importance of a low magnesium sulfate content in the syngenite is evident from the values for recovery of potassium sulfate in Table V. With 1.2 per cent of magnesium sulfate in the syngenite in experiment 82, only 2 per cent of the potassium sulfate charged as syngenite was lost in the final calcium sulfate residue. Increase in the magnesium sulfate content of the syngenite to 4.1 per cent in experiment 84 resulted in the retention in the final residue of 10 per cent of the potassium sulfate charged as syngenite. The magnesium sulfate content of the residue indicated that 7 per cent corresponded to polyhalite formation. The remaining value of 3 per cent is in good agreement with the corresponding loss in experiment 82.

It is estimated from the experimental results that syngenite intended for decomposition by water at approximately 200° C. should not contain more than 1.5 per cent of magnesium sulfate. Since the concentration of sodium chloride in the syngenite mother liquor is only a fraction of the concentration of magnesium sulfate, limitation of the latter will result in a low sodium chloride concentration in the syngenite, and hence in the extract liquor and the potassium sulfate recovered from it.

PROCESS OUTLINES

The high-temperature decomposition of syngenite, which will be referred to as Bureau of Mines process 4C, may be substituted for the low-temperature process 4A (*16*) in the recovery of potassium sulfate from syngenite produced by processes 4 or 4B. By suitable modification of the quantities involved, it may also be substituted for the low-temperature decomposition in process 7A (*10*). In addition, the high concentration of potassium sulfate attainable by operation at 200° C. makes possible a new and probably more advantageous procedure designated as process 5A, which is outlined in Figure 5 subsequent to the preliminary steps of crushing, washing to remove sodium chloride, grinding, and calcination.

Process 5A combines two fundamental operations. The first is the conversion of polyhalite into a mixture of syngenite and gypsum; the second is the high-temperature two-stage extraction of this syngenite-gypsum mixture to produce a concentrated potassium sulfate liquor. By evaporating a comparatively small amount of water from this liquor and cooling, a crop of potassium sulfate is obtained, the mother liquor being recirculated for use in forming the syngenite-gypsum mixture.

The material balance for process 5A in Figure 5 is based upon the following considerations:

1. An allowance of 26 per cent of excess calcium sulfate over the amount equivalent to the potassium sulfate in the washed and calcined polyhalite.
2. A concentration of 32 grams of magnesium sulfate and 4 grams of potassium sulfate per 100 grams of water in the mother liquor from the syngenite-gypsum mixture.
3. A syngenite-gypsum mixture containing 62 per cent of calcium sulfate in excess over the amount corresponding to pure syngenite.
4. Moisture contents on the wet basis of 40 per cent of water in the syngenite-gypsum cake and 25 per cent in the pentasalt-syngenite and in the calcium sulfate residue cakes.
5. Reduction of the magnesium sulfate content of the syngenite-gypsum cake to 1.4 per cent, dry basis, by washing with potassium sulfate liquor recycled to the formation step.
6. Drying of the syngenite-gypsum cake before extraction.
7. Extraction of 55 per cent of the potassium sulfate from the syngenite-gypsum in the first stage, and an over-all extraction of 97 per cent.
8. No removal of water between the first and second stages of extraction.
9. A concentration of 25 grams of potassium sulfate per 100 grams of water in the liquor from the first stage of the extraction.
10. A concentration of 13 grams of potassium sulfate per 100 grams of water, corresponding to saturation at 30° C., in the mother liquor recycled from the centrifugals to the formation of the syngenite-gypsum mixture.
11. A moisture content of 10 per cent of water, wet basis, in the potassium sulfate leaving the centrifugals.

Many modifications of the flow diagram are possible. The polyhalite may contain less excess calcium sulfate than indicated; moisture contents differing from those assumed may necessitate minor revision of the material balance; instead of drying the syngenite-gypsum mixture, an extract

liquor of lower concentration may be obtained, as in experiment 93, the extra water being removed in the evaporation rather than the drying step; more water may be used in the second stage of the extraction, if the second-stage extract liquor obtained at 200° C. is allowed to flash to atmospheric pressure before introduction in the first stage; and more or less potassium sulfate may be recirculated to the syngenite formation step by varying the temperature at which the final crop of potassium sulfate is separated. The flow diagram of Figure 5 is presented simply as one of the most probable outlines indicated by the extraction tests in this paper, together with previously published data on the formation of a syngenite-gypsum mixture (*16*).

The over-all recovery of potassium sulfate calculated from the flow diagram of Figure 5 is 87 per cent. A total of 4.2 tons of water must be removed by evaporation and drying per ton of potassium sulfate produced, but it should be noted that of this quantity approximately 1 ton would be removed by single-stage self-evaporation of the extract liquor from 200° C. to the atmospheric boiling point. Process 5A should, therefore, compare favorably with processes previously described (*10*, *13*, *15*, *16*, *19*) in spite of the increased cost of equipment and difficulties introduced by operation at a pressure of approximately 200 pounds per square inch (14 kg. per sq. cm.).

Patents relating to the decomposition of syngenite and pentasalt by water or aqueous solutions at temperatures above 200° C. were granted to the Chemische Fabrik Buckau (*7*) during the course of the work described in this paper. The process outlined in Figure 5, however, appears to be novel and therefore has been made the subject of a patent application by the authors.

Acknowledgment

The authors are indebted to Arthur E. Hill of New York University for the privilege of using his experimental data prior to its publication, to Alton Gabriel of this station who performed numerous petrographic examinations of solid phases and prepared the photomicrographs of Figure 4, and to A. A. Berk and F. Fraas of this station who measured the solubility of potassium sulfate at 250° C.

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Indium Glass

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The addition of indium sesquioxide to a glass mixture containing sulfur colors the glass yellow in proportion to the amount of indium sesquioxide used. This color appears to be developed by the interaction of indium sesquioxide as the glass is being made, because the adding of the indium sulfide (In_2S_3) to the glass-forming mixture does not produce the same result. The color is progressive, from light canary to dark tangerine-orange.

INDIUM is listed as number 49 in Mendeléeff's periodic table of elements. Reich and Richter are accredited with having discovered it in 1863, and because of the indigo blue lines in its spectrum, it was named "indium." Its isolation was made probably early in its history, but its commercial development was left until a few years ago. It was one of the elements that was supposed to be widely distributed in several kinds of ores, but always in minute quantities. While small amounts had previously been produced as residues, the author believes that he and his associates were the first to consider seriously its production from the ore.

Properties of Indium

The properties of this element are fairly well known. It is a white lustrous metal, very soft and ductile, and lighter than silver; it melts at 155° C. and is said to boil at about 1450° C. It has great surface stability at ordinary temperatures, but oxidizes and burns at temperatures above its melting point, especially if finely divided.

There are two known oxides of indium—the monoxide and the sesquioxide. The monoxide (InO) is black and probably not as stable as the other oxide since but two of the three valences of indium are satisfied. With further oxidation the monoxide becomes the sesquioxide. Indium sesquioxide (In_2O_3) is very stable and volatilizes without decomposition at 850° C. It has a specific gravity of 7.179 and a beautiful yellow color. Its solubility in fused alkali salts makes possible the new use in glass.

Indium, when heated high enough in the presence of oxygen, will produce the sesquioxide easily. Another method of producing indium sesquioxide is as follows: The indium metal may be dissolved in a suitable acid such as hydrochloric and then precipitated by an alkali such as ammonium hydroxide. The indium hydroxide is filtered away from the solution, and, after drying, the hydroxide is burned to the yellow sesquioxide.

Yellow Glass

The production of yellow glass has depended, at least to some degree, on compounds of uranium, cerium, and titanium. The uranium hydrate has a greater coloring power than any of the usual compounds. Cerium and titanium have been used together in rather substantial amounts but the color is lighter than is desired. Uranium gives a canary yellow color.

So far as has been determined, indium sesquioxide gives a more intense yellow color than any of the other oxides used. One-half pound imparts a beautiful yellow to 1000 pounds of glass-forming materials. This amount is about one-seventh that of the metallic oxides previously used for coloring glass yellow.

A laboratory sample of the glass may be made from the following proportions (parts by weight): silicon dioxide, 100; sodium carbonate, 5; sodium sulfate, 37.50; calcium carbonate, 35.80; indium sesquioxide, 0.09. The mixture is melted together into a complete solution and the result is a beautiful yellow glass. This combination may be the basis for the crystal-clear yellow glass which is desirable.

The intensity of color of indium glass depends upon the amount of indium sesquioxide introduced, ranging from very light yellow to dark yellow-amber.

Indium metal in a finely divided condition may be used instead of the indium sesquioxide. When tried with the above formula, a yellow glass is obtained, but great care must be exercised in preparing it. Instead of starting with the sesquioxide, it is probable that indium hydroxide may be used. This would make it unnecessary to burn the hydroxide beforehand.

The above mixture was fused together without any indium compound; the resulting glass was not yellow but a very light green. When indium sesquioxide was added the yellow color developed. There is some question as to why this happened. There is a rather high amount of sodium sulfate present in the mixture which would undoubtedly produce a yellow color if reducing agents were present. It is difficult to explain how indium sesquioxide could act as a reducing agent. However, the fact remains that the yellow glass is produced, and that the depth of color depends on the amount of indium sesquioxide present.

While the price of indium compounds is relatively high, there is present in the above mixture only about 0.05 per cent of indium sesquioxide, or about one-seventh of the amount of any other metallic compound necessary for the purpose. The price of indium compounds has been greatly reduced during 1934 and should be reduced farther as production increases. There is a large supply of ore available which contains consistent amounts of indium. It is therefore expected that indium and its compounds will soon find a definite and useful place in commerce.

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Tests for the Accuracy of Vapor-Liquid Equilibrium Data

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The accuracy of vapor-liquid equilibrium data for binary systems which deviate from the ideal solution laws can be appraised by means of certain easily applied criteria derived from the Duhem-Margules equation, and can rigidly be tested by a method based on this equation which depends on the calculation of one partial pressure curve from the other.

In a previous communication (*1*) it was shown that, when a binary system of volatile substances is ideal or nearly so, this fact can be demonstrated by a simple and accurate experimental method. It was also shown that in such cases the vapor-liquid equilibrium diagram can be calculated with great accuracy, the precision obtained depending only on the magnitude of the deviation from ideality. This method gives results which are more accurate than those which have been obtained heretofore experimentally, particularly in the case of substances of nearly equal volatilities.

In the case of systems which exhibit a significant deviation from ideality, it is no longer possible to proceed in this manner, and it becomes necessary to determine equilibrium data experimentally. Consequently it is important to have means of checking the reliability of the data so obtained. Though these data may be located within the presumed experimental error on a smooth curve, nevertheless this alone is not a sufficient test of their accuracy, since an unsuspected error may be present which affects all of the results more or less equally. This point is illustrated by the discordant data found in the literature—e. g., for water–acetic acid (*7*), alcohol-water (*15*), carbon disulfide–carbon tetrachloride (*18*), etc.

It has long been recognized that the Duhem-Margules equation is a powerful tool for the investigation of partial pressures and, hence, equilibrium data in binary systems. This equation may be written:

$$\frac{d \ln p_1}{d \ln p_2} = -\frac{1-x}{x} \qquad (1)$$

where x and $1-x$ = mole fractions of components 1 and 2, respectively, 1 being the more volatile component; p_1, p_2 = corresponding partial pressures at a given fixed temperature.

With the substitution of fugacities for pressures, the relation becomes thermodynamically exact; however, at temperatures near the normal boiling points, pressures may, in general, be used without significant error (*9*).

This equation, integrated as a power series with three or more arbitrary constants, usually in the form

$$\log \frac{p_1(1-x)}{p_2 x} = A + Bx + Cx^2 + Dx^3 + \ldots$$

has been used by Zawidski (*20*), Rosanoff and Easley (*18*), and others to construct calculated partial-pressure curves for comparison with experimental data. This method of application of the equation, if carefully performed, yields satis-

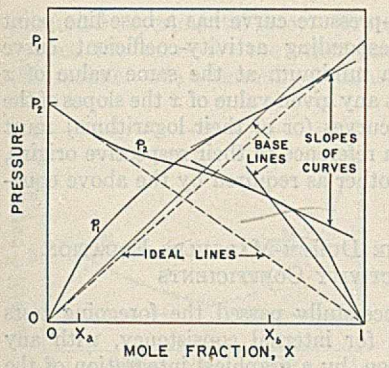

FIGURE 1. TYPICAL PARTIAL-PRESSURE CURVES

factory results, but is somewhat cumbersome and laborious. In like manner, Rosanoff, Bacon, and Schulze (*17*) have used the empirical equation:

$$\frac{d\pi}{dx} = \left(\frac{P_1 - P_2}{\log P_1 - \log P_2}\right) \log \frac{p_1(1-x)}{p_2 x}$$

where π = the total pressure of the system

P_1, P_2 = the vapor pressures of the pure components at the temperature in question

This, of course, requires an equation of π in terms of x, which is obtained empirically from the data, using arbitrary constants. The partial pressures have also been obtained from the π curve by Marshall (*14*), using a trial-and-error graphical method founded on the Duhem-Margules equation and the relation: $\pi = p_1 + p_2$. Finally, Lewis and Murphree (*13*), using a simplifying assumption regarding the nature of the x-y curve, have performed a stepwise integration of a special form of the Duhem-Margules equation, in which the vapor composition, y, and the total pressure, π, are used as variables instead of the two partial pressures.

The present paper will attempt to show that a good preliminary indication of the reliability of partial-pressure data can be gained directly by inspection, using a few simple corollaries of the Duhem-Margules equation. This critical inspection alone is sufficient to reveal the inaccuracy of some of the published results. For those data which pass this test, and when greater accuracy is desired, the conformity to the Duhem-Margules equation can rigorously be tested by employing a method developed by Lewis and Randall. This method, which is based on a conversion of the partial pressures into activity coefficients, followed by graphical integration, appears to be more accurate and expeditious than those described above.

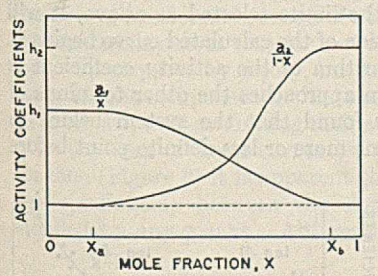

FIGURE 2. TYPICAL ACTIVITY-COEFFICIENT CURVES

PRELIMINARY INSPECTION OF PARTIAL-PRESSURE CURVES

When the data have been obtained at constant temperature, the partial pressure may be plotted directly as a function of x, and the resulting curves tested for conformity to the rules outlined below.

As previously shown (*1*), if one partial-pressure curve is a straight line, the other is also. Conversely, if π is a straight line, both partial-pressure curves are also; i. e., the system is ideal.

For nonideal systems we may advantageously use the Duhem-Margules equation in the form

$$\frac{dp_1/dx}{p_1/x} = \frac{dp_2/d(1-x)}{p_2/(1-x)} \qquad (2)$$

which brings out the comparison of the slope of the partial-pressure line at one point with the slope of the straight line through that point and through the origin of the curve. For the sake of convenience this line will arbitrarily be called the "base line" of the point, and the ratio of the slope of the curve at that point (e. g., dp_1/dx) to the slope of the base line (e. g., p_1/x) will be called the "slope ratio," since it is understood that these slopes are measured with respect to the origin of the curve in question, and hence are always positive. Figure 1 shows examples of these slopes for a typical pair of partial-pressure curves.

From the above equation, the slope ratios of the two curves at the same value of x must be equal. By placing a straight edge through any point on a curve and the origin of that curve, it can readily be seen whether the slope ratio is greater than 1, equal to 1, or less than 1 (rule A). If the slope ratios of the two curves for the same value of x differ from unity in opposite directions, this is sufficient indication that the data are inaccurate. If the curves pass this test, but appear abnormal in some respect, then actual measurement of slopes can be made, and the slope ratios can be compared quantitatively (rule B). While the use of measured slopes is generally avoided on account of the difficulty of obtaining accurate figures, the direct comparison of two slopes through the same point is easier to perform, especially if the several portions of the curve which are to be tested are plotted on such different scales that the actual slopes to be measured are not too far from 45°. An examination of the two curves in Figure 1 by this method, for example at x_b, will readily show that they are not compatible with one another, although they pass the preliminary test since the slope ratios are less than 1 for both curves from x_a to x_b.

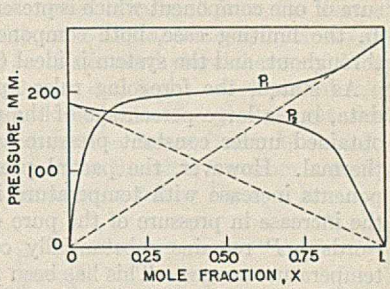

FIGURE 3. METHANOL-BENZENE

When the slope ratio equals 1, $dp_1/dx = p_1/x$ and $dp_2/d(1-x) = p_2/(1-x)$. That is, if, at a given value of x, the tangent to one partial-pressure curve passes through the origin of that curve, then the tangent to the other curve at the same value of x also passes through its origin (rule C). The existence of such a point can be determined readily by rotating a straight edge around the origin and observing whether in any position this straight edge becomes tangent to the curve. Such a point may be defined as a point of inflection of the curve in regard to the base line. The statement of this rule then becomes: "Whenever one curve has a point of inflection in regard to its base line, the other curve does likewise at the same value of x." [This was sensed by Ostwald (*16*) who, however, mistook the condition for that of a true analytical inflection $[(d^2p/dx^2) = 0]$. Marshall (*14*) pointed out Ostwald's mistake, but did not go so far as to show what the correct condition was.]

In nonideal solutions this condition occurs only seldom, but the following extension of the rule is of considerable importance: If one partial-pressure curve is, in part, a straight line which, extended, passes through its origin, then the other is likewise over the same range (rule D).[1] This condition, in which the partial pressure is proportional to the mole fraction, is seldom, if ever, found in the middle of a curve without

[1] A slight misstatement of this rule appears in Lewis and Randall's "Thermodynamics" (*9*), where, following Equation XVIII, it is stated that "if one of the curves is a straight line through a certain range of composition, the other is also a straight line through the same range." It can readily be shown by geometrical application of the Duhem-Margules equation that, if the one straight line, when extended, does not pass through the origin of the curve, then the other line must be curved over that range.

extending to either end. When it extends to the lower end, we say that the curve follows Henry's law over that range, and in consequence the other constituent must follow Raoult's law over the same range (for example, from $x = 0$ to x_a in Figure 1). Since most binary solutions follow these laws without significant deviation over an appreciable range of concentration, this relation may be of considerable value, particularly in determining the partial pressure of one component which is present in very small amount. In the limiting case, both components follow Raoult's law throughout, and the system is ideal (rule E).

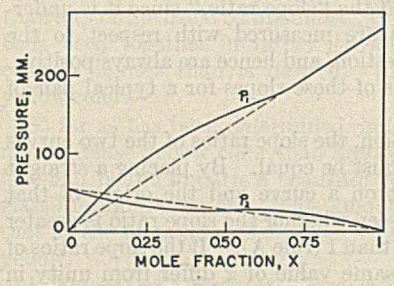

FIGURE 4. METHANOL-WATER

As stated, the foregoing rules apply only to isothermal data, but a large percentage of the published data has been obtained under constant pressure and is therefore not isothermal. However, the partial pressures of the two components increase with temperature in a manner similar to the increase in pressure of the pure constituents, or in other words p/P remains substantially constant, over moderate temperature ranges. This has been pointed out by Rosanoff and Easley (*18*) and can be confirmed by inspection of data in the literature—for example, for the system acetone-chloroform (*2*, *20*). For greater convenience the figures obtained in this manner from isothermal (as well as from isobaric) data are used in the form p_1/P_1x and $p_2/P_2(1 - x)$. In the nomenclature of Lewis and Randall (*10*) these expressions become a_1/x and $a_2/(1 - x)$, respectively, in which a is the activity, provided we take as the standard state for each component, respectively, this component in the pure liquid state at the temperature in question. The deviation of these "activity coefficients" from unity thus gives a measure of the departure of the system from ideality. If the boiling point curve is known, the corresponding values of P_1 and P_2 can be determined or obtained from the literature. The observed partial pressures can then be converted into activity coefficients and plotted as a function of x, as, for example, in Figure 2.

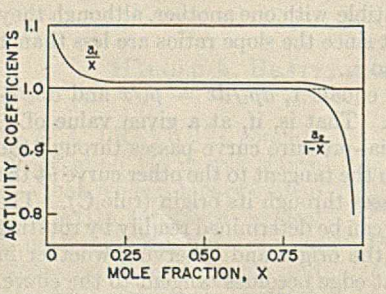

FIGURE 5. *n*-HEPTANE–METHYLCYCLOHEXANE

The Duhem-Margules equation now becomes:

$$d \log \frac{a_1}{x} = -\frac{1 - x}{x} d \log \frac{a_2}{1 - x} \qquad (3)$$

from which it may be seen that the following rules must be satisfied by the data.

Starting at $x = 0$, the activity coefficient $a_1/x = h_1$, where h_1 is the Henry's law constant, up to a point x_a, through the range over which Henry's law holds (rule F). Since Raoult's law applies to the other component over the same range, $a_2/(1 - x) = 1$, from $x = 0$ to $x = x_a$. Conversely, at the other end of the diagram, $a_1/x = 1$, and $a_2/(1 - x) = h_2$, from $x = x_b$ to $x = 1$. This is illustrated by Figure 2. In the limiting case of an ideal system, both coefficients equal unity throughout (rule G).

Whenever the partial-pressure curve has a base-line point of inflection, the corresponding activity-coefficient curve shows a maximum or a minimum at the same value of x (rule H). In general, at any given value of x the slopes of the two activity-coefficient curves (or of their logarithms) must be of the same sign with reference to their respective origins, and are related to each other as required by the above equation (rule I).

INTEGRATION OF THE DUHEM-MARGULES EQUATION USING ACTIVITY COEFFICIENTS

Data which have successfully passed the foregoing tests may then be examined for internal consistency, with any desired degree of precision, by a graphical integration of the Duhem-Margules equation. It is evident that direct graphical integration of Equations 1 or 2 is not practical, because $\log p_1$ (or $\log p_2$) approaches $-\infty$ as x approaches 0 (or 1). This difficulty is avoided by using the form of Equation 3 suggested by Lewis and Randall (*11*). Using as the standard state for each component this component in the pure state, Equation 3 gives:

$$\log \frac{a_1}{x'} = -\int_{x=1}^{x=x'} \frac{1 - x}{x} d \log \frac{a_2}{1 - x}$$

and

$$\log \frac{a_2}{1 - x'} = -\int_{x=0}^{x=x'} \frac{x}{1 - x} d \log \frac{a_1}{x}$$

where the limiting values of $x' = 0$ and 1, respectively

Thus, in each case, by taking one of the activity-coefficient curves as established, we can proceed therefrom to calculate the other curve by graphical integration of the proper one of the above equations.

The recommended procedure to follow is to select that one of the two experimental curves which appears to be the better defined, particularly at its termini, and from it to calculate the other curve. With the limits selected as above, it will be seen that the construction of the calculated curve begins at its origin, where the logarithm of the activity coefficient is zero. As the construction approaches the other terminus of this curve, it is usually found that the system begins to follow Raoult's law at some more or less definite point before the end of the calculation is reached. At that point the logarithm of the first curve becomes zero, and there is no further change in the value of the integral. This final value of the integral is therefore the Henry's law constant for the dilute solution, and the accuracy with which it is determined depends on the precision with which the first curve may be drawn, particularly at its terminus where the logarithm becomes zero. In the event that this terminus cannot be located with sufficient accuracy, the best that can be done is to extend the calculated curve just so far as the experimental data warrant, leaving its final value (the Henry's law constant) undetermined. The curve thus calculated is then compared with its corresponding experimental curve, and the magnitude and sign of the deviations between these two are noted. Based on these deviations, the initially selected experimental curve is arbitrarily redrawn in slightly modified form, the modifications being kept, if possible, within the

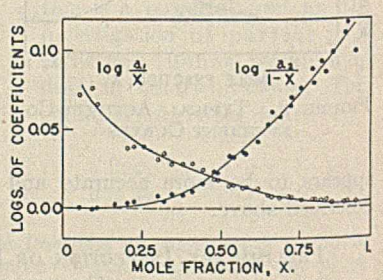

FIGURE 6. TOLUENE–*n*-OCTANE
(Experimental only)

presumed experimental error. From this new curve is recalculated the curve for the other component. Proceeding in this manner, one eventually obtains that thermodynamically related pair of curves which best satisfies the data as a whole. In actual practice it will usually be unnecessary to make more than one such recalculation, if the data are reasonably good and if a certain degree of familiarity with the method has been obtained. If, however, the data are not in good agreement, this fact will be evident as soon as the first calculated curve has been obtained (if not before), and no further effort need be wasted in attempting to reconcile them.

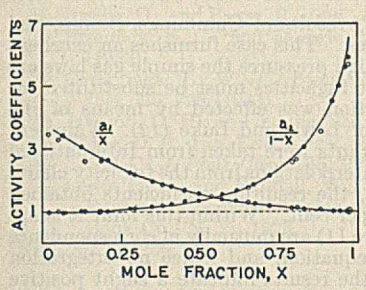

FIGURE 7. CARBON DISULFIDE–ACETONE

● Experimental, Zawidski; ○ Experimental, Rosanoff; —— Calculated, graphical integration

EXAMPLES OF THE APPLICATION OF THE FOREGOING METHODS

To demonstrate the utility of the preceding tests, there follow some typical results of the application of these tests to data taken from the literature. Throughout the present discussion, the symbol x refers to the first named component, which is the more volatile.

ISOTHERMAL SYSTEMS. Examples of straight-line partial-pressure curves are furnished by the results of Zawidski (*20*) for benzene–ethylene dichloride and ethylene dibromide–propylene dibromide. These systems, accordingly, are ideal (rule E).

Of the nonideal systems, many appear to follow Raoult's law over a considerable range of concentration, as illustrated by Zawidski's curves (*20*) for carbon tetrachloride–ethyl acetate. As required by theory, the corresponding data over this range for the component in dilute solution are found to follow Henry's law, thus confirming their accuracy (rule D).

In the case of Lee's curves (*8*) for the system methanol-benzene (Figure 3) it is apparent that the requisite quantitative relationship between the slope ratios (rule B) is not satisfied by any means. Although both ratios are less than one, it can be seen by inspection that, with increasing x, the ratio for methanol increases, while that for benzene decreases. Application of the slope-ratio rule A to the results of Bredig and Bayer (*3*) for the methanol-water system (Figure 4) shows that at about $x = 0.1$ to 0.4, the slope ratio for the alcohol is much less than one, while that of the water is equal to or slightly greater than one. Hence in both cases, either the data are in error or else the vapors of the two components do not follow Dalton's law.

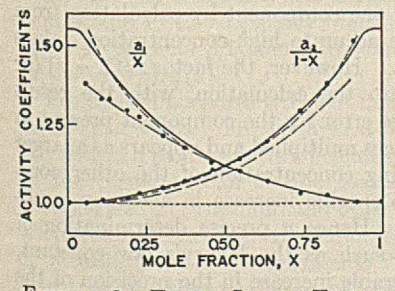

FIGURE 8. ETHYL IODIDE–ETHYL ACETATE

● Experimental; ——Calculated, graphical integration; —— Calculated, Zawidski; ---Calculated, Rosanoff

ISOBARIC DATA. For each of these systems it was necessary to select vapor pressures from the literature, and to construct equations of the type $\log P = A - B/T$ which gave the best fit over the temperature ranges involved. In some cases the value of A was then changed to give agreement with the value of the boiling point of the pure compound given by the authors of the data in question. The constants used are given in Table I. Using these P_1 and P_2 values and the x-y data, the activity-coefficient curves were constructed and examined by the above-described methods.

TABLE I. VAPOR PRESSURES OF PURE COMPOUNDS USED IN THE CALCULATION OF ACTIVITY COEFFICIENTS

(A and B are constants of the equation $\log P = A - B/T$, where T is in ° K.)

COMPOUND	TEMP. RANGE ° C.	A	B
n-Heptane	98–110	7.5917	1750.0
Methylcyclohexane	98–101	7.4542	1710.0
Toluene	98–124	7.7309	1860.0
n-Octane	110–126	7.7503	1941.4
Carbon disulfide	39–54	7.4018	1444.2
Acetone	39–56	7.8482	1635.7
n-Hexane	67–79	7.7215	1654.6
Benzene	67–79	7.6559	1686.8

The activity-coefficient curves calculated from the data of Bromiley and Quiggle (*4*) for *n*-heptane–methylcyclohexane are illustrated in Figure 5. Since methylcyclohexane follows Raoult's law from $x = 0$ to $x = 0.8$, the activity-coefficient curve for *n*-heptane should be horizontal throughout that range, the value indicated by the figure being $h_1 = 1.01$. Likewise, since *n*-heptane follows Raoult's law from $x = 0.9$ to $x = 1$, methylcyclohexane must follow Henry's law over that range. Furthermore, the slope of the activity-coefficient curve of *n*-heptane from 0.8 to 0.9 makes it necessary for h_2 to be greater than 1, while the data indicate a value lower than 1. Actually, since the apparent deviation from ideality for *n*-heptane is so small (1 per cent), and may be due to an uncertainty regarding the vapor pressure of the material used, it seems likely that both components follow Raoult's law over the whole range, and that the system is actually ideal, a conclusion which the present authors have previously confirmed experimentally (*1*).

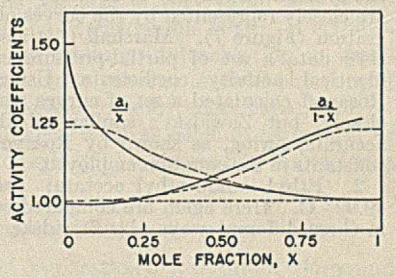

FIGURE 9. *n*-HEPTANE–TOLUENE

—— Experimental, Bromiley and Quiggle; —— Calculated, graphical integration

A preliminary inspection of the results of Bromiley and Quiggle (*4*) for the system toluene–*n*-octane reveals a considerable degree of inaccuracy. When the logarithms of the activity coefficients are plotted against x, as in Figure 6, it appears that *n*-octane follows Raoult's law up to about $x = 0.1$, but the corresponding points for toluene show no indication of constancy as required by Henry's law (rule F). The same is true at the other end of the curve, and in this case the toluene curve becomes constant at a value somewhat above the ideal line (probably due to an error in the value selected for P_1). More serious discrepancies, which cannot be brought within the presumed limits of experimental error, appear when the slopes of the log curves are compared at convenient points such as $x = 0.25$, 0.5, and 0.75 (rule I). The ratios of the slopes of the two curves at these particular points should be -3, -1, and $-1/3$, respectively, whereas the actual values are found by inspection to be about -3.5, -0.6, and -0.1, respectively. Under these circumstances there is no hope of reconciling the two curves with one another.

INTEGRATION OF ACTIVITY-COEFFICIENT CURVES. Examples are given below of the results obtained by application of the graphical integration method to five typical systems, both isobaric and isothermal, which have passed the

preliminary tests. The activity coefficients which have been calculated by this method for the following systems are listed in Table II:

TABLE II. VALUES OF THE ACTIVITY COEFFICIENTS CALCULATED BY GRAPHICAL INTEGRATION

	Carbon Disulfide–Acetone		Ethyl Iodide–Ethyl Acetate		*n*-Heptane–Toluene		*n*-Hexane–Benzene	
	a_1	a_2	a_1	a_2	a_1	a_2	a_1	a_2
x	x	$1-x$	x	$1-x$	x	$1-x$	x	$1-x$
0.00	4.0	1.000	1.5542	1.0000	1.236	1.000	1.367	1.000
0.03	...	...	1.5542	1.0000	...	...	...	...
0.05	3.57	1.003	1.5444	1.0003	...	...	1.367	1.000
0.10	3.22	1.011	1.4689	1.0044	1.236	1.000	1.334	1.003
0.15	2.911	1.026	1.4029	1.0110	...	...	1.293	1.0075
0.20	2.636	1.048	1.3455	1.0200	1.182	1.008	1.260	1.013
0.30	2.183	1.116	1.2487	1.0457	1.135	1.022	1.206	1.028
0.40	1.832	1.226	1.1751	1.0804	1.097	1.041	1.155	1.052
0.50	1.570	1.391	1.1220	1.1220	1.066	1.065	1.112	1.085
0.60	1.380	1.629	1.0804	1.1751	1.040	1.098	1.075	1.132
0.70	1.230	2.017	1.0457	1.2487	1.019	1.140	1.040	1.203
0.80	1.113	2.725	1.0200	1.3455	1.005	1.189	1.013	1.303
0.85	1.068	3.314	1.0110	1.4029	...	...	...	...
0.90	1.035	4.12	1.0044	1.4689	1.000	1.222	1.0005	1.395
0.95	1.014	5.36	1.0003	1.5444	...	...	1.000	1.403
0.97	1.007	6.4	1.0000	1.5542	...	...	...	...
1.00	1.000	...	1.0000	1.5542	1.000	1.222	1.000	1.403

1. Carbon disulfide–acetone: results of Zawidski (*20*) at 35.17° C. and of Rosanoff and Easley (*18*) at 760 mm. (39° to 54° C.) shown in Figure 7. The good agreement between these two sets of data illustrates the fact that the activity coefficients do not vary appreciably over the small temperature range involved, despite the very large deviation from ideality shown by the system. Both sets of data appear very accurate, since they are closely represented by the curves obtained by graphical integration (Figure 7). Marshall (*14*) also calculated from Zawidski's data a set of partial-pressure curves which give almost identical activity coefficients. Using still another method, Rosanoff calculated a set of curves which fit his own data very closely, but Zawidski's similar calculations are distinctly inaccurate, owing, as shown by Rosanoff, to the use of too few constants in the equation employed.

2. Ethyl iodide–ethyl acetate: results of Zawidski (*20*) at 49.99° C. Here again are compared calculated curves obtained in three different ways—by Zawidski, by Rosanoff, Bacon, and Schulze (*17*), and by the present authors. From an inspection of the curves (Figure 8) it appears that Zawidski used only the experimental points for ethyl iodide (a_1/x) to obtain the constants for his equation, with the result that the calculated curve for ethyl acetate [$a_2/(1-x)$] diverges from the corresponding experimental curve throughout. The present authors have used two identical, mirror-image curves which fit the data perfectly over the high-concentration (50 to 100 per cent) range for each component, where the experimental accuracy is greatest. The extension of these curves into the low-concentration range is then arbitrarily determined by the Duhem-Margules equation; having accomplished this by graphical integration, it is found that the low-concentration data for ethyl acetate are accurate, but those for ethyl iodide are somewhat in error. Rosanoff's calculated curves are very similar but do not quite fit the high-concentration points for ethyl acetate.

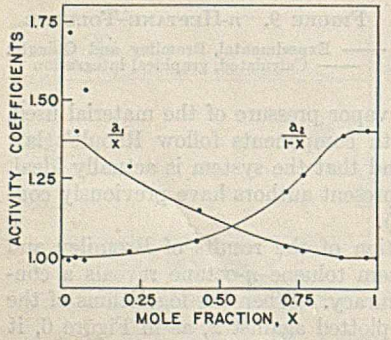

FIGURE 10. *n*-HEXANE–BENZENE

● Experimental; —— Calculated, graphical integration

3. *n*-Heptane–toluene: results of Bromiley and Quiggle (*4*) at 760 mm. The experimental points are numerous and, for the most part, lie within the probable experimental error on the smooth curves shown in Figure 9. Nevertheless, it is found impossible to reconcile the two experimental curves, the calculated pair of curves shown in the figure being about the best that can be obtained.

4. *n*-Hexane–benzene: results of Tongberg and Johnston (*19*) at 735 mm. In this case, instead of using the experimentally determined boiling points, the more accurately known values at 724 and 760 mm. (*6*, *19*) were taken and corrected to 735 mm. After plotting all of the experimental points, as shown in Figure 10, and arbitrarily drawing a curve through one set of them (those for benzene), we obtain by calculation the corresponding curve for *n*-hexane. The latter shows fairly good agreement with all but two of the experimental points, indicating that the data are reasonably accurate.

5. *n*-Pentane–*n*-heptane: results of Cummings, Stones, and Volante (*5*) at 10 atmospheres. This case furnishes an excellent example of the fact that at high pressures the simple gas laws are no longer applicable, so that fugacities must be substituted for pressures. This transformation was effected by means of the generalized fugacity charts of Lewis and Luke (*12*). Values of P_1, P_2, and the critical constants were taken from International Critical Tables. Since the interpolations from the fugacity charts were necessarily not precise, the resulting coefficients obtained may be in error by about 2 per cent. Within this limit it is apparent that the results (Figure 11) are mutually in correspondence with the Duhem-Margules equation, and hence no integration was performed. However, the results indicate a slight positive deviation from ideality, whereas a similar calculation by Cummings, Stones, and Volante, expressed in the form of an x-y diagram, shows a negative deviation: the latter would be predicted by previous results (*1*) for paraffin-paraffin systems.

ACCURACY OF DATA

If, as is usually the case, the analytical data used to calculate partial pressures are obtained by the measurement of a substantially additive physical property of the binary mixture, it follows that the absolute accuracy with which the composition of each phase is known remains the same throughout the range of concentration. Hence the relative accuracy with which each component is determined varies with its concentration. For example, if the absolute accuracy of the measurement is 0.1 per cent, then at a point where x (or y) is about 0.5 the accuracy for each individual component is 0.2 per cent. However, at x (or y) = 0.1, the accuracy for component 1 is 1 per cent and for component 2 is 0.11 per cent; at x (or y) = 0.01, these accuracies become 10 and 0.101 per cent, respectively. Since substantially the same inaccuracy applies to a given value of x and to the corresponding value of y, it is evident that at low concentrations the ratio y/x may be in error by an amount far exceeding the accuracy with which the composition of the binary mixture can be determined.

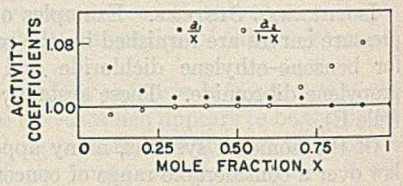

FIGURE 11. *n*-PENTANE–*n*-HEPTANE

For this reason it would appear desirable to obtain the low-concentration values for one component by calculation from the corresponding, more accurate high-concentration values for the other component. However, the factor $x/(1-x)$ (or its reciprocal) enters into the calculation, with the result that the small percentage error for the component present in high concentration becomes multiplied and appears as a larger error in the corresponding concentration of the other component. As a result no specific increase in accuracy is obtainable by calculation. Hence a precise determination of low-concentration data, such as the Henry's law constant, requires either a considerable increase in the precision of the customary analytical methods based on some physical property of the mixture, or the use of a specific method for determining the compound present in the smaller amount, irrespective of the amount of the other. Two illustrations of the first method would be, for example, the effect of the solute on the melting point of the solvent, or the use of a Pulfrich-Zeiss differential refractometer whereby the difference in refractive index of a known and an unknown mixture can be directly measured. The best example of the second method is perhaps chemical analysis, which, unfortunately, seldom yields accurate results in the case of one hydrocarbon dissolved in another.

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Preparation of Anhydrous Metallic Soaps

Titanium Soaps

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THE term "metallic soaps" is applied to the salts of the fatty, resin, or naphthenic acids, and the metals other than the alkali metals or the ammonium radical. These metallic soaps have many useful applications in the arts. They are used in waterproofing materials, as thickening agents in oils and greases, as stabilizers for suspensions and emulsions, as wetting agents, and to give many special properties to paints and varnishes. Soaps of cobalt, manganese, and lead form the commonly used driers for paints.

There are two types of metallic soaps which are usually referred to as precipitated and fused soaps, respectively. The precipitated soaps are prepared by the double decomposition of aqueous or alcoholic solutions of alkali metal or ammonium soaps with aqueous solutions of salts of the other metals. The reaction results in the replacement of the alkali metal or ammonium in the water-soluble soap with the other metal, thus producing a water-insoluble or relatively insoluble metallic soap. The precipitated soaps are, when properly made, chemical compounds containing a definite percentage of metal which completely saturates the acid used. The fused metallic soaps are made by heating free fatty or resin acids with a suitable metallic compound, usually the oxide or hydrate and less frequently the acetate. The ease of preparation of the fused soaps and their suitability for many purposes gives them preference in some instances over the precipitated soaps (*2*).

For certain purposes trivalent metallic soaps are preferable to divalent soaps. For example, a small amount of aluminum stearate in a paint is more efficient in preventing hard-settling of the pigment than is zinc stearate. The preparation of metallic soaps of titanium and other tetravalent elements was therefore undertaken in this laboratory in order to determine if metallic soaps of tetravalent elements possess any advantages over the metallic soaps of di- and trivalent elements.

Titanium oxide is an extremely inert pigment, and therefore no reaction could be expected between a free fatty acid and titanium oxide to form a titanium soap. However, hydrous titanium oxide, and more particularly the orthotitanic form which is precipitated by the addition of an alkali to a titanium solution in the cold, is readily soluble in dilute mineral acids and the strong organic acids. Therefore it was attempted to form a titanium soap by mixing hydrous titanium oxide with a free fatty acid and heating under varying conditions. In no case was there any indication of the formation of any titanium–fatty acid compound.

[1] Present address, United Color & Pigment Company, Newark, N. J.

It was then found that titanium tetrachloride reacted with fatty acids at moderate temperatures with the elimination of hydrogen chloride. This reaction is very rapid and is accompanied by the evolution of considerable heat. It is therefore necessary to add the titanium tetrachloride in small portions with rapid agitation to prevent marked charring of the organic acid. The presence of substances capable of reacting with hydrochloric acid, such as calcium carbonate or aniline, was also found to be helpful in decreasing the violence of the reaction.

METHOD OF PREPARATION

In general, a method of preparation of a titanium compound of a fatty acid is to suspend calcium carbonate in amount equivalent to the chloride of the titanium tetrachloride to be used in the fatty acid at a temperature at which the fatty acid is completely liquid. Titanium tetrachloride, in somewhat more than the theoretical amount for the reaction,

$$4HR + TiCl_4 \longrightarrow TiR_4 + \uparrow 4HCl$$

is added in small portions with vigorous stirring. The reaction mass is then heated on a water bath until the evolution of hydrogen chloride ceases. The bulk of the hydrogen chloride formed by the reaction escapes as the gas, the remainder reacting with the calcium carbonate to form calcium chloride. The cooled reaction mass is dissolved in a suitable volatile solvent, preferably benzene, and filtered or centrifugalized to remove the calcium carbonate and any calcium chloride or titanium oxide or oxychlorides formed in the course of the reaction. The solvent is removed and recovered by distillation. However, solution of the reaction mass in a volatile solvent in order to permit removal of solids is not necessary, as the mass may be clarified by filtering at a high enough temperature to maintain fluidity. A product of higher titanium oxide content is obtained by triturating the above material with alcohol, or by precipitation from the solvent by the addition of alcohol. While the primary product is quite soluble in most organic liquids, the alcohol-precipitated product is very nearly insoluble in most.

For example, 500 grams of stearic acid were heated to 90° C., and 100 grams of calcium carbonate were suspended in the melt. To this were added 85 grams of titanium tetrachloride in small portions and with vigorous stirring. The reaction mass was heated on a water bath until the odor of hydrogen chloride had practically disappeared, then cooled, dissolved in 1800 grams of ether, and filtered on a Büchner funnel im-

mersed in ice water to prevent loss of ether. The ether was then distilled off and the residue heated under vacuum on a water bath. The product so obtained contained 6.5 per cent titanium oxide (theoretical for titanium stearate, 6.6 per cent) and 0.2 per cent chlorine. It melted between 63.5° and 66° C. without giving a sharp melting point. The melt appeared to be perfectly clear. This product was triturated with alcohol, filtered, and air-dried, and then contained 13.1 per cent titanium oxide. Inasmuch as the titanium oxide content of the alcohol-treated material was almost twice that of the untreated material, this may indicate that the alcohol treatment does not merely remove free fatty acid but also brings about some decomposition of the primary product, similar to hydrolysis in an aqueous system, to form a basic titanium salt.

Titanium linoleates and resinates were similarly prepared. The tung acids combine with titanium in much the same way as stearic, linseed, and rosin acids, except that the resulting compounds have quite a low titanium content—about 2.5 per cent titanium oxide—which may be due to polymerization of the tung acids. Gardner and Bielouss (*1*) found that small amounts of titanium tetrachloride polymerized linseed and tung oils.

Since one of the principal uses for metallic soaps in paints is to prevent hard-settling, some titanium soaps were ground into a number of Titanox-B flat wall paints by the Paint, Varnish, and Lacquer Laboratory of this company and stored for 30 days. Comparisons were then made with similar paints to which aluminum stearate, which is considered to be the most efficient antisettler of the common metallic soaps, had been added. Titanium linoleate had very poor antisettling properties; titanium resinate was only a shade better. On the other hand, titanium stearate suspended the pigment more efficiently than the best grade of aluminum stearate.

X-ray examination of a titanium stearate did not show the presence of titanium oxide in either crystalline or amorphous form, which indicates that the formation of a titanium stearate compound had taken place.

Inasmuch as the reaction of titanium tetrachloride with free fatty or rosin acids was successfully used for the formation of titanium soaps, it was thought that the anhydrous chlorides of other metals might react similarly. In fact this was found to be true, and cerium, thorium, zirconium, and aluminum stearates were prepared by the reaction of their anhydrous chlorides with stearic acid.

Literature Cited

(1) Gardner, H. A., and Bielouss, E., Am. Paint Varnish Mfrs.' Assoc., Sci. Sect., *Circ.* 366 (1930).
(2) Gardner, H. A., and Coleman, R. E., Paint Mfrs.' Assoc. U. S., *Circ.* 120 (1921).

Received June 4, 1934.

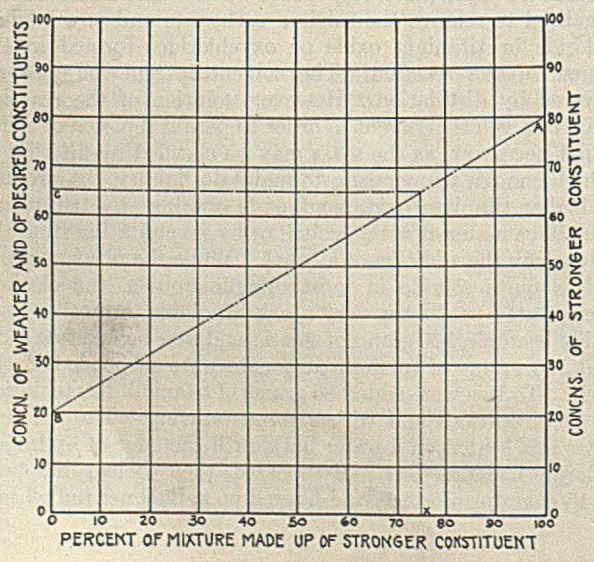
A Chart for the Rapid Calculation of Mixtures

J. S. Baker, E. R. Squibb & Sons, Brooklyn, N. Y.

THE calculation of the amounts of two or more substances of known concentration, which when mixed will produce a mixture of an intermediate desired concentration, is a problem often encountered in chemical plants and laboratories. By "concentration" of an ingredient, as used here, is meant the number of units of that ingredient, solid, liquid, or gas, dissolved in or uniformly mixed with another substance or mixture of substances to form one hundred units of mixture.

The chief difficulty with the usual graphical presentations for the rapid solution of problems of this type is that one or more irregular scales, such as logarithmic or reciprocal scales, are employed in their construction, resulting in poor accuracy over at least part of the range.

It is the aim of the chart here presented to overcome this objection. Since the scales are all regular and straight, this chart may be constructed on regular coördinate paper in a few minutes.



This chart is based on the relation:

$$X = \frac{C - B}{A - B}$$

where A = concn. of stronger constituent
B = concn. of weaker constituent
C = intermediate desired concn.
X = fraction of final mixture made up of stronger constituent

To construct this chart, draw perpendicular identical scales at the ends of a base line having one hundred equal divisions. Let the perpendicular scales represent the concentrations involved, B and C on the left and A on the right, and the baseline scale, as measured from the left end, equal the percentage of the final mixture consisting of the stronger constituent.

To use this chart, draw a horizontal straight line at the elevation above the base line representing the desired concentration, C. Connect another straight line from the point representing the weaker concentration B, on the left scale with the point representing the stronger concentration, A, on the right scale. The horizontal distance, as measured on the base line, from the left perpendicular to the point of intersection of these two lines gives the percentage (100 ×) of the final mixture made up of the stronger constituent.

A simple geometric consideration of the similar triangles involved in the above construction establishes the validity of this method.

A similar chart may be made for the mixture of liquids of different gravities, A and B, to obtain a desired gravity, C. The units on the base line in such a chart will represent volume per cent. Obviously such a chart cannot be used for mixtures of liquids such as alcohol and water, in which there is an over-all volume change, without the introduction of a correction factor.

Received April 7, 1934.

MARKET REPORT—JULY, 1934

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, JULY 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.	.38
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.07
Adipic	lb.	.72
Furoic, tech., drums	lb.	.35
Linoleic	lb.	.16
Naphthenic, drums	lb.	.12
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.	.65
Calcium furoate, tech., drums	lb.	.25
Capryl alcohol, tech.	lb.	.85
Pure	lb.	2.50
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
Diglycol oleate, drums	lb.	.18
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
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.	.35
Glyceryl phthalate	lb.	.28
Glycol phthalate, drums	lb.	.28
Glycol stearate	lb.	.20
Isopropyl ether, drums	lb.	.07
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
Phloroglucinol, tech., drums	lb.	15.00
C. P.	lb.	20.00
Phosphorus oxychloride, 175 cyl.	lb.	.20
Potassium abietate	lb.	.06
Pyrocatechin, C. P., drums	lb.	2.75
Sodium abietate	lb.	.06
Sodium alginate	lb.	.64
Sodium naphthenate, drums	lb.	.13
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 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.	2.66
56%, c/l., bbls.	100 lbs.	5.50
Glacial, c/l., bbls.	100 lbs.	9.13
Glacial, U. S. P., c/l., carboys	100 lbs.	9.63
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.	.60
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.	1.55
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls., c/l.	lb.	.09
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.	1.35
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	4.485
Amyl, from pentane, tanks	lb.	.143
Amyl, tertiary, tech., tanks, del.	lb.	.052
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
Amylene, tanks, wks.	lb.	.09
Amyl acetate, tech., from pentane, tanks, delivered	lb.	.135
Amyl chlorides, mixed, tanks, wks.	lb.	.10½
Amyl chloride, normal, drums, wks.	lb.	.56
Amyl lactate, drums, wks.	lb.	.50
Amyl mercaptan, drums, wks.	lb.	1.10
Amyl stearate, drums, wks.	lb.	.31
Aniline oil, drums	lb.	.16½
Anthracene, 80–85%, casks, wks.	lb.	.75
Anthraquinone, subl., bbls.	lb.	.45
Antimony, metal	lb.	.08⅝
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.	.07
Arsenic, metal, kegs	lb.	.44
Red, kegs, cases	lb.	.15
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.	.19
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.	1.20
Bismuth, nitrate, 25-lb. jars	lb.	1.20
Oxychloride, boxes	lb.	3.05
Subnitrate, U. S. P., 25-lb. jars	lb.	1.55
Blanc fixe, dry, bbls.	ton	65.00
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
Butyl carbinol, nor., drums, wks.	lb.	.60
Butyl carbinol, sec., wks.	lb.	.60
Butyl carbinol, iso, tanks, wks.	lb.	.326
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.	2.50
Arsenate, bbls.	lb.	.05
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.	.51
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.	27.00
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec.	100 lbs.	9.00
Copper carbonate, bbls., 52/54%	lb.	.15½
Chloride, bbls.	lb.	.17
Cyanide, drums	lb.	.37
Oxide, red, bbls.	lb.	.15
Sulfate, c/l., bbls.	100 lbs.	3.85
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls.	lb.	.19¼
Cyanamide, bulk, N. Y.	Ammonia unit	1.07½
Diaminophenol, kegs	lb.	3.80
Diamylamine, drums, wks.	lb.	1.00
Diamylene, tanks, wks.	lb.	.08½
Diamyl sulfide, drums, wks.	lb.	1.10
Dianisidine, bbls.	lb.	2.35
Dibutylphthalate, drums, wks.	lb.	.20½
Dichloropentanes, tanks, wks.	lb.	.02½
Diethylaniline, drums	lb.	.52
Diethylene glycol, drums	lb	.14
Diethyl carbinol, drums, wks.	lb	.60
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.29
Dimethyl ethyl carbinol, drums, wks.	lb.	.60
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	6.50
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.	.13½
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.	3.80
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls.	lb.	.08
Oxide, litharge, bbls., 20-ton lots	lb.	.05½
Peroxide, drums	lb.	.20
Red, bbls., 20-ton lots	lb.	.0655
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	60.00
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	75.00
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.	.55½
Methyl chloride, cylinders	lb.	.45
Methyl propyl carbinol, drums, wks.	lb.	.60
Methyl salicylate, cases	lb.	.42
Michler's ketone, bbls.	lb.	2.50
Monoamylamine, drums, wks.	lb.	1.00
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.	.09
Coconut, tanks	lb.	.02⅝
Cod, N. F., bbls.	gal.	.48
Corn, crude, tanks, mills	lb.	.04⅝
Cottonseed, crude, tanks	lb.	.04½
Linseed, bbls.	lb.	.103
Menhaden, crude, tanks	gal.	.20
Neat's-foot, pure, bbls.	lb.	.12
Oleo, No. 1, bbls.	lb.	.06
Olive oil, denat., bbls.	gal.	.86
Foots, bbls.	lb.	.07⅛
Palm, Lagos, casks	lb.	.03⅞
Peanut, crude, tanks	lb.	.05⅛
Perilla, bbls.	lb.	.09¾
Rapeseed, bbls.	gal.	.38
Red, bbls.	lb.	.06⅞
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-tertiary amyl phenol, drums, wks.	lb.	.50
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.	.08½
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	25.00‡
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.	.75
Rochelle salt, bbls., U. S. P.	lb.	.14½
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.	.33⅜
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.	.05
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
Nahpthionate, 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, disodium, bags	100 lbs.	1.90
Phosphate, trisodium, bbls.	100 lbs.	2.70
Picramate, kegs	lb.	.67
Prussiate, bbls.	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.80
Silicofluoride, bbls.	lb.	.05
Stannate, drums	lb.	.33½
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.	.83
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.	.25
Oxide, bbls.	lb.	.56
Titanium dioxide, bbls., wks.	lb.	.17¼
Toluene, tanks	gal.	.30
Triamylamine, drums, wks.	lb.	1.00
Triamyl borate, drums, wks.	lb.	.40
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.	4.30
Zinc ammonium chloride, bbls.	lb.	.05
Chloride, granulated, drums	lb.	.05¾
Oxide, Amer., bbls.	lb.	.06¾
Stearate, bbls.	lb.	.18
Zinc dust, bbls., c/l.	lb.	.0630

† This is the approximate F. O. B. shipping point price. Quotations are now all on a delivered basis and vary with the section.

* F. O. B. destination.

‡ Less certain discounts depending upon time of purchase and delivery.

DU PONT SODIUM CYANIDE SERVES CHEMICAL AND METAL INDUSTRIES

Important Chemical in Organic Processes

DU PONT Sodium Cyanide has properties ideally suited for chemical operations which involve reactions of the cyanogen (CN) radical. It is readily soluble in water and alkaline solutions. It reacts with many soluble salts to form other cyanides. It can be handled with ease, and without danger, when proper precautions are followed.

Large scale manufacturing operations in which Sodium Cyanide is now employed include the manufacture of organic cyanogen derivatives, dyestuff intermediates, rubber accelerators, sulfocyanides, metal cyanides and double cyanides.

Technical Literature on the Applications of du Pont Sodium Cyanide

WIDELY USED IN METAL INDUSTRIES

The importance of Sodium Cyanide in metal industries has long been recognized. Here it is widely used in combination with metal cyanides as the principal ingredient of many plating baths; for cleaning metal surfaces preparatory to plating; for making up and replenishing molten Cyanide baths for case hardening, nitriding, reheating, and mottling steel parts; and for extracting gold and silver from their ores.

POPULAR FOR INDUSTRIAL FUMIGATION

An important practice in producing clean food products is the control of insect infestation in stored products and processing plants. One of the most effective and economical ways of controlling such infestations is to fumigate with hydrocyanic acid gas generated from du Pont Sodium Cyanide.

•

"Cyanegg" is the registered trade mark name of du Pont for its Sodium Cyanide, minimum 96%, molded in the form of eggs weighing approximately 1 ounce each. This form is highly popular because of its convenience in making up plating solutions, heat treating baths, fumigation charges, and for general use.

PROPERTIES OF SODIUM CYANIDE

Formula	NaCn
Molecular Weight	49.01
Form	White, solid
Specific Gravity: 25° C.	1.50
850° C.	1.19
Melting Point	560° C.
Boiling Point	1500° C.
Solubility in 100 g. Water: 0° C.	43.4 g.
20° C.	58.3 g.
34.7° C.	82.7 g.

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TECHNICAL COOPERATION

We shall be glad to cooperate with you on any application of du Pont Sodium Cyanide which you may be considering. Special service groups are maintained to assist in steel treating, plating, fumigation work and organic synthesis. Please advise us of your interests.

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THE "R. & H." CHEMICALS DEPT.
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- ☐ Steel Treating
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  "Duozinc"
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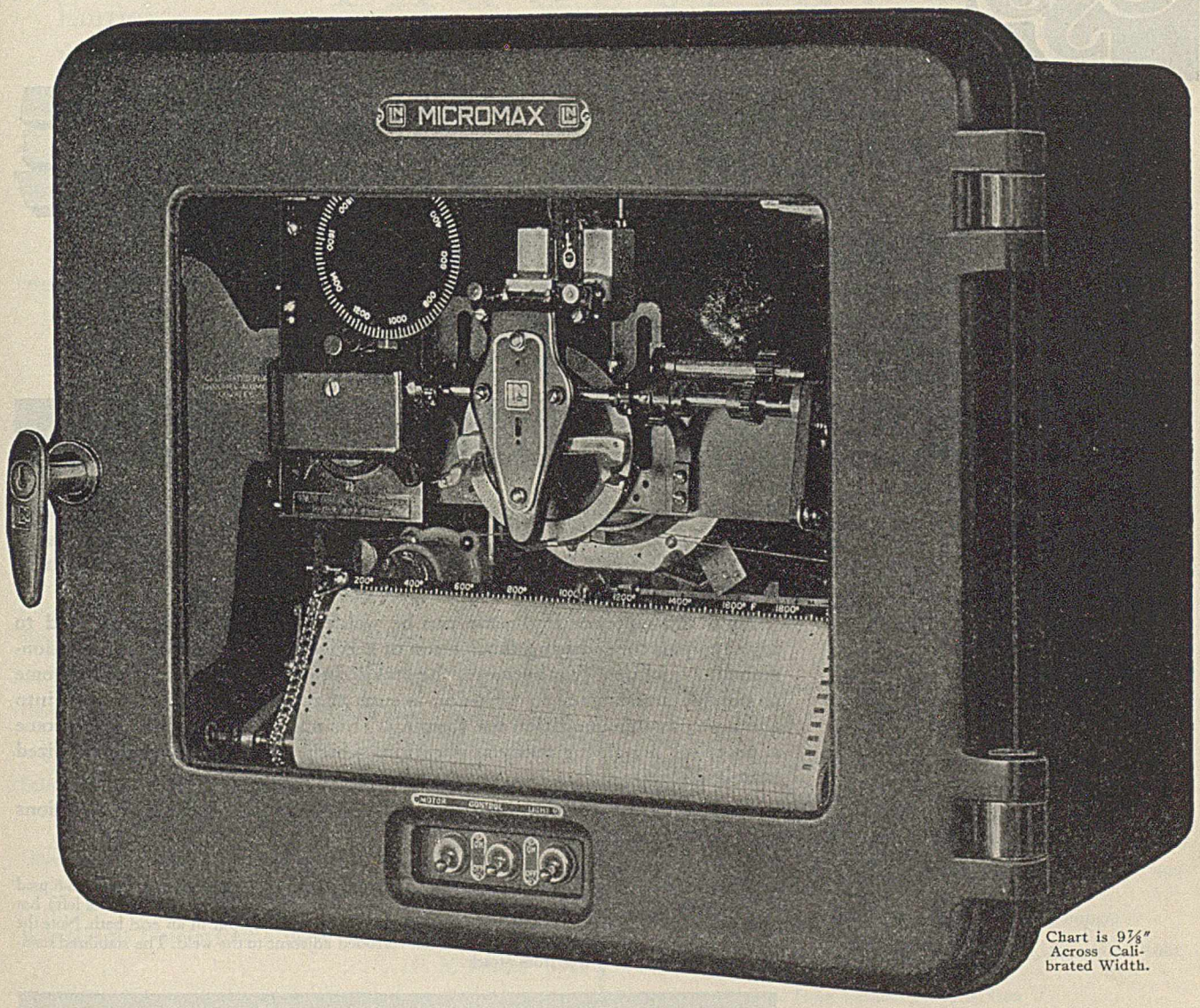

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