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HARRISON E. HOWE, EDITOR

The Editor's Page

POTASH AND A SHORT MEMORY. It was but relatively few years ago when we were wringing our hands over the scarcity of potassium-bearing compounds and when the price of potash soared to $600 per ton. Over $50,000 of private and public funds were expended in attempts to develop an adequate domestic supply of potash. Many of the 128 plants that came into operation extracted potash from wood ashes, some worked on cement dust, some on the by-products of distilleries, and there were sundry other sources. All that was in the time of the World War. When it was possible to resume importing, all of these wartime enterprises folded up, with the exception of the remarkable plant at Trona, which has ever since continued to utilize the salt deposits of dry Searles Lake and has become an expanding chemical industry.

Until about 1925, when potash-bearing minerals were discovered in New Mexico, we could only lament that Nature had seen fit to bless Europe with all the deposits of usable potash, just as she had presented to Chile the monopoly in nitrate. Since that time a substantial sum of private capital and federal appropriations has been expended in prospecting for potash-bearing salts in southwestern United States. The activities in New Mexico and in California have led to the development of capacity that fully meets our domestic requirements of those grades of potash most needed in this country. Senator Hatch, in discussing this matter before the Senate, reported that two mines are now working the Sylvinite which lies approximately 1000 feet deep and a refinery in connection with one of them has an annual capacity of 140,000 tons of potassium chloride. The investment in the potash industry in New Mexico now exceeds $4,000,000, while the American Potash and Chemical Corporation is reported to have invested nearly $15,000,000 in plant, equipment, and other property at Trona, Calif. The industry as a whole employs something more than 1200 men. Starting from nothing at the time of the World War through scientific research, exploration, and great enterprise, resources have been found through which the United States can be independent of the world as regards compounds of potassium.

Potash is duty-free. Those who pay miners per 8-hour shift $5.85 in New Mexico must compete with miners at $2 a day in Germany, $1.33 per day in French Alsace, $1.05 in Spain, and nominal sums in addition to food, shelter, and clothing in Soviet Russia.

The Soviet Union is the newest entrant into world potash markets. It is claimed that the world's greatest deposits are to be found near the Ural Mountains and that by 1935 production from these sources will approach 3,000,000 tons annually, whereas the world market requires at present about 1,330,000 tons of potash. The agricultural program in the Soviet could easily use the output of their potash mines, but the necessity of building favorable trade balances abroad in order that equipment and certain raw materials may be imported has already led to the exportation of Soviet potash. This is offered in some cases below current prices for the sake of obtaining business. Spanish potash has also been imported into the United States. Material from both these sources is reported to have circumvented all codes of fair practice.

It can easily be seen that our domestic industry faces difficulty. We have higher wage scales and higher transportation costs here, as compared with low wages and favorable water rates from other countries to eastern and southeastern seaports plus a willingness to sell for just about what the potash will bring. It is greatly to the credit of the American producers that they have made such headway without tariff protection or subsidy and without inordinately high prices. But it is by no means sure that they can continue, in the face of new and determined competition, without some sort of protection or assurance. The United States did not fare particularly well when at the mercy of a monopoly, which continued under a joint marketing agreement into which Germany and France entered after the war. We should have learned a few years ago at the expense of considerable effort, money, and anxiety that there are conditions under which dependence on foreign sources is far from satisfactory. Steps necessary to maintain our potash industry as an active and progressive unit of our economy should be taken without delay and with firmness.

PATENT TRAINING. As operated at the present time, the United States Patent Office resembles a school in which chemists and engineers might be trained to practice the specialty of patent law. Young graduates from technical schools enter as examiners, and usually as soon as some skill has been demonstrated and experience has been gained there is a demand for their services elsewhere. In the majority of such cases, unless there is some other reason for their remaining, they leave the Patent Office, taking with them their experience, and to the aggravation of the patentee he may find relatively inexperienced individuals in charge of his application when he comes again to headquarters.

Patent Office training is, in a considerable measure, a valuable type of service to industry, and most useful in its development. Nevertheless, this frequent change of examiners, this continual process of education, is costly in several ways. In exchange for this unique opportunity for training, the patent examiner should agree, upon appointment, to remain in the service at least five years. During the first part of that period he would receive more in experience than he could return in service; during the latter part the account would become balanced, because of his ability to give in service more than he was receiving in experience. This is not possible where the tenure of office is brief. The junior examiners who, through the Civil Service Commission, have been seeking reallocation to a group with a higher status deserve to succeed in their endeavor; but should they not be willing, in exchange for the promotion, to remain two or three years longer in the service?

As for the enforcement of his contract, the Government could refrain from registering any of those who resign before carrying out their agreements. Such an offender should not be registered later for any reason and while he might work in patent law he could not practice before the office. The United States Patent system, with all its faults and the objections to it, has nevertheless played a vital part in the industrial development of the United States. Such a minor change as is suggested here would tend toward its betterment.

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THE GROUP PLAN for local section meetings, initiated by the Chicago Section, is well known but has not been as widely tried as it should be. This year the Detroit Section experimented with it and found it good.

The group meeting plan makes possible simultaneous provision for a considerable diversity of activity. A given speaker, no matter how renowned, is not likely to interest deeply more than a small percentage of his audience, unless his discussion is in terms so general that his colleagues in the specialty find the address devoid of much that is new. The group plan, however, does not eliminate a principal speaker whom people wish to hear on his own account, though they may not be very familiar with his specialty. Such an address is given to the entire meeting immediately after the dinner or early in the evening. After that the audience breaks up into prearranged sections according to interests and each of these groups has its own program, which is usually confined to one or two topics so that there will be ample opportunity for discussion. These group meetings are often followed by a general social hour.

It is a plan we should like to see more universally adopted for the good of the individuals, the local sections, and the AMERICAN CHEMICAL SOCIETY. There is no difficulty so far as the machinery and procedure are concerned. It is largely a question of careful planning and enthusiastic leadership. We recommend its trial by other local sections next season.

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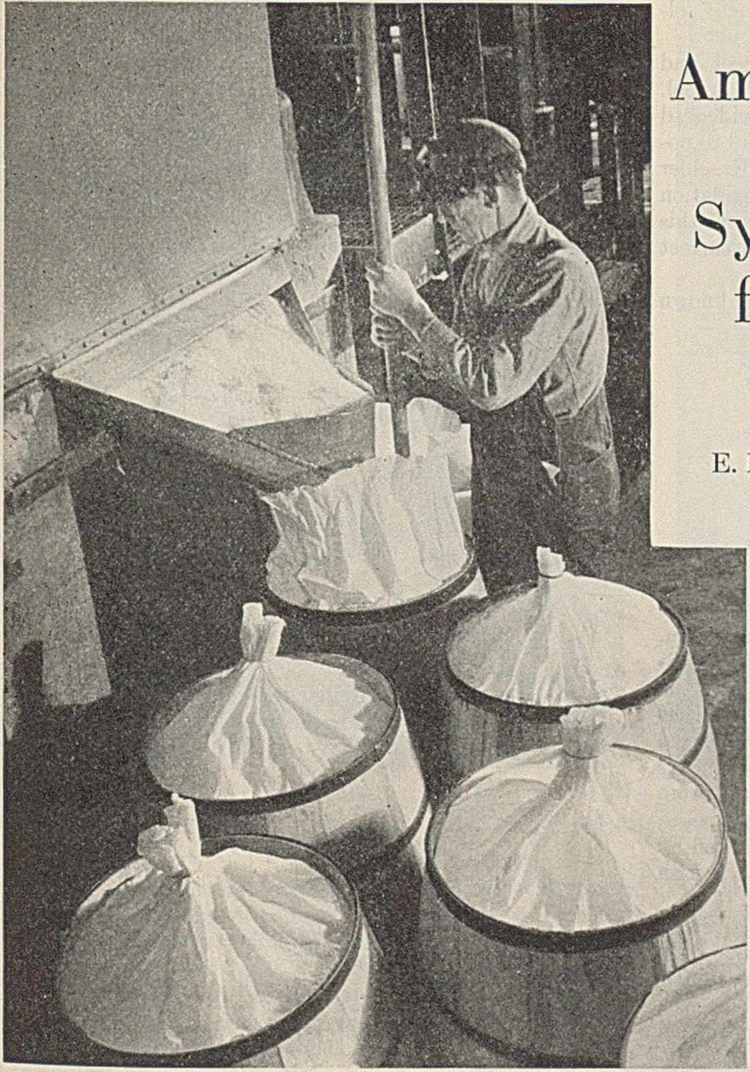
RADIO LIBRARY. At Buffalo the Council of the AMERICAN CHEMICAL SOCIETY authorized a committee to investigate radio possibilities. It concluded that, pending an opportunity for broadcasting over national chains, a real service could be rendered by using the facilities of local stations.

The committee had much to guide it in the experience of several successful local sections. Perhaps the earliest to undertake broadcasting seriously was the New York Section. The Chicago Section has been successfully broadcasting, while the most sustained program is that of the Northeastern Section where a program has become a weekly feature. More than 125 talks have been given and the *Boston Evening Transcript* regularly prints these addresses. The Virginia Section has been active, and individual chemists in Georgia, Ohio, Pennsylvania, and Washington, D. C., as well as other points, have done their best to present an interpretation of chemistry in a popular style.

Nearly every radio station has free time for suitable educational features. We urge our local sections to investigate such possibilities and, realizing that those who have not had experience may think it difficult to prepare an acceptable program, INDUSTRIAL AND ENGINEERING CHEMISTRY proposes to build up a library of successful radio talks. These will be available to those who can use the material advantageously. The Northeastern, Virginia, and Chicago Sections have already placed on file transcripts of addresses. Others are requested.

It is not expected that all those who have an opportunity to broadcast will necessarily use this material, but it is available to serve as guides or actually to be used with proper credit. Notwithstanding all of the publicity that has been given science, it is quite necessary to continue and sustain the effort. It is with such service in mind that this office cheerfully undertakes the additional labor involved.



VIEW IN SYNTHETIC CAMPHOR PLANT, DEEPWATER POINT, N. J.

American Production of Synthetic Camphor from Turpentine

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The history of the production of natural camphor is briefly mentioned, and the reasons for the production of a synthetic material are developed. The determination of the structure of the camphor molecule and the methods for synthesizing the product are described.

Commercial production in America and its relation to the turpentine industry are reviewed. The effect of low-priced, imported material on domestic production is stated, and an opinion offered on the conditions under which manufacture can be continued.

IN ANTIQUITY the scene was laid for one of the modern romances of chemistry. In 1421 the Chinese, visiting the beautiful island of Formosa (*9*), found among the numerous articles that attracted them a substance with which the natives were familiar and which had a fresh and pleasant odor. In the interior of that country of mountains there are wonderful stretches of virgin forest with gigantic tree ferns. In these virgin forests grow stately camphor trees, filling the air with their balmy scent that can be smelled for miles around.

Man the world over is attracted by beautiful crystals, pleasant odors, and gleaming white products. It was a delight to the aborigines of Formosa to produce such a substance by chopping these magnificent trees into thin pieces, putting them through a simple distillation process, and separating the camphor from the oil. Then a refinement was accomplished by taking advantage of one of the physical properties to sublime the pure material from the crude and to produce the pure crystalline product that could be pressed into small cakes and serve as symbols of pagan belief and amulets to insure health. The Chinese prized it highly, and traders from the Near East and Europe procured it and carried it home as evidence of the attractiveness of the Orient. It was first used in India and then in Egypt. It was employed in Turkey by the end of the fourteenth century for medicinal purposes, and similarly by the Arabs as early as the eleventh century.

Although visited by the Dutch and Spaniards, Formosa remained in the hands of the Chinese until 1895, when, as the result of the Sino-Japanese war, it was ceded to Japan. Since then, owing to the unremitting and intelligent efforts of the Japanese, Formosa has prospered as never before and has now gained for itself a world market in many commodities, principal among which are tea and camphor. In 1933 the value of camphor and its by-products amounted to 10,000,000 yen.

DETERMINATION OF CAMPHOR STRUCTURE

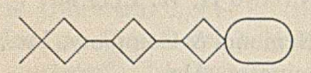
During the nineteenth century the structure of camphor occasioned much curiosity on the part of chemists. Modern man has never been content to be restricted by nature and the obvious desirable properties of camphor gave the incentive to scientists to work out the secret of its structure and to build it up from more available substances by synthetic processes.

Dumas in 1832 established the molecular formula as being $C_{10}H_{16}O$. It was early noted (*3*) that, by dehydration with phosphorous pentoxide, camphor was converted into *p*-cymene, while by treatment with iodine, carvacrol (2-hydroxy-*p*-cymene) was formed. These results clearly pointed to a benzene skeleton.

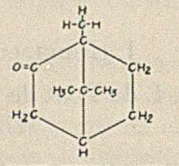
Rosengarten in 1785 oxidized camphor with nitric acid and obtained camphoric acid, a compound which has played an important part in the final determination of the structure of camphor. Various derivatives and reaction products followed.

In 1838 Martius announced the existence of borneol, and in 1843 Gerhardt made camphor by oxidation of borneol. Weyl in 1868 showed camphor to be a ketone, as evidenced from the formation of derivatives such as an oxime, a bromophenylhydrazone, and a semi-carbazone. In 1871 Krachler found a second acid, camphoronic, among the oxidation products, and it was the elucidation of the structure of this acid by Bredt in 1893 which led ultimately to the correct interpretation of the structure of camphor.

Camphor structures, as thought to be in 1690 and as known to be in 1893, follow:



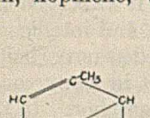
ALCHEMISTIC FORMULA-1690



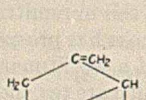
BREDT FORMULA-1893

The year 1893 was in the midst of one of the most remarkable periods of chemical developments the world has known. German chemists, as well as some others, undertook the problem of duplicating camphor. Curiously enough, although the practical goal has been attained, the natural product has never been exactly duplicated since it has the physical property of optical rotation whereas the synthetic product is practically inactive. This difference detracts not at all from the synthetic product since it can be used for all purposes, including medical, with equally good results, as indicated by the fact that it is included in the German and the British Pharmacopeias.

The cue to the successful synthesis of camphor was given by the fact that it was possible to obtain some camphor from borneol and it was also known that borneol, as well as similar substances, could be derived from turpentine. The constituent of turpentine of real importance was pinene (*4*). The pinenes are the main constituents of the various turpentine oils which are obtained by steam distillation of pine stumps or the resinous exudations of various coniferous trees. α-Pinene is by far the most widely distributed of all the natural terpenes; in addition, turpentine contains an isomeric beta form, nopinene, which occurs in much smaller quantities:



ALPHA-PINENE



BETA-PINENE

The pinene contents of gum and wood turpentine, respectively, are as follows:

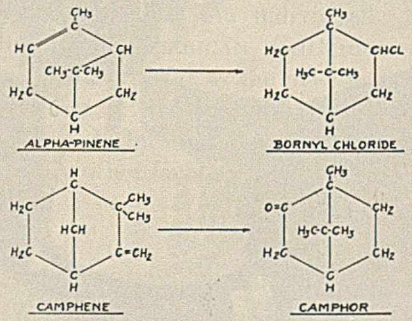
	Gum Turpentine	Wood Turpentine
	%	%
α-Pinene	74	77
β-Pinene	18	..
High-boiling terpenes	8	8
Dipentene	..	15

Both α- and β-pinene are useful in the manufacture of camphor, and it is evident, therefore, that the effective portion of gum turpentine is 92 per cent whereas only 77 per cent of the wood turpentine is of direct value. The use of one or the other depends on economic considerations, such as original cost and credit obtained for by-products.

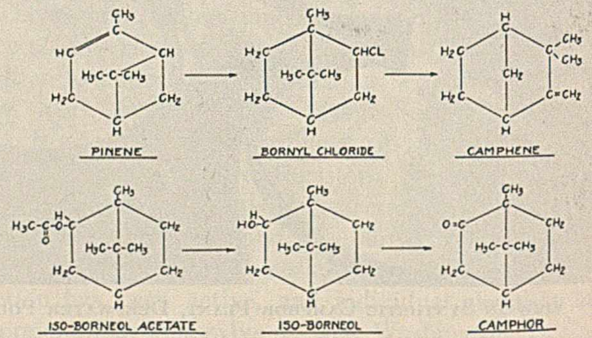
Greek turpentine contains 95 per cent total pinene. The French product is next highest, and, as indicated, the American contains 92 per cent.

Methods of Synthesis

Two laboratory methods of synthesis of camphor have been employed (*6*). One starts with pinene and goes to bornyl chloride and camphene, and the latter is directly oxidized to camphor:



The other is the same through the camphene step but then converts the camphene to borneol or isoborneol and oxidizes these to camphor:



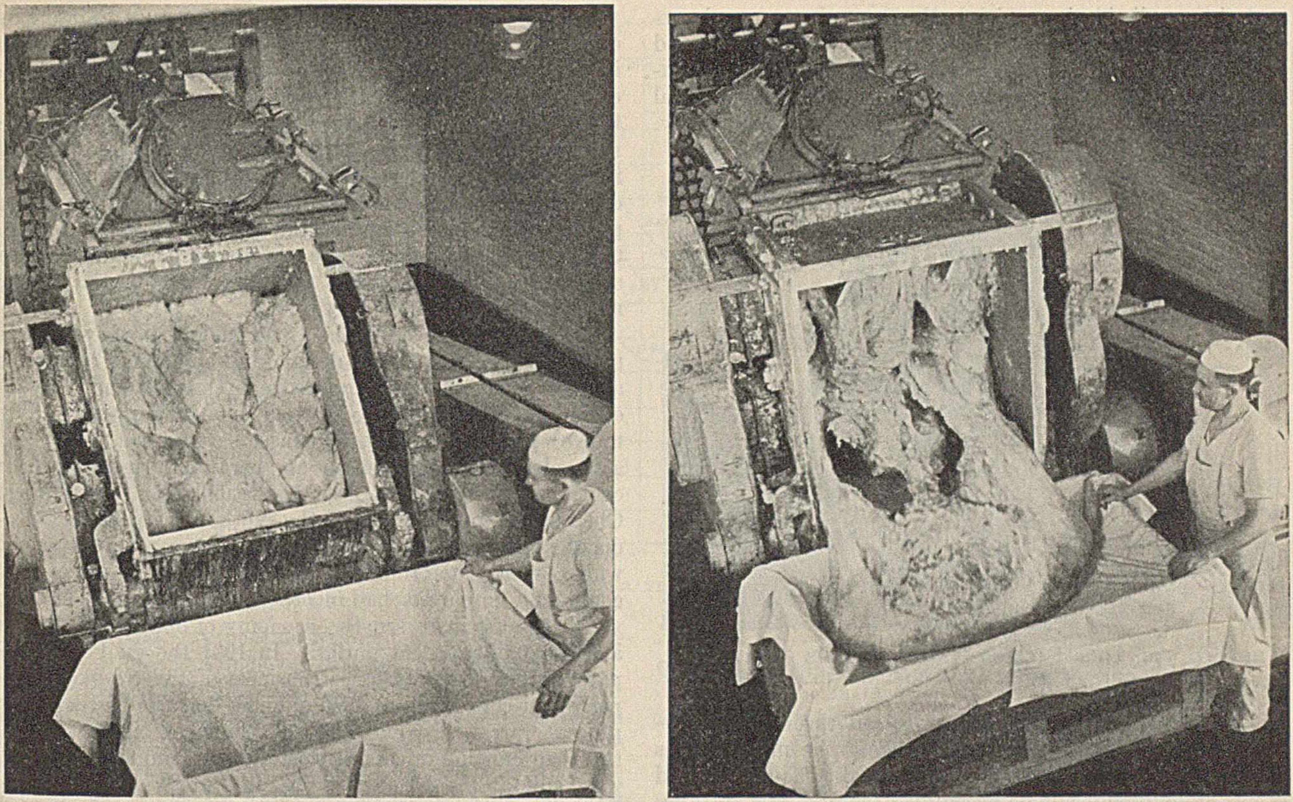
Simple though these syntheses appear, it was one thing to prepare small quantities of camphor in the laboratory and quite another to manufacture it economically. Early in the twentieth century the Germans had reached the point of manufacturing at a price which could then compete with the natural product, as had several smaller concerns in France, Switzerland, and Italy. These commercial processes involved the second procedure just mentioned and the now commonly accepted general practice of starting with turpentine, fractionating to obtain pure pinene, saturating with hydrogen chloride to form bornyl chloride, hydrolyzing to form camphene, esterifying, saponifying to form isoborneol, and oxidizing to camphor.

Table I. Importations of Camphor to the United States (*2*)

(In pounds)

Year	Synthetic	Natural Crude	U. S. P. Natural Refined	Total
1926	2,944,478	2,018,971	1,169,779	6,133,228
1927	2,933,784	1,689,714	1,480,851	6,104,349
1928	2,264,916	4,364,661	1,176,047	7,805,624
1929	3,957,282	4,203,795	1,431,438	9,592,515
1930	2,393,691	1,058,393	1,031,584	4,483,668
1931	1,828,091	1,963,796	1,161,876	4,953,763
1932	1,459,674	1,799,201	1,034,059	4,292,934
1933[a]	267,508	996,694	945,201	2,209,403

[a] Up to and including July, 1933.



Dough mixer

Dumping the dough

Pyroxylin Mixing Operation

Utilizing this general method, the Europeans improved their working conditions and were able gradually to replace a portion of the natural product until in 1931 it is estimated they produced 12,000,000 pounds. Substantial quantities were exported to the United States as shown by Table I. During the 7-year period, 1926 to 1932, inclusive, the total camphor imports averaged about 5,000,000 pounds annually.

Commercial Production in America

The earliest attempt to produce synthetic camphor in the United States was in 1900 when, according to Brooks (*5*), the Thurlow process was operated at Niagara Falls. No accurate detailed account is available in regard to this venture.

It is certain that consideration has been given by various other manufacturers to the production of synthetic camphor, and undoubtedly considerable sums of money have been spent in the development of processes and plant lay-outs. However, prior to 1918 no extensive development took place. It is estimated that the amount expended by various companies for research, development, plant, and information is probably in excess of $3,000,000, not including the cost of facilities now employed in manufacturing operations.

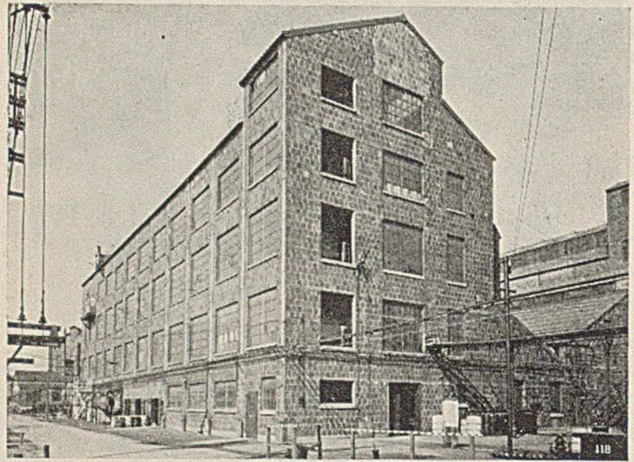
The large domestic supply of turpentine, the growing consumption of camphor in the United States, and its high prices, coupled with the absence of any domestic producer which constituted a formidable and continuing threat to the fabrication of products in which camphor is an essential ingredient, led the du Pont Company into the manufacture of synthetic camphor. In 1918 operations were started and encouragement was lent by the fact that the prices in 1918 to 1920 increased from $0.40 to $1.36 per pound.

The process used at that time followed closely the one described by F. Ullmann (*10*): Turpentine was distilled to yield a substantially pure pinene. This was placed in large, agitated, horizontal iron vessels and treated with dry hydrogen chloride. Great care was necessary in the drying of both materials. Cooling was maintained by means of a jacket. The formation of solid bornyl chloride thickened the reaction mixture and introduced difficulties due to insufficient agitation and cooling. Much trouble was encountered in the generation and handling of the hydrogen chloride. At first the whole mixture was saponified to form camphene, but this procedure was found to be objectionable and later it was the practice to centrifuge the reaction mixture and wash the chloride with benzene.

The conversion of bornyl chloride to camphene was carried out by adding it to a mixture of cresol and sodium hydroxide, from which all water had been removed by distillation. The camphene was separated and given a distillation to remove terpene oils. This step of the process caused great difficulty because of plugging of the condenser and because the design of the still did not permit complete separation of the impurities. It was essential to recover cresol for re-use in subsequent runs.

The next step in the process involved treating the camphene with glacial acetic acid to convert it to isobornyl acetate. The reaction mixture was treated with water and the isobornyl acetate mechanically separated. It was then saponified to isoborneol by treatment with alcoholic sodium hydroxide. Again, it was necessary efficiently to recover both alcohol and sodium acetate. By drowning the saponification mixture, the isoborneol was obtained as a solid product and was then purified by a sweating process in agitated tanks.

The final chemical step of the process was carried out by adding the isoborneol to a mixture of nitric and sulfuric acids in a regulation type nitrator. The temperature had to be carefully controlled, and nitrous gases were evolved. When the oxidation was complete, the mixture was drowned in ice water. The solid material was dissolved in benzene and given a distillation which both removed water and partially purified the camphor. Great difficulty was encountered in obtaining a high quality such as was required in the manufacture of Pyralin. It was attempted to purify the material by sublimation, but this was both ineffective and costly.



The Size of This Factory Indicates the Commercial Scale of Synthetic Camphor Manufacture

Subsequently, the impure product was put through a thirty-plate fractionating column. While all of the material was used in Pyralin, it was not of as high quality as desired and would undoubtedly not be acceptable today. The costs by this process were high, owing partly to turpentine which at that time sold for $1.50 per gallon but also to the many operating difficulties, some of which would no doubt have been overcome in time.

The fact that the war was then over, together with the availability of limited supplies of the synthetic product which it was reasonable to expect would be increased if prices continued high, caused the Japanese to revise their selling prices. Table II shows the price fluctuation of camphor over a period of years.

Table II. Range of Camphor Price per Pound, Exclusive of Duty

Year	Natural Crude	Natural Refined and Synthetic[a]	Natural Refined	Synthetic
1918	$0.40	$0.685	...	...
1919	0.93	1.800	...	...
1920	1.36	1.960	...	...
1921	0.59	0.77	...	...
1922	0.63	0.70	...	...
1923	0.64	0.72	...	...
1924	0.53	0.62	...	...
1925	0.55	...	$0.60	$0.50
1926	0.58	...	0.65	0.53
1927	0.48	...	0.555	0.43
1928	0.3775	...	0.5075	0.3575
1929	0.375	...	0.555	0.345
1930	0.3975	...	0.535	0.355
1931	0.355	...	0.475	0.325
1932	0.285	...	0.345	0.2775
1933	0.216	...	0.3005	0.2454

[a] Grouped together by Department of Commerce until 1925.

To understand why the price of Japanese camphor can be adjusted over such wide ranges, we look to Formosa for the answer. In 1904 the Japanese Government made the manufacture of natural camphor a monopoly. Prices were steadily increased and this brought about the incentive for European firms to manufacture the synthetic product. Since 1905, when the first attempt was made to employ synthetic camphor, there has been a continuous battling of forces to determine whether natural camphor through Japanese control and monopoly or the synthetic product should triumph. As the latter became more available and cheaper, the Japanese price dropped, always by the necessary amount to insure its dominant position. Cheap Formosan and Japanese labor, with its low standard of living, is the explanation of how the price of camphor could be and is being dropped to any necessary figure to compete with the synthetic product. As it became necessary, the price per pound of camphor was lowered until it eventually became set at one yen (formerly 50 cents based on our gold standard currency). While it might have been possible to compete with natural camphor at $1.00 a pound, using our original process, it became impossible at $0.50. The original du Pont effort was therefore abandoned as holding no promise of becoming profitable.

Since 1920 there has been a tremendous improvement in materials of construction, design, and building of equipment and also in the skill and knowledge of chemists and chemical engineers. Operations are carried out comparatively easily today which ten or fifteen years ago would not have been attempted. For these reasons and because the use of camphor continued to expand, it seemed justifiable to the Newport Chemical Company to study the synthesis of camphor. Under the direction of Ivan Gubelmann a process was developed which, while conforming in general to the broad method commonly employed, had incorporated in it various features which greatly increased the economy of operation and gave a product of excellent purity. In 1931 the du Pont Company purchased the chemical business of the Newport Company and concurred in their opinion that the new camphor process warranted commercial development on the basis of the then existing prices of turpentine and camphor. A plant was built at the Deepwater, N. J., Dye Works having an annual capacity of 1,500,000 pounds.

In developing the present process, a great deal of attention was given to the simplicity of operations. American conditions require the amount of labor to be kept at a minimum. Equipment had to be designed which would have a long life, thus assuring low repair costs, and which would also make possible the direct and economic handling of materials. By this process an exceptionally high grade of camphor is produced. The plant has been in operation since the fall of 1932, and capacity production and goal yields are being realized currently.

Outlook for Domestic Manufacture of Camphor

Fundamentally, domestic production of synthetic camphor is on a sound basis compared to other countries. Our southern states count their turpentine and rosin industry as a major asset. The group comprising principally Alabama, Florida, Georgia, Mississippi, North Carolina, South Carolina, Louisiana, and Texas produced large quantities of turpentine in 1899–1932, as shown in Table III.

Table III. U. S. Production of Turpentine (*8*)
(In gallons)

Year	Total	Distilled from Crude Gum	Distilled from Wood
1931–32	27,499,514	24,349,024	3,150,490
1929–30	35,940,124	31,320,871	4,619,253
1927–28	35,882,258	31,549,082	4,333,176
1925–26	27,261,425	23,922,250	3,339,175
1924–25	29,333,450	26,072,200	3,261,250
1923–24	29,781,944	27,174,580	2,607,364
1922–23	24,252,835	22,394,137	1,858,698
1921–22	24,820,620	24,378,854	441,766
1920–21	26,200,000	24,450,000	1,750,000
1919	19,228,174	17,693,841	1,534,333
1918–19	18,650,000	17,050,000	1,600,000
1917–18	24,900,000	23,700,000	1,200,000
1914	27,648,939[a]	26,980,981	575,557
1909	29,714,132[b]	28,988,954	706,868
1904	31,129,236	30,687,051	442,185
1899	37,733,500	37,733,500	?

[a], [b] Totals include 92,401 and 18,310 gallons, respectively, of turpentine produced in manufacture of lumber and timber products.

Data relative to the number of the concerns, wage earners, wages, value of the products as well as the materials made from turpentine and rosin are shown in Table IV.

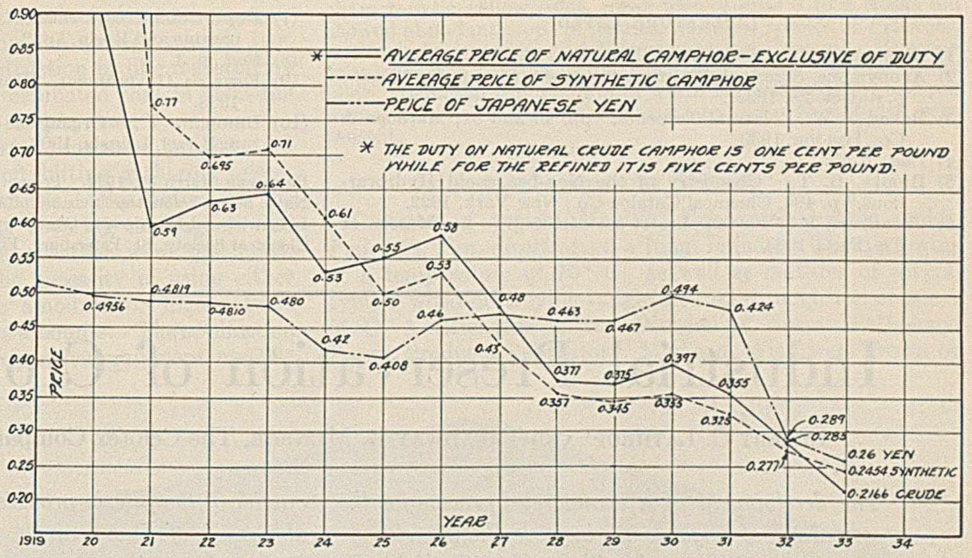


Figure 1. Comparative Data on Natural and Synthetic Camphor

According to a previous article (*1*) the number of operations in Florida is now 325 and 20,000 people are employed, producing material worth $11,000,000 annually. It is evident, therefore, that large amounts of capital are invested in this industry, many workers derive their livelihood from it, and much wealth results from it. The part which camphor might play in this picture is of interest. Based on the data available, it is not unreasonable to suppose that present outlets might, on the average, consume 6,000,000 pounds of camphor annually. On this basis the following data are derived: turpentine required, 9,600,000 pounds or 1,370,000 gallons; value of the turpentine, $750,000.

While these figures may seem small compared to the labor charges, tonnage, and values pertaining to the turpentine and rosin industry, they nevertheless represent a reasonable amount for a single outlet. It should also be noted that the development of plastics which employ camphor has not been fully exploited. Besides present uses which include toiletware novelties, sheeting, etc., there is the rapidly expanding use in safety glass. Many automobiles are completely furnished with shatter-proof glass which contains a sheet of Pyralin between two glass plates. This outlet is large and is being rapidly expanded. Such glass is already being used in railway coaches and, with the development of the modern high-speed trains, will no doubt become even more universally employed.

Even with expanded outlets for camphor the ability to continue manufacturing depends on being able successfully to meet competition from the natural product. Japanese imports are very small compared with total consumption and consequently increasing prices have comparatively little effect on the cost of living in that country. It is obvious, therefore, that depreciation of the yen will have very little effect on their domestic prices. A study of prices quoted for Japanese exported products indicates that their policy is to quote just under prices quoted for competitive lines and their domestic situation makes this economically possible. This is the situation which must be faced by Japan's competitors.

In light of the foregoing remarks it is interesting to examine the varying prices of camphor over a period of years, together with the concurrent prices of the yen in terms of American gold standard money. Figure 1 presents these data.

It is evident that a manufacturer who decided to manufacture camphor in 1928 to 1931 felt that a selling price of 35 to 40 cents per pound was to be expected. The figures show that, by the time domestic production on a reasonable scale was an accomplished fact, the price of the natural crude had dropped to about 22 cents without duty or 23 cents with duty, at which price it was necessary to sell the American synthetic material in order to obtain business.

Present selling prices are lower than the goal costs set up for the synthetic product, and, if this situation persists, it is extremely doubtful whether domestic manufacture can survive. In the event of its demise we will again face the curtailment of a domestic outlet for substantial quantities of American turpentine, with the consequent loss to labor; at the same time we will be dependent on a foreign source of supply for an indispensable commodity.

Table IV. Statistical Data on Turpentine and Rosin Industry (*7*)

(The figures for 1919 and earlier years refer to calendar years; those for 1921 and subsequent years, to crop years ended March 31. Data for establishments with products under $5000 in value are included for 1919 and prior years but not for 1921 and subsequent years.)

Year	Establishments	Wage Earners (Av.)	Wages	Cost of Materials, Containers, Fuel, and Purchased Electric Energy	Value of Products	Value Added by Manufacture[a]
			United States			
1931–32	953	28,257	$ 7,280,389	$ 5,792,633	$16,505,745	$10,713,112
1929–30	1183	40,157	15,036,175	10,293,954	36,281,632	25,987,678
1927–28	1149	37,913	16,953,054	12,173,394	39,902,971	27,729,577
1925–26	1007	29,413	15,190,076	11,887,395	42,364,413	30,477,018
1923–24	1203	34,328	15,448,590	8,972,758	35,166,715	26,193,957
1921–22	1062	27,422	9,512,177	6,199,179	23,300,845	17,101,666
1919	1191	28,067	16,972,881	13,929,888	53,051,294	39,121,406
1914	1394	34,817	8,582,970	5,535,561	20,990,191	15,454,630
1909	1585	39,511	9,363,359	4,910,838	25,295,017	20,384,179
1904	1287	33,382	8,382,700	3,774,637	23,937,024	20,162,387
1899	1503	41,864	8,393,483	6,186,492	20,344,888	14,158,396
			States, 1931–32			
Alabama	67	1,957	$ 522,605	$ 592,022	$ 1,364,821	$ 722,799
Florida	280	10,218	2,551,998	1,826,615	5,258,466	3,431,851
Georgia	536	13,655	3,564,856	2,841,336	8,308,527	5,467,191
Mississippi	18	814	184,203	114,606	473,288	358,682
No. Carolina	3	90	28,538	21,703	78,447	56,744
So. Carolina	41	877	228,405	191,845	533,388	341,543
Louisiana and Texas	8	646	199,784	204,506	488,808	284,302

[a] Value of products less cost of materials, containers, fuel, and purchased electric energy.

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Industrial Preservation of Crop Fibers

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The development of a commercial process for the preservation of sugar cane bagasse during storage is described. This work will apply with slight obvious modifications to the industrial preservation of other crop fibers exposed to the weather. The best method consists in so piling the bales that the heat of carbohydrate fermentation is used to raise the temperature of the interior bales to that corresponding to pasteurization. The insulating qualities of the mass maintains this temperature for 2 or 3 months. The moisture content of the mass is greatly lowered, so that spores of organisms living through the heating stage may not germinate. The outside of the pile is protected from rains by a portable roof of steel panels, and also by sprinkling boric acid on the edges of the outside bales and on the tops of the top bales of the pile. The average fiber loss per annum is less than 10 per cent, being reduced more than 60 per cent.

The chemical cost is 6.4 cents per ton of dry fiber. The yearly cost of chemicals and roof is offset by savings in labor in removing the piles, owing to the time saved in handling solid rather than broken bales. The dollar savings for the first year amounted to more than five times the entire development cost.

THE industrial preservation of sugar cane bagasse fiber vital to the manufacture of Celotex insulation products will be discussed, beginning with the inception of the experimental work in 1921 and concluding with the successful commercial solution of the problems. The process, while applied specifically to the use of bagasse fiber, may be applied with modifications, generally obvious, to other crop fibers.

A considerable number of patent applications covering the processes developed have been granted, and reference is made to these for greater detail than can be given here. One of the authors has described elsewhere (*2*) in some detail the manufacturing operations and products of Celotex, so that only such details will be given in this paper as pertain to the specific problems discussed.

INDUSTRIAL REQUIREMENTS OF AND NECESSITY FOR A STORAGE PROCESS

Bagasse, the residue from cane sugar manufacture, as received from Louisiana sugar mills, consists of bundles of coarse fibers, up to several inches in length, associated with pith and rind particles. It contains about 50 per cent moisture, a small amount of unextracted sugar, some nonsugars, together with some gums, waxes, almost no nitrogen, and about 2 per cent ash. It differs from wheat and other straws, from corn stalks and similar agricultural by-products, in that the sugar cane is cut and milled before maturity and death of the plant. During the milling process practically all of the plant juices and soluble material are removed from the fiber. Perhaps for this reason the fiber has not given good results as a fertilizer when plowed under, since its rate of decay is slow. Piles of bagasse fiber 30 years old have been examined by one of the authors in Australia, and the fiber was found to be in a relatively good state of preservation. Bagasse is used in the sugar industry as fuel.

The sugar campaign in Louisiana runs from about the last of October to sometime in January, a period varying from 60 to 90 days. During this short period it is necessary to handle and store a year's supply of fiber. The operations must be so arranged that bagasse is taken from the sugar mill as fast as produced and so that there will be no interference with the operation of the sugar mill. A Louisiana sugar mill may grind from 1000 to 2000 tons of cane per 24 hours, producing from 200 to 400 tons of wet bagasse. The yearly Celotex Company requirements of dry fiber run from 80,000 to 150,000 tons (from 8000 to 15,000 carloads). The labor for this short intense storage campaign is mostly inexperienced, and, as will be shown later, decay is accelerated by faulty piling; accordingly, a type of treatment that could be handled by this type of labor was advisable.

About one-third of the bagasse secured during the grinding season is stored at the Celotex plant at Marrero, La., and the remainder at outlying sugar mills.

The importance of constantly uniform raw material in a manufacturing operation is obvious. The first year's operation (1921–22) showed the manufacturing difficulties caused by changes taking place in this raw material. It was found that the fresh raw fiber received from the mills during the grinding season was difficult to fibrillate, while the fiber which had weathered in the piles a full season had weakened, and overrefining was difficult to avoid.

A process of preservation of the bagasse during the storage period was obviously necessary. Such a process would be economical only if its cost did not exceed the value of the bagasse being lost by the weathering process; thereby, uniformity of raw material and manufacturing process would result, and some saving in handling costs might be expected

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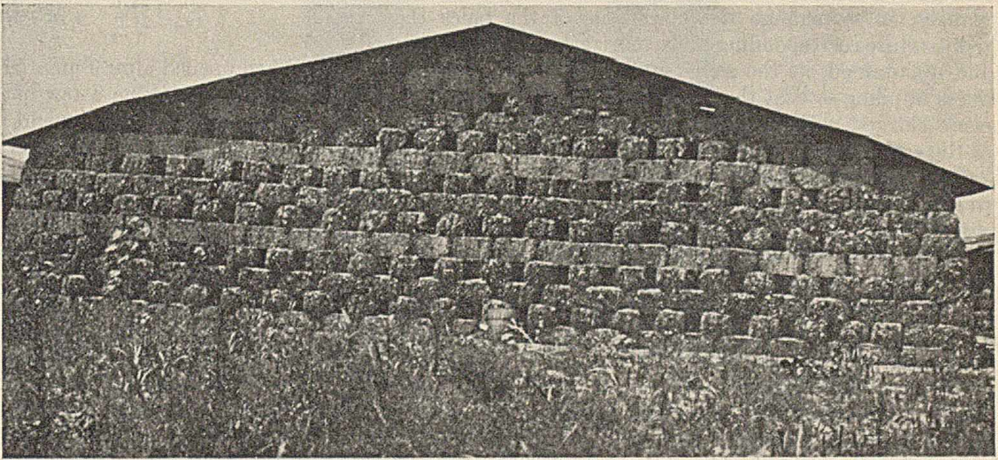
to accrue. At this time no data existed relative to the magnitude of average fiber loss during the storage period, but, from general experience with destruction of like material by microbiological processes, it was estimated that in 1922 the fiber loss in storage was close to 30 per cent.

The requirements of a successful process of preservation were rather exacting. Because of shifting gathering operations from season to season and the bulky nature of the bagasse, permanent structures for covering the bagasse and protecting it from the rains and weather were precluded. Chemical treatment indicated the necessity of using either low-cost chemicals in moderate amounts or highly toxic chemicals of greater cost in minute amounts. The application of such chemicals must involve inexpensive equipment, must be rapid, and must be susceptible to handling by common, green labor. The chemicals should not be toxic to humans or domestic animals, and must not interfere with manufacturing operations, particularly cooking of the fiber and waterproofing.



Standard-Roofed Boric Acid Pile of Baled Bagasse

Light streaks on the tops of the lower bales show undissolved boric acid.

Natural Causes of Fiber Deterioration and Loss

The years 1923–24 were devoted to laboratory work and to determining by field studies the causes for the losses, so as to plan field experiments properly. The sugar cane comes to the mill covered with dust from the fields, so that there may be expected to be present spores of all the microflora of these rich, semi-tropical soils, as well as the natural yeasts and other microflora finding the sugar cane plant as host. The milling operation, while it relieves the cane from juices and uses some wash water, in no way sterilizes the fiber and does not remove the contaminating spores. During the milling, the sap cells are burst and filled with air. The bagasse contains 50 per cent water. The climate is warm during a large portion of the grinding season. The conditions of rapid growth of microörganisms is therefore optimum, and nature takes her course rapidly. Within a few hours the small amount of sugar in the bagasse starts to ferment, and an odor of alcohol is marked. Within a few days, depending somewhat on conditions of exposure, a strong acetic acid odor is evident, the alcohol largely being converted into this compound. Conditions of storage modify somewhat these and subsequent microbiological changes.

In 1924 Charles Thom of the U. S. Department of Agriculture spent about two weeks studying with the authors the microflora in these bagasse piles because of the department's interest in the spontaneous combustion of stored crop fibers. The findings of this investigation are briefly (*10*):

> Concurrent with the alcohol fermentation, forms of *Monilia* were prolific and spread over the piles with great rapidity. When exposed to the rains, the looser parts of the piles showed abundant fruits of mucors and *Trichoderma*. Such molds as *Penicillia* and *Aspergilli* were inconspicuous, when apparent at all, although their presence was demonstrated by culture. The central areas of the bales were tightly compressed and apparently furnished conditions unfavorable for the growth of the common molds. Where the bales were wet and cool, the central areas were penetrated with mycelia which, as could be seen by the naked eye, followed the cleavage lines entirely through the bale. The whole mass penetrated by these mycelia assumed a characteristic yellow color. The tops of piles 3 to 4 weeks old showed abundant crops of agarics, mostly a species of *Psilocybe*, but including occasionally *Hypholomas* and *Coprini*. *Myxomycetes* were seen fruiting on the sides and even on the tops of the piles. Bacterial examination of warm bales showed typical rod forms, still viable but not in great numbers. Nematodes were present.

Laboratory Studies

Cultures of typical *Monilia, Trichoderma.* slime molds, *Psilocybe*, *Pen. divaricatum*, a fungi found by Thom growing at a temperature of 70° C., as well as cultures of several typical wood-destroying fungi (secured through the courtesy of C. A. Richards of the Division of Forest Pathology, Forest Products Laboratory, Madison, Wis.) were grown on prepared agar. As a background for the work, studies were made duplicating certain of the toxicity tests with organisms and chemicals reported by the Forest Products Laboratory (*1*). After making sure that their results could be duplicated, culture media containing chemicals such as sodium fluoride, boric acid, sodium dinitrophenolate, certain organic mercurials obtained from the du Pont Company, etc., in various proportions were prepared, and the toxicity of these chemicals in their various concentrations to the whole series of organisms was determined. These data gave the basis for the amounts of selected chemicals to be used in field tests.

Field Experiments

Effect of Mechanical Handling and Piling on Preservation and Quality of Bagasse—Aërobic Methods. In 1920 it was known that, if the bales were piled too closely together, there might be danger of burning and spontaneous combustion, so that when the first season piles were made, attention was given this point. No cases of spontaneous combustion have ever resulted. The few fires in piles were the result of carelessness with matches, cigarettes, etc. Nevertheless, there was some evidence that bales reached high enough temperatures to turn the fiber to a dark coffee color and to make it harsh and brittle, somewhat like burned sulfite cooks of wood chips. The cause for this was found to be the falling of loose bagasse between two bales, cutting off ventilation, and confining the vapors. In the presence of the evolved acetic acid mentioned above, a type of acid cooking took place which was quite undesirable. Only great care in instructing the labor making the piles was able to stop this, and some of this type of burning turned up in one or more piles every year. This fact demonstrated the necessity of studying the spacing of bales and of studying their placement as well, since some piles caved in or fell off, causing acid-burning or other types of spoilage. The most striking characteristic of the piles was that during the first month or so, depending on the method of piling, the center of the piles would reach temperatures of about 140° F. Later, studies using recording thermometers, with the sensitive bulb embedded in a bale in the center of the eighth row from the top, showed that an almost uniform temperature of 142° F. was reached within a week or so, and that the temperature was maintained for a period of 2 or 3 months, the bale finally cooling down to air temperature. The cause for the heating is the exothermic reaction involved in the fermentation of the sugar to alcohol, acetic acid, and perhaps lactic acid. This temperature corresponds to that of pasteurization. This fact gave a clew to an important method of preservation—namely, to so arrange the placement of the bales that a temperature corresponding to pasteurization would be reached and maintained, at the same time to provide proper cleanliness in piling so that the ventilation channels would not become clogged with loose bagasse and lead to acid-burning, or the condensation of moisture.

One of the controlling factors of microbiologic growth is water supply. The fermentation produced large volumes of carbon dioxide. When this gas was produced under elevated temperatures, its escape resulted in a rapid drying out of the bale, since carbon dioxide must saturate itself with water at the temperature of the bale. The mechanical method, therefore, not only resulted in pasteurization but also in drying out the bale to a moisture content of 30 per cent or even less. Therefore, when the pile cooled below the pasteurization temperature and organisms could again begin their destructive work, the moisture content was below an optimum, so that the spores that had lived through would not germinate. Here was a positive mechanism for control. The discoveries made in studying mechanical piling are the subject of patents (*3*, *6*, *9*).

Anaërobic Mechanical Methods. During the grinding season of 1920, bagasse had been piled loose, without baling. Examination of some of this material two years later, where conditions had kept the fiber continually wet, suggested that an anaërobic method of preservation might be worked out. By chance in 1924 there had to be made on the Marrero property large piles of loose bagasse, owing to lack of baling equipment at one of the sugar mills. Arrangements were made to soak this pile repeatedly with water so that, except for the outside surface, anaërobic conditions would be maintained. The course of fermentation in this pile was radically different from that previously described with the piles of bales. A very disagreeable odor of putrefaction developed, which ceased to be given off after a few weeks. After some 4 months of storage, retted fiber was used in a mill run. The fiber showed little evidence of strength loss, was very light in color, and when dried was much like raw bagasse. Some pith seemed to have gone. The odor was that of butyric acid combined with protein putrefaction. Evidently the process was entirely bacterial, since there was no evidence of the growth of fungi. The fiber was quite satisfactory. The process is covered by a patent (*4*). This process seemed at that time worth following up, but later developments seemed more practical, involving less capital investment.

A quite different anaërobic method suggested itself, and experiments were carried out during 1925–26 to determine its commercial use. The method consisted in baling the bagasse according to standard practice but, instead of piling the bales in the open, to place them in a closed container. Under these conditions it was thought that the alcoholic fermentation would proceed as usual, and that, since the carbon dioxide being produced was heavier than air, it would displace the air in the pile and under proper control would not diffuse, thus preventing fungi growth. For containers 15,000-gallon wooden tanks with tight covers were used. Recording thermometers were used to obtain records of bale temperatures. Loose bagasse was packed in between bales. Gas analyses were made at several intervals as shown in Table I.

Table I. Analyses of Gas

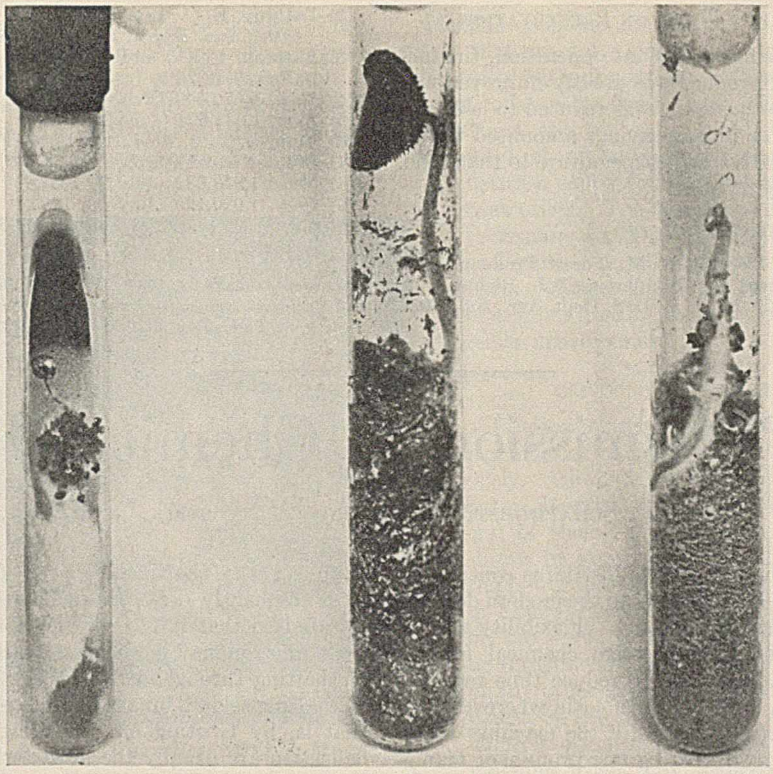
Date		Analysis in Closed-Tank Storage of Bagasse under Anaërobic Conditions			Analysis from Interior of Boric-Acid–Treated Pile in Open	
		CO_2	O_2		CO_2	O_2
		%	%		%	%
12/31/26		24.8	0.2		0.6	20.0
		24.9	0.1		0.8	19.8
	Av.	24.85	0.15	Av.	0.7	19.9
1/27/27		21.8	0.6		0.3	20.8
		21.6	0.6		0.2	20.4
	Av.	21.7	0.6	Av.	0.25	20.6

When opened after 9 months of storage, there was evidence of fungus growth on a few of the bales at the top owing to the fact that the covers could not be made air-tight, but the bales below were fairly dry and showed no visible change from the day they were stored, and a distinct odor of alcohol was still evident. A recovery of more than 95 per cent of the original fiber was obtained. The process is covered by a patent (*7*).

Process of Retting Fiber by Fungi. To learn the secret of a microbiological process and to put it to commercial work is appealing. Perhaps the outstanding visual characteristic of much of the piled, stored fiber was the characteristic yellow color. Associated with this color was the fact that such bagasse was almost devoid of pith particles so that, when a mass of such fiber was rubbed in the hands, it fell apart in long, slender, soft individual fibers. Evidently the organism growing on the mass had utilized the parenchyma tissue as a food supply and did not materially attack the fiber itself. Mill runs made with selected bales resulting from this type of fermentation gave excellent board. Evidence was gathered in field and laboratory studies that this change was due to some mushroom type of fungus, and the studies of Thom and one of the authors confirmed this. The bales in a large experimental pile were inoculated by spraying at the time of piling with a culture of *Psilocybe*. The fiber, after storage, was the completely retted yellow bagasse sought and gave excellent results in a mill run. The process is described in a patent (*5*). Later a method of commercially recovering pith from the white water and a valuable market for this material as a filler for dynamite were worked out, so that it seemed best to avoid this loss of pith.

Preservation with Chemicals and Quantitative Determination of Preservation Losses. Attempts to obtain quantitative ideas of losses in 1923–24 by the use of small experimental piles were a failure. The authors were forced to work on full-scale piles, which meant gearing up experimental work with the flow of bagasse from the sugar mill. Extreme difficulty in obtaining yields was involved. Time was not available to weigh every bale; bales were not exactly uniform in size or weight as made; sugar mill analyses made for an entirely different purpose had to be accepted to arrive at moisture, sugar, and nonsugar content; bales would break in loading; and during the baling operation, accurate count of all bales going into each pile was imperative. These were a few of the difficulties in setting up the piles. On taking them down, the most serious problem was an accurate determination of the average moisture content of the pile. Many times the piles were taken down during torrential rains. Of necessity the results obtained had to be analyzed with considerable judgment and visual knowledge of conditions. In spite of these difficulties, the Research Department in the grinding season of 1925 took over the entire baling station at the Raceland Sugar Mill as a field experiment. This station produced about 40,000 tons of wet bagasse, or about twenty piles of bales. During the erection of the first few piles, attention was given to means of obtaining as quantitative figures as possible, and several changes had to be made in the plans to meet the practical requirements.

The program was to determine the loss in storage under the best conditions of piling found in the 1924 season—i. e., involving no chemical treatment and not roofing the pile, but making the piles as mechanically perfect, with proper ventilation, as was possible. In addition, it was decided to build a wooden roof over one such pile to keep the rain off the top and so to determine directly the loss due to the wet top.



Psilocybe Cultures

A. Pure culture grown on agar.
B. *Psilocybe* growing on bagasse under wet conditions.
C. *Psilocybe* growing on bagasse under moist conditions.

Two schemes of chemical treatment were used. The first was to treat integrally the loose bagasse on the conveyor with dry chemical or a chemical solution and to bale the treated bagasse.

For the integral treatments, dry sodium fluoride (18 pounds per ton), boric acid (21 pounds per ton), and a solution of sodium dinitrophenolate (3 pounds per ton) were used. Salt was also used for one treatment at the rate of 235 pounds per ton. The theory of using salt was based on the fact that salt in sufficient concentrations, because of the high osmotic pressure, was known to be a controlling factor in the manufacture of Roquefort cheese, the salt concentration inhibiting the growth of other fungi and permitting the development of *Pen. roqueforti.* Also, salt is used in many food-pickling processes. Salt was cheap and the mines were close. The amount added was calculated on the basis of producing a 40 per cent solution when the moisture content of the treated bales had been reduced to 35 per cent.

The second scheme of treatment was one which, if it worked, would be simple of application and very economical. If it was assumed that pasteurization preserved the bagasse in the interior of the pile satisfactorily, as was thought and hoped that it would, then there was no need of integrally treating the bales that would become so pasteurized. The only bales needing chemical treatment would be those not so pasteurized. Assuming that only the bales on the top and bottom layers and on the sides of the pile were not pasteurized, calculations showed that these comprised half of the pile. Therefore, a method for chemically treating only half the bales in a pile was needed. If it was assumed that these bales would dry out if not exposed to the rains, then the water deposited by the rains was the controlling factor. Following this line, a method of chemical treatment was needed such that the rains would dissolve and carry the chemical into the bales as the water from the rains penetrated. The method of sprinkling chemicals along the outside ledges of the bales on the sides of the pile and over the top bales of the pile should accomplish this. The method of piling used at that time was to step each row in the pile back from the edge of the bale below about 6 inches.

The amount of chemical to be used had to be guessed at, and for these experiments 3.6 pounds per ton of sodium fluoride and 4 pounds per ton of boric acid, respectively, were used. It was decided to set aside one pile for each chemical used, to treat integrally one half of the pile, and to edge and top-treat the other half.

After 9 months the piles were taken down with great care, thorough notes being taken on the fiber characteristics, and on the man hours and equipment time required for each. The losses of fiber from the various piles were calculated and are presented in Table II.

Table II. Relation between Method of Storage and Calculated Loss of Fiber

Method of Piling	Total Loss
	%
Roof and boric acid surface treatment	6
Roof alone	10
Boric acid alone	15
Untreated and without roof	30

The results were so promising that it was decided to design a portable roof and to use boric acid at the rate of 2 pounds per ton of fiber in the pile on the edges of the side bales, and at the rate of 2 pounds per ton on the top bales, a total of 4 pounds per ton.

The final method adopted for preservation was to level off and supply good drainage for the ground bottom of the pile. The bales were arranged according to a blue print. Boric acid was applied to edges and tops of piles, and the pile was immediately roofed. Thus, the principle of pasteurization, chemical treatment, and roofing were all used. The experiments were continued for several more years in order to determine the minimum amount of boric acid necessary and to check up on yields and make other possible improvements.

The chemical costs are surprisingly low (6.4 cents per ton dry fiber) and are more than offset by the saving in labor in taking down the piles and in handling the fiber in the Celotex manufacturing operation. The roof cost is low, especially with its long life, and is probably also covered by the saving in unloading.

RESULTS OF RESEARCH WORK ON PRESERVATION

The first year the system was put into operation, the uniformity of operation and product was greatly improved and the average fiber loss due to storage was reduced to less than 10 per cent per year. The money savings amounted to five times the cost of the entire research expenditure to that time. The process is covered by a patent (*8*).

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Power Transmission in Chemical Industries

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USE of power in the chemical industries is continually increasing. This is due largely to the modern demand for utmost production economy. Flexibility and efficiency are being sought by aggressive chemical factory executives to reduce handling cost, to reduce time required for production processes, and to reduce costs wherever possible. The utmost cannot be attained if the machine drives are not right. As correctly stated by one prominent manufacturer, "No plant or machine is efficient unless the drives are efficient." In other words, although power is applied for the sake of economy, to secure maximum economy we must "economize in the economy department."

SHAFTING

Let us begin at the bottom, with the most lowly and most common of all power transmission devices—steel shafting. Shafting has been in use longer, perhaps, than any of the other elements to be discussed. Nothing has yet been found which promises to supersede shafting. Even in electrical transmission, which is now commonly used in preference to purely mechanical transmission, the rotors are mounted upon shafts.

Transmission of power through shafting under favorable conditions is more efficient than is generally supposed. Much depends upon the care exercised in hanging the shafting and in the arrangements of the pulleys. Goodman (*1*) shows that, if properly aligned, a solid shaft with ordinary bearings will transmit power a distance of 6000 feet with an efficiency of 80 per cent when all forces are purely torsional. Using ball bearings instead of plain bearings, this distance jumps to 120,000 feet or 22.7 miles.

Shafting lends itself admirably to use in the chemical plant because it can be made of almost any desired metal for resisting corrosion. Steel shafting is sometimes plated. Numerous standard sizes are available. The proper size is generally dependent upon the torsional stress to be resisted. In a large chemical plant it is well to take advantage of these various sizes, but in the small plant it is better to use line shafting of the same size throughout. This simplifies the matter of changing pulleys from one place to another, since it eliminates bushings. In the event that it should be desired to move the motor from one place to another, this can be done without changing the shafting. If the shafting is stepped down, as is frequently done, the matter sometimes becomes complicated so that it is really cheaper in the end to spend a little more money in the first place and to use the same size of shafting throughout.

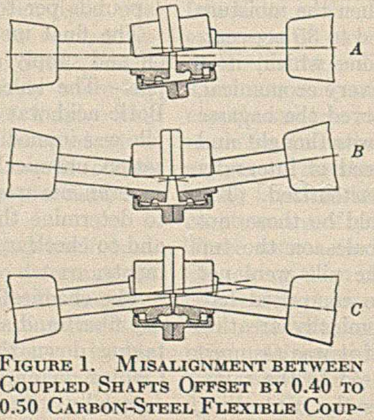


FIGURE 1. MISALIGNMENT BETWEEN COUPLED SHAFTS OFFSET BY 0.40 TO 0.50 CARBON-STEEL FLEXIBLE COUPLING

Shafting seldom breaks because of torsional stresses alone—that is, by twisting off. Bending stresses caused by shaft deflection are usually the most serious. To avoid excessive bending stresses, it is important that plenty of bearings be used and spaced sufficiently close together. To minimize shaft deflections, it is advisable always to place the pulleys, heavy clutches, couplings, etc., as close as practicable to the bearings. Deflection should not be greater than 0.01 inch per foot of length.

BEARINGS

Bearings, like shafting, are one of the indispensables in all forms of power transmission. But the problem of selection is somewhat more complex because of the numerous bearing types. However, in general almost any bearing in good condition will transmit with high efficiency. To be in good condition a plain bearing must be properly babbitted, lubricated, and aligned. The efficiencies of the various types of bearings in good condition are:

	%
Common bearing (singly)	96–98
Common bearing in long lines of shafting	95
Roller bearings	98
Ball bearings	99

It would be absurd to use ball bearings exclusively simply because such bearings are most efficient. For greatest economy, shafts that are used only occasionally should usually be run in plain bearings. If power is turned on frequently, even though not continuously, and if electric motors are used for driving, ball or roller bearings are preferable to plain bearings because the starting friction of plain bearings is high. In fact, the starting friction of roller and ball bearings is not much greater than the running friction. Hence smaller motors can be used with ball and roller bearings.

Where plain bearings can be kept in good condition, the cost of the frictional loss as compared with ball or roller bearings is often a small item and may be neglected. Thus the frictional cost of running the main bearings of an engine, generator, motor, turbine, pump, and similar large unit is ordinarily small as compared with the total power involved, whereas the difference in cost between ball bearings and plain bearings is high. Under such circumstances, therefore, plain bearings may be more economical even though slightly less efficient. The interest on the difference in cost may be insufficient to cover the difference in power losses.

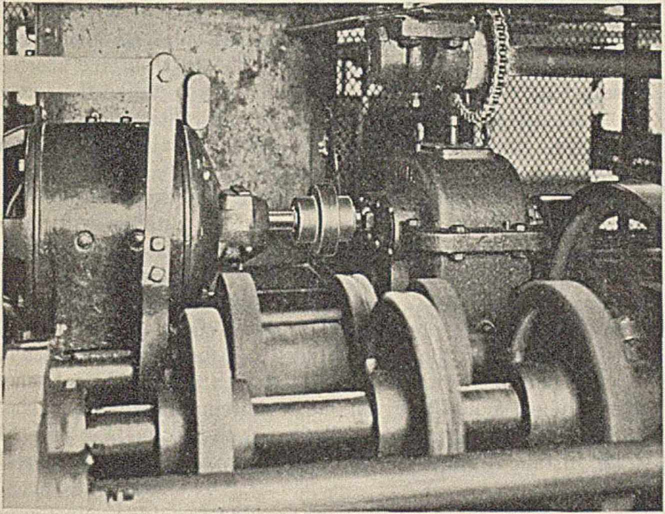


Figure 2. Drive on a Special Chemical Mixing Machine

Electric motor, flexible coupling, reduction gear, multiplicity of open gearing, and overhead chain drive are involved.

On line shafting where lubrication may be comparatively more difficult and where as a result the difference in friction may be considerable and hence the cost of power considerably less with ball or roller bearings, it is advisable to use the low-friction type. An important advantage of roller and ball bearings is that they require less lubricant than the plain type and need not be oiled so frequently.

For service in chemical plants, ball bearings are now made with chrome-alloy steel balls and carbonized race rings, the rings being cadmium plated. Also, ball bearings are made of monel metal, with hardened stainless-steel balls and races. Ball or roller bearings that are sensitive to corrosion should be avoided in surroundings which subject them to corrosive attack.

Flexible Couplings

Slight errors in aligning shafting are unavoidable. To compensate for such errors, flexible couplings are recommended. They save power when properly applied. The offset should never be greater than $^1/_{16}$ inch, nor should the angularity between shafts be greater than 5°. Sometimes exceptional misalignment cases can be cared for by using two flexible couplings with an intermediate shaft between.

When installing a machine, alignment should always be made as perfect as possible; even if considered perfect, it is well to use a flexible coupling at the end of the shaft because misalignment is almost certain to occur eventually owing to shrinkage of grouting under motors or generators, shifting of building foundations, likelihood of shrinking and twisting of wood stringers, and possibility of loosening of bolts and shifting of hangers, thereby throwing the shafting out of line. If no flexible coupling is used under these conditions, or if certain machine parts twist or warp, much stress is thrown upon bearings and shafts; as a result expensive machines may be distorted and ruined.

Flexible couplings are commonly made up of two flanged pieces that are not rigidly connected together and that will yield freely without slipping. There are many makes on the market today using flexible pins, rubber, leather, sheet metal laminations, etc.

Figure 1 shows exaggerated conditions of misalignment between coupled shafts. *A* shows two shafts offset to each other. The flexible coupling permits the shafts to remain straight, allowing all members free to float and causing no strain in the bearings, shaft, or other parts. *B* shows how the flexible coupling takes care of angular misalignment. *C* takes care of angular and offset misalignments.

Clutches

Friction clutches are recommended for use where machines or groups of machines do not operate continuously. Clutches may be so arranged as to cut off an entire department or a portion of a department. Several of them may be placed on a single-line shaft as shown in Figure 3. In that way almost any part of the power may be thrown on instantly. For example, in Figure 3 each driving pulley on the shaft is mounted on the sleeve of a friction clutch so that any unit may be disconnected without interfering with the operation of any other part of the plant. Clutches may also be placed on the main shaft. To operate an empty machine is often almost as costly as operating the same machine when fully loaded—hence the power saving that accompanies the use of clutches.

Before the advent of the friction clutch, machines were thrown on and off by removing the belt and then replacing it. Because of the time required and the annoyance, many operators preferred to leave the belt on. As a result the belt was removed only when the machine or machines were to be idle several days or weeks. The friction clutch eliminates these difficulties.

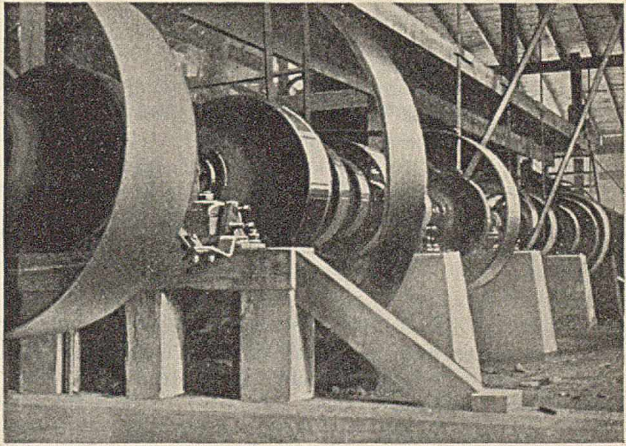


Figure 3. Modern Group Drive in a Rock Asphalt Plant

Power is supplied by a 300-h. p. Diesel engine.

When a friction clutch is thrown off, the pulley becomes a loose pulley, and we still have more or less friction between the shaft and the pulley. For this reason some friction-clutch pulleys are provided with ball bearings.

In some plants considerable money has been spent on mule drives in preference to quarter-turn drives because the former are reversible. On starting the engine and turning it backward to center, the belt would run off. A friction clutch on the main shaft solves such problems; it costs less and simplifies matters considerably. A friction clutch on the main connecting unit between a synchronous motor and the

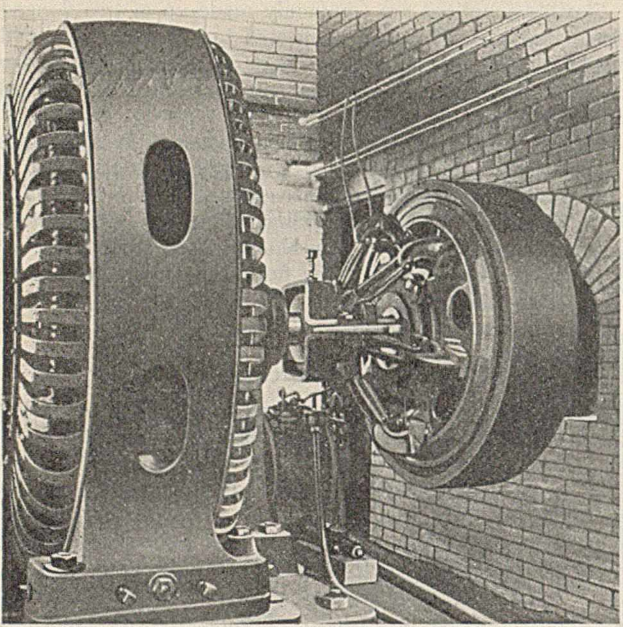


FIGURE 4. FRICTION CLUTCH WHOSE DISKS ARE LINED WITH SPECIAL FRICTION LINING

It has been giving continuous service for nearly 12 years; ordinary wood blocks, formerly used in the friction disks, had to be replaced every month.

transmission machinery is shown in Figure 4. Here, of course, there is no dead center problem.

There are hundreds of clutch designs from which to select. An interesting recent design is shown in Figure 5 which is an ingenious clutch employing shot and centrifugal force to take care of starting loads, shocks, and overloads without possibility of damage to the motor or running off of belt. In *A* the rotor and shell are at rest; the shot are resting on the bottom of the shell. In *B* the rotor is at full speed, the shell being started. In *C* the shell and rotor are at full speed and in synchronism.

BELTING

Of importance in many chemical plants, owing to corrosive fumes, is the selection of belting. Oak-tanned leather belting is sold as waterproof or nonwaterproof. The nonwaterproof variety is not recommended for use in chemical plants. The waterproof variety is better for resisting mineral oils, steam, moisture, alkali, acids, etc., but is unsuitable in high-temperature surroundings. A special tannage leather belt which costs about 50 per cent more is preferable in many plants because it is waterproof, resists acids and fumes well, is flexible, and has high tractive power. Boiling water and exhaust steam do not harm this belt.

Sometimes coated belts are necessary to take care of special conditions. For instance, a chemical condition existed in the nitric acid plant of a large powder company. There was a motor drive in one of the departments subject to fumes, and, owing to the circumstances, nothing but a special coated belt drive could be used. On this drive the best service that could be obtained from any type of belt, until they used the coated special, was 7 days, and the minimum service was 24 hours. With the special coated belt, as regularly made for chemical service, they were able to obtain 4 weeks of service. There was a mutual interest in improving on this, if possible, so they applied additional coatings on the surface of the belt and eventually developed a special so-called "acid-resisting belt," which consistently gave 8 weeks of service.

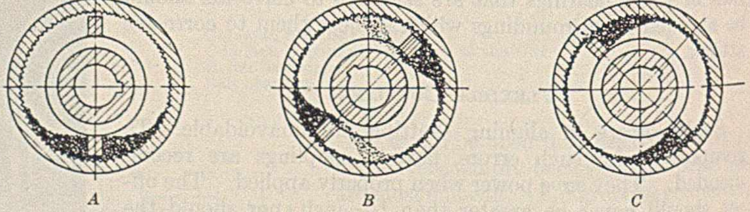
Two of these belts, operating in a temperature of 250° F., gave 1.5 years of service each, whereas the best service from a specially processed, high-priced leather belt was only 6 months. That particular leather belt had been selected previously as the best obtainable for the conditions. For service on drives exposed to sulfur fumes, one concern recommends an untreated stitched canvas belt thoroughly sealed in cellulose.

It is seldom that corrosive liquids are splashed onto a belt. Nevertheless, moisture present on the belt surface absorbs sufficient vapor to present a condition not unlike the action of corrosive liquids in active contact with the belt. In general, friction surface rubber belts are satisfactory unless fumes in contact with the belt deteriorate cotton fabrics. Where fumes detrimental to cotton are excessive, rubber-covered belting should be employed. Rubber will withstand practically all industrial chemicals except nitric acid. The cover should be no heavier than necessary to protect the fabric carcass (0.032 inch is usual practice). Rubber belts operating in the presence of fumes of chemicals detrimental to cotton should be made endless to insure rubber protection at all points. If mechanical fasteners are used, the cut edges of the belt should be given one or more applications of rubber cement. For all rubber belt drives, endless belts should not be installed unless a take-up is provided for permanent elongation.

In general, inflammable belts should be avoided. Instances are on record where belts have run off pulleys and wrapped around the drive pulley, and the resultant friction has created sufficient heat and high temperature to ignite the belt and cause damage by fire.

STATIC ELECTRICITY. Most chemists have doubtless had experience with difficulties that are commonly encountered owing to static electricity. Many fires and explosions in industrial plants have been caused by static sparks from power transmission belts.

After considerable research it is now known definitely how to eliminate static electricity. One method is to use a belt that is a good conductor of electricity. Rapidly moving metal parts, such as metal disks, never cause static troubles. This is because the disks themselves are excellent conductors of electricity. Metal band saws which run at velocities of thousands of feet per minute never give static troubles because metal saws conduct electricity. Therefore, if a given belt can be converted into a perfect conductor of electricity, there will be no static. One belting concern recently put out a belt containing a copper wire stitching along each edge, claiming such belting to be permanently static-proof.



A *B* *C*

FIGURE 5. CLUTCH USING SHOT AND CENTRIFUGAL FORCE

Not long ago the research department of a prominent powder manufacturing concern found that a graphite solution is effective as a preventive of static. Another powder manufacturing company uses glycerol which is satisfactory as long as its use is continued; that is, the belt must be maintained in a moist condition and must not be allowed to become dry. As long as the belt is moist, it is a good conductor of electricity. One concern, having used both methods, declares that graphite is superior to glycerol in that graphite need not be applied so frequently.

P. W. Edwards and J. O. Reed of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, report that for rubber belts "a good grade of spar varnish with a satisfactory vehicle" should be used. Powdered aluminum, bronze, copper, graphite, and lampblack were tried as the conducting mediums. Various proportions of each of these materials were mixed with spar varnish. The most satisfactory results for a nonstatic rubber dressing were obtained by using 18 parts of lampblack with 82 parts of good spar varnish. For a good noninflammable thinner they recommended equal volumes of carbon tetrachloride and Varnish Makers' and Painters' naphtha. This was carefully tested on belts in actual installations on an air compressor and on a rubber conveyor belt.

For leather belting the following formula is recommended: 100 cc. liquid fish glue, 88 cc. glycerol, 100 cc. sulfonated castor oil, 170 cc. water, 82 grams lampblack, and 20 cc. of 2 per cent ammonium hydroxide. The material for leather belting may be applied while the belt is moving and in use, but the dressing for the rubber belting must be allowed to dry before the belt can be used.

Any material applied to a belt for the removal of static must not decrease the coefficient of friction between the belt and the pulleys, it must not injure the belt in any way, and it must wear well.

Static may also be successfully removed from belts by combing. A thorough discussion of removal of static electricity is published by the National Safety Council (*2*).

Care of Belting. Owing to the naturally shorter life of belting and its importance as a transmitter of power, it is plain that money can be saved by (1) lengthening its life and (2) maintaining high efficiency throughout that life.

It is well known that each per cent of belt slip consumes one per cent of the power. Thus, if the annual power bill of a given plant is $100,000, each per cent of slip costs $1000. In addition, owing to the high slip, the rate of wear will be high. It is therefore worth while to keep belts in good condition—clean, strong, and slipless.

Before cleaning belts it is well to remember that 212° F. is too hot for most rubber belting. One prominent rubber belt manufacturer states that his belting is not affected by heat up to 200° F. He states that, where higher temperatures are to be encountered, he should first be consulted. That is good advice regardless of the kind of belt. Even where steel chains are used, one must be careful at high temperatures or lubrication difficulties will be experienced. Steel chains can be cleaned safely with steam if desired, but such practice is decidedly unsafe when applied to leather, rubber, and other kinds of belting.

Balata belting is more sensitive to high temperatures than rubber. Its temperature should be kept down to less than 110° F. At 125° balata gum can be molded; therefore balata belting should never be heated in any way.

According to one authority, oak-tanned leather belting should not be subjected to a temperature higher than 115° F., which means that oak belting must not be cleaned with hot water because the water will probably melt out the impregnating compound. Without the compound, cotton belting does not give satisfactory results. Stitched canvas belting should not be used in temperatures higher than 140° F.

Waterproof leather belting of the special mineral-tanned variety can safely be cleaned with hot water, as it is not harmed at 212° F. But the mineral oils which are almost certain to be driven out must be replaced. Unless the belt is treated after hot cleaning in accordance with the directions of the manufacturer, the fibers will be left dry and brittle, and failure thereafter may be premature.

All belts should be inspected frequently so that faults may be remedied at an early stage. All belts should be kept free from oil and grease. The fastenings should be watched, and replaced before it is too late. Lengthwise rips in belts are invariably started because of uneven fastening, or because the fastening breaks out on one side first and puts all the strain on the other side. Once a rip starts, it progresses rapidly, and in a surprisingly short time the belt is ripped for a considerable distance and put out of commission.

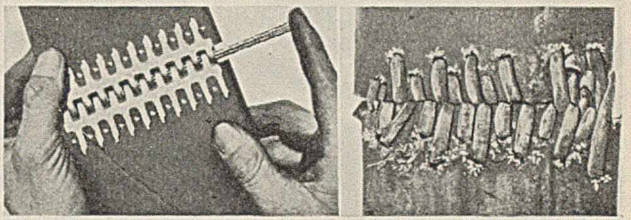

A *B*

Figure 6. Belt Joinings

A. Modern method of belt joining; the fastener is quickly applied by means of an ordinary hammer and then joined by inserting a pin which is notched to prevent slipping.
B. Example of poor belt joining; the "jog" in the alignment and the unevenness in the lacing make a joint of this kind bulky, weak, unsightly, and unsatisfactory.

A fastener whose teeth cut crosswise of a belt is much more destructive than one whose teeth penetrate the belt lengthwise. If a belt breaks behind the fastener, it is usually the result of using the wrong type or size of fastener. Care should be used that the ends of the belt are cut square and the fastener is evenly placed across the joint as illustrated in Figure 6*A*.

Pins, while coming out, have been known to strike against an object thus generating a spark and causing damage by fire. One manufacturer of belt fasteners states that he has made up a few special hooks from a material that is not only spark-proof but rust-proof. These hooks are now on test in several chemical plants.

Pulleys

To transmit power at the least ultimate cost, the correct pulley as well as the correct belt must be chosen. Too many users of pulleys are interested only in first cost, giving little or no attention to the cost of installation, cost of fuel due to avoidable belt slip, cost of air fanning, cost of friction due to the weight of the pulleys, high belt tension, cost of belt maintenance, life of pulleys, and the elements of safety and general dependability.

A few of the most common pulley faults and advantages are as follows:

Paper pulleys should be kept dry. If they become wet they will swell, warp, crack, and give trouble. Wood pulleys are subject to uneven wear because of the fact that in some places the fibers are tangent. The tangential portions slip and therefore wear more easily. An important advantage possessed by wood, paper, and other nonmetallic pulleys for use in chemical plants is that they do not corrode.

Steel pulleys are commonly used in chemical plants. To prevent corrosion it is sometimes advisable to protect steel against acid fumes. Thus in one pickle house where the pulleys and hangers are constantly enveloped in sulfuric acid fumes, special nonoxidizing coatings are being used with entire satisfaction. The pulleys have been used under such conditions for many years. Generally unless steel pulleys are properly protected they should not be used where there are acid fumes or where the air is unusually humid. Sometimes power transmission apparatus is plated, as with nickel or chromium. Not only does plating resist corrosion, but it insures a presentable appearance at all times.

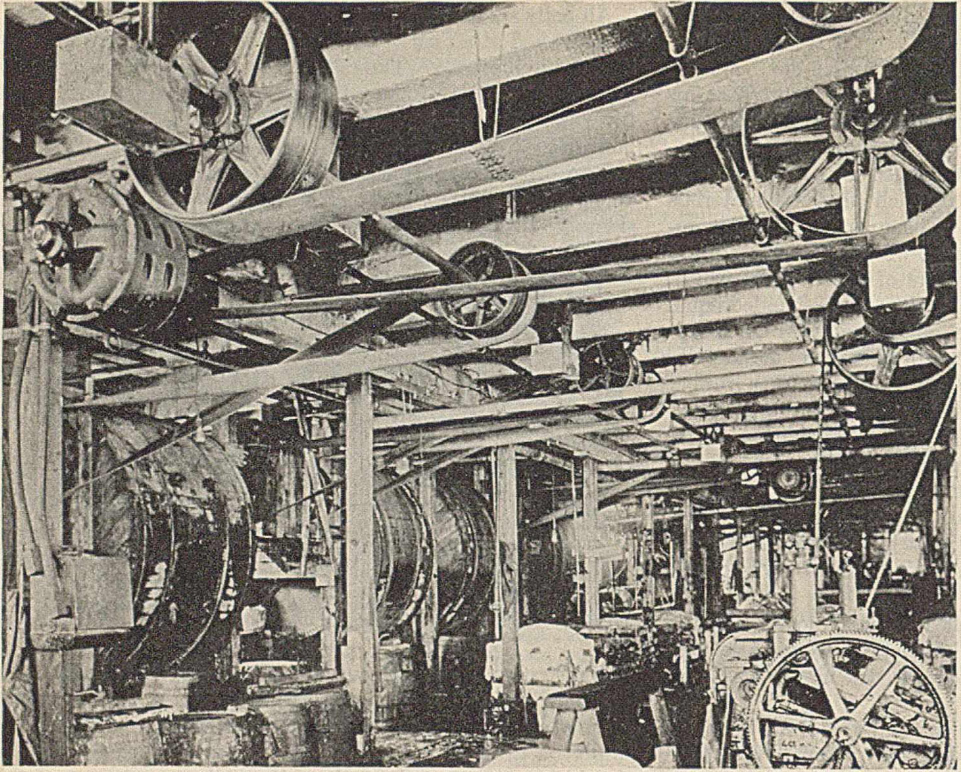


FIGURE 7. STEEL PULLEYS IN A TANNERY

Friction surface rubber belting, gears, electric motors, and shafting are also shown.

The principal advantage of the steel pulley is its high strength which permits it to operate without danger with a rim speed of 6000 to 7000 feet per minute. Other advantages are that steel is not brittle and will bend before it will break, steel pulleys are light in weight, they have high tractive power, and they are good conductors of heat, long lived, and not inflammable. Nonmetallic pulleys are poor conductors of heat and inflammable. An excellent example of the use of steel pulleys in a tannery plant is shown in Figure 7.

Pulley surfaces are sometimes made rough in an effort to reduce slip; this is a mistake. W. M. Sawdon of Cornell University found in making careful tests that with rough pulley surfaces the belt would not remain on the pulley after a slip of 2 per cent was reached. Upon smoothing and polishing the surfaces, no difficulty was experienced in keeping the belt on at 10 per cent slip, and at the same time the pulley would transmit a much greater load.

In general, large pulleys and high-speed belts are more economical than small pulleys with low-speed belts. Much equipment in the chemical plant is operated at high speed—blowers, grinders, pulverizers, mixers, etc. These necessarily are equipped with small pulleys. Only thin, pliable, strong, tough belting should be used on such drives. Where line-start motors are used, the belt should be sufficiently wide or thick to take care of the starting load and the pulleys should be proportionally strong.

WRAPPER-PULLEY DRIVES

The old method of using a multiplicity of pulleys, belts, and jack shafts to reduce from a high-speed engine or motor to a low-speed shaft has been superseded by the modern wrapper-pulley drive. It was formerly considered good engineering to use several pulleys to maintain an ample arc of contact on all pulleys. In fact, in some plants this method is still in vogue.

One modern method, shown in Figure 8, requires a wrapper pulley. Here it is plain that even though the wrapper pulley does consume power, it consumes less than does a jackshaft because the latter is necessarily under high tension. The wrapper pulley, on the other hand, being placed on the slack side, consumes little power, and, if properly designed, the friction loss is negligible. Where a wrapper pulley is used, its diameter should be about one and a half times the diameter of the smaller pulley in the drive, and it should be placed close to the small pulley as shown in Figure 8, always on the slack side and not on the tight side.

Figure 9 shows three typical wrapper-pulley drives which were originally operated over long centers, the center distances being from 24 to 32 feet. Dust settling on the belts caused so much slip that it was almost impossible to drive the mills, and the power used was out of all proportion to the work being done. Wrapper pulleys permitted the center distances to be shortened to an average of 12 feet. Slippage was reduced to the vanishing point, belt life prolonged, and the power consumption reduced fully one-third. In a number of installations of this type where open drives were superseded by wrapper-pulley drives, an increase of 40 per cent in transmitting capacity has resulted.

It is sometimes argued that the reverse bend due to the wrapper pulley is disastrous to the belt. That is true where the wrapper pulley is too small. The reverse bend is of no consequence, however, where the wrapper pulley is sufficiently large and where a properly flexible belt is used.

Sometimes it is expensive to operate machinery at a speed slower than normal. Thus the operator of an air compressor driven by an electric motor and wrapper-pulley drive wondered why belt upon belt would break after being in use for only a week. An investigation disclosed that the compressor speed was too low. Designers of compressors generally base flywheel computations on the normal speed of the compressor. That is, they give the flywheel a weight which is sufficient to turn the compressor at a predetermined speed fluctuation. Therefore this compressor which was operated at a low speed fluctuated so violently that the wrapper pulley would be thrown up into the air with each fluctuation and would come down hard against the belt. No belt can endure such punishment. For violently fluctuating drives of this sort, a spring-operated wrapper pulley (Figure 10) is recommended. There are no weights on this drive. The spring is on the shaft around which the wrapper pulley arm oscillates. This type of drive is scarcely known as yet in the eastern states. It was developed on the Pacific coast where it is now being used and is gradually working across the country. With properly designed springs and a light wrapper pulley, contact with the belt is continually maintained. There is no hammering.

PIVOTED-MOTOR DRIVE

So-called "pivoted-motor drives" are now coming into general use. The motor is mounted on an arm and pivoted to a rigid base in such a way that the weight of the motor itself provides the necessary tension in the belt as illustrated in Figure 11. Thus in position 1, when the motor is idle, the belt is unstretched, and the center of the motor is almost directly above the hinge; that is, distance L is smallest. Upon starting (position 2), the motor automatically "backs into the belt," and distance L becomes greatest. Finally, when the load becomes normal (position 3), the motor swings slightly toward the right, and distance L decreases to normal.

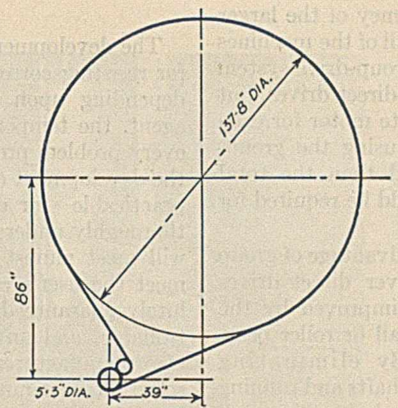


FIGURE 8. WRAPPER-PULLEY DRIVE WITH A PULLEY RATIO OF 26 TO 1

With this system the ratio is limited only by the practicable size of the driving and driven pulleys.

Advantages possessed by this drive are: (1) it is applicable to shorter centers than any other type of belt drive; (2) slip is minimized; (3) the belt cannot be overstressed; (4) belt stretch is automatically taken up; (5) there is no wrapper pulley and hence (6) there is no reverse bend in the belt; and (7) the first cost for belt and pulleys is less. The principal disadvantages are: (1) the pulley ratio should not be greater than 6 to 1; (2) slightly less capacity is obtainable than from the wrapper-pulley drive for the same belt width; (3) somewhat greater pull on the bearings is present owing to the smaller arc of belt contact; and (4) it is not so easy to regulate.

Unquestionably the pivoted-motor type of drive is excellent for the smaller horse powers. One manufacturer has elaborately standardized this drive to the extent that a data book is now available which lists more than five thousand various combinations of pulley sizes, center distances, speeds, and horse powers. This makes it possible for the chemical plant executive to select quickly a suitable drive for almost any condition up to and including 40 h. p. From 50 h. p. and upward, innumerable wrapper-pulley drive combinations are listed in complete detail.

V-BELT DRIVE

Another excellent short-center drive for the smaller horse powers is the V-belt. The two outstanding advantages of this belt are: (1) it will not run off the pulleys, and (2) it is noiseless in operation. It is more efficient than ordinary flat-belt drives but less efficient than the higher grade drives. Unfortunately, extravagant claims have been made for this type of drive which have caused it to be applied to installations for which it is not suited. Now that thousands of installations have been made and it has passed through the experimental stage, available data are more dependable. For instance, when this type of drive was first brought out it was claimed that the V-belt would not slip owing to its wedging action. It was claimed that an absolutely constant speed ratio was maintained because of the total absence of slip. Today manufacturers readily agree that these belts do slip when starting, under peak loads and under shock.

Figure 14 is a typical chemical plant installation in which this modern type of drive is economically utilized. As in the case of the pivoted-motor drives, exhaustive data on V-belt drives are now available in manufacturers' catalogs enabling the chemical plant executive to do his own selecting. The same care must be exercised as cautioned above regarding fumes, acids, oil, dust, high temperature, and their respective action on the rubber belt strands and the metal sheaves.

As is usually the case in all departments of industry involving designs and patents, numerous so-called "freak drives" have been developed and placed on the market, and impossible claims have been made for them. Thus we have belts with holes punched through them to permit escape of air, pulleys with punched and drilled rims, cupped belts, grooved pulleys, and a wide assortment of coverings. Out of these a few have proved their worth and have demonstrated ability to transmit power efficiently and economically. From these "successes" the chemical plant official can possibly make a selection, but in general it is usually best to avoid unproved "freaks."

One prominent manufacturer recently pointed out that much of the equipment used in chemical plants can be "sampled" before the final order is given. Belting, pulleys, clutches, couplings, bearings, and other transmission equipment can be installed on an experimental drive and given a thorough trial. But this manufacturer also states that the more important equipment cannot be "sampled" in this way because it might prove too expensive an experiment. Sampling of this sort is really nothing more or less than research. Thousands of users of industrial products throughout the world are continuously, though perhaps unconsciously, performing research tasks of this sort for manufacturers and for one another. The results of most of this "sampling," costing many millions of dollars annually, are available to prospective purchasers.

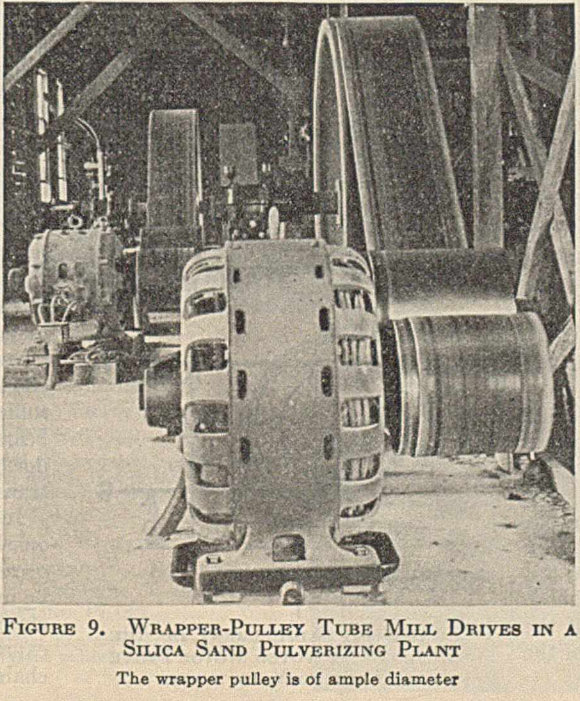


FIGURE 9. WRAPPER-PULLEY TUBE MILL DRIVES IN A SILICA SAND PULVERIZING PLANT

The wrapper pulley is of ample diameter

ELECTRIC *vs.* BELT TRANSMISSIONS

No rule has yet been devised which unerringly determines whether or not any given group of machines shall be driven by individual motors, or through belts and pulleys by a large single motor or from an engine or turbine. As stated by Norman (*3*), "On the whole, electric drive is less efficient than individual belt drive, although the power consumed by idling shafting is a very serious item in many cases."

Where a small motor is used on each machine, the efficiency of each motor is always less than the efficiency of the larger motor such as would be required for driving all of the machines through a group drive. Not only is the group-drive system usually more efficient and economical than direct drives, but the first cost is less. To purchase a separate motor for each machine would obviously be costly. By using the group-drive system, a smaller motor is required than the total capacity of all of the small motors that would be required for individual drives.

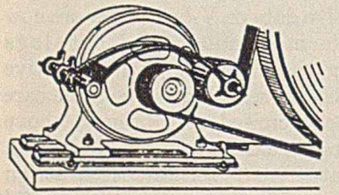


Figure 10. Spring-Operated Wrapper-Pulley Drive for Fluctuating Installations

The advantage of group drives over direct drives may be improved by the use of ball or roller bearings. By eliminating countershafts and running the main shaft at approximately 1000 r. p. m., it becomes possible to drive directly from the main shaft to the machine. Also, by operating at the higher speeds allowed by ball and roller bearings, the size of pulleys, shafting, and belting are reduced. The higher the speeds, the narrower the pulleys and belting necessary. This reduces both the initial cost and the cost of power to the minimum.

Machines driven by individual motors are sometimes allowed to run all day with no attendant near and the machine doing nothing. One of the advantages of individually driven machines is the power saving that accrues from shutting off the motor as soon as the operator has finished with the machine. The current required to run some motors at no load is nearly as much as when fully loaded. Besides, there is the additional loss due to wear, the structural losses due to vibration, and the unnecessary use and cost of lubricants.

As a rough general rule, individual motors should be used on large machines requiring 50 h. p. or more. On portable machines, too, individual drive is usually a convenience regardless of the size of the motor or the percentage of full load. It seldom pays to belt machines that must be moved frequently. Also, where machines operate at full load steadily, or most of the time, electric drive is generally more economical. Electric drive should be used where speeds are too high for efficient or economical belt drive and where overhead cranes interfere with belting.

The cost of repairing electric motors as compared with repairing belt drive is an item to be considered. According to published data concerning a factory in which nearly five thousand electric motors are operated, there were over one hundred burn-outs per year. Each motor averaged 8.92 h. p. The cost of rewinding each burned-out motor averaged $83.80. Nothing was said about the other costs involved—namely, holding up production, idle labor during the breakdown period, etc. The cost of repairing belt drives, on the other hand, is comparatively small because of the simplicity and low purchase price of the parts.

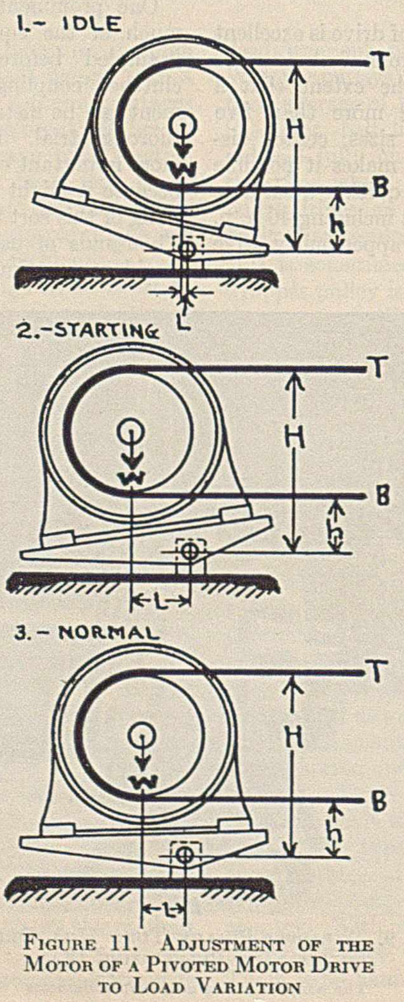


Figure 11. Adjustment of the Motor of a Pivoted Motor Drive to Load Variation

Chain Drives

The development of almost any power transmission device for resisting corrosion is more or less an individual problem depending upon the kind and intensity of the corrosive agent, the temperature, service, speeds, loads, etc. Nearly every problem presents some new condition to be met so that the development of a general type of equipment is not always practicable—for example, chain drives. With the problem thoroughly understood, a chain can doubtless be built which will meet almost any operating condition. That it would meet the user's requirements 100 per cent cannot be absolutely guaranteed because some of the factors are not controllable, and any variable is likely to change the results. One manufacturer states that the trial-and-error method of selection is commonly necessary, the first recommendation being based upon laboratory tests. Certain materials which will withstand the necessary corrosive attack will not withstand the abrasive wear. Combining the two or more requirements makes the problem difficult. Where corrosion is an important factor because of the presence of gases or liquids, stainless steel, monel metal, pure nickel, and bronze are most commonly employed. These noncorrosive chains are for the most part special and naturally are more expensive than standard stock.

Chain drives have become a reality because metals from which chains can be made are stronger than leather, rubber, cotton, hair, and other materials of which belting is made. Thin steel belts are used in Europe to some extent, but according to reports they are unsatisfactory. Great precision is required in aligning the pulleys. Center distances must be almost perfect. There must be no slackness, and steel belt joints are unsatisfactory.

American manufacturers have overcome these objections to the metal belt by converting it into a chain by putting teeth in metal belts, teeth that will actually mesh with metal spur gears and entirely eliminate the creep and possible slip inherent in the metal belt as well as in other belts. The action of the so-called "silent chain" on the driven sprocket is similar to that of an annular gear or rack. In fact, the chain might properly be called an "endless rack gear."

The modern silent chain drive is in some respects a masterpiece of engineering skill. The evolutionary process of continual betterment has resulted in an efficiency which may be maintained as high as 90 to 98 per cent. Silent chains are now made with pins that roll instead of slide. Friction and noise are thereby considerably reduced. It is obvious that, if a steel chain could be made absolutely frictionless, it would never wear out and its transmission efficiency would be 100 per cent. The rolling pin in the silent chain, therefore, bears the same relation to the chain as does the antifriction bearing to power transmission through shafting.

In general, chains should not be used on shock drives. Where elasticity and occasional slip are desired, belts should be used. Where shafts are sufficiently close, gears should be employed. As expressed by one manufacturer, "Use chains when the shafts are too close

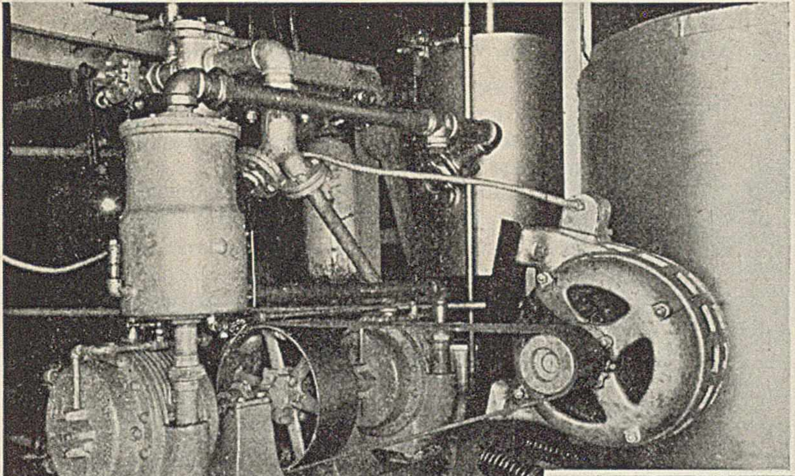
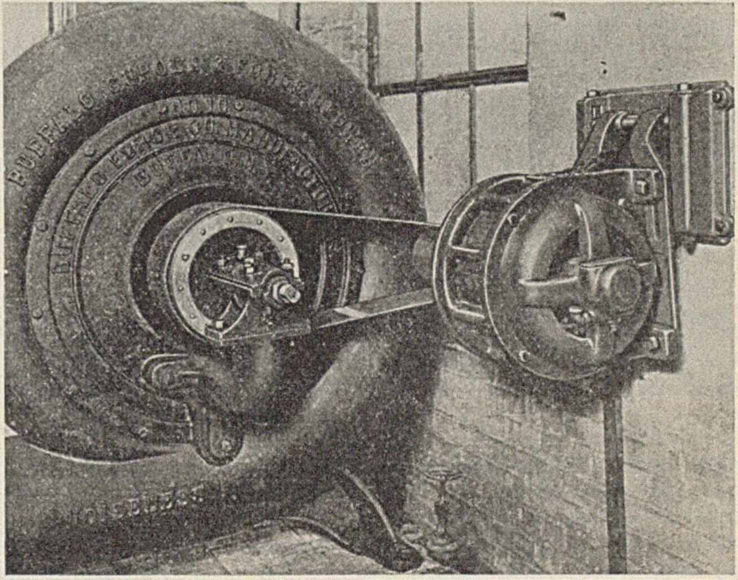


FIGURE 12 (LEFT). PIVOTED 7.5-H. P. MOTOR, COUNTERBALANCED BY SPRINGS, DRIVING A VACUUM PUMP

There is no limit to the possible variety of designs of this type of drive.

FIGURE 13 (BELOW). PIVOTED MOTOR FOR DRIVING A BLOWER

It is mounted on the wall so that proper belt tension is continually maintained; the belt is made of high-grade leather which resists fumes and high temperature.



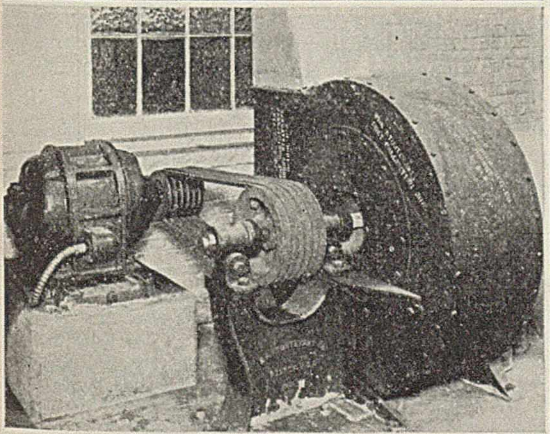


FIGURE 14 (ABOVE). EXHAUST FAN ON DUST COLLECTOR DRIVEN BY SIX V-BELTS

Thirty-horsepower motor; 1750 revolutions per minute.

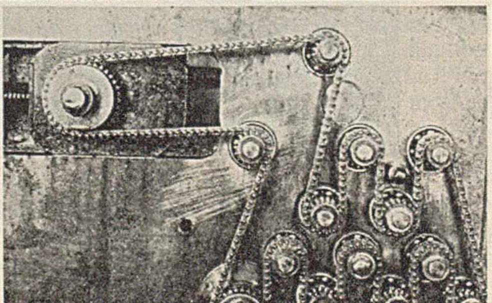


FIGURE 15 (ABOVE). SINGLE SILENT CHAIN CONNECTING FOURTEEN WHEELS

The advantage in using chain drive here is that a constant speed ratio is always maintained; there is no slip and the double face of the chain permits contact on both sides.

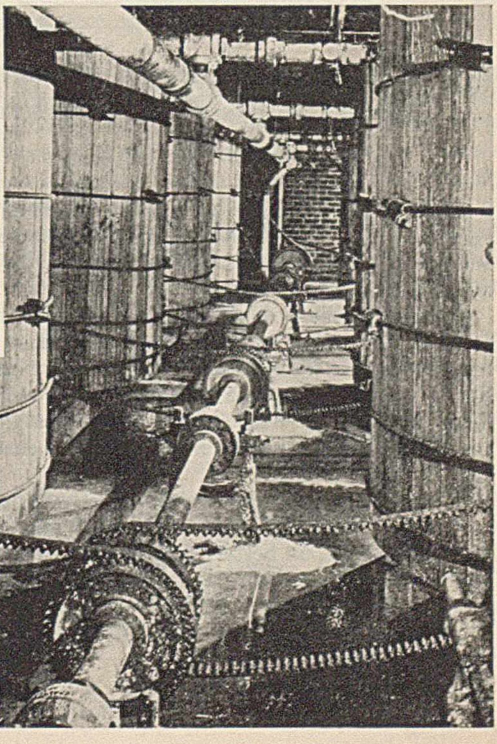


FIGURE 16 (RIGHT). SILENT CHAINS FROM A SINGLE-LINE SHAFT OPERATING PROPELLERS OF AGITATOR TANKS IN A LACQUERING AND ENAMELING PLANT

An important advantage of chains in situations like this is that either the top or the bottom side may be the pulling side.

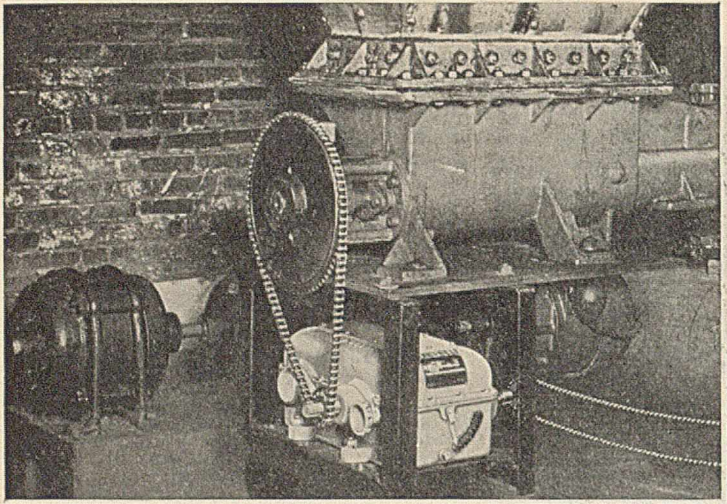
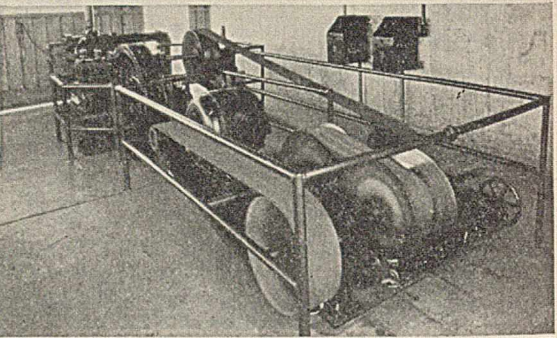


FIGURE 17 (LEFT). ALL-METAL VARIABLE-SPEED GEAR AND ASSORTMENT OF CHAIN DRIVES

The vertical chain drives the feed screw on a powdered coal apparatus.

FIGURE 18 (BELOW). VARIABLE-SPEED TRANSMISSION DEVICE IN PIPE LINE GATHERING STATION



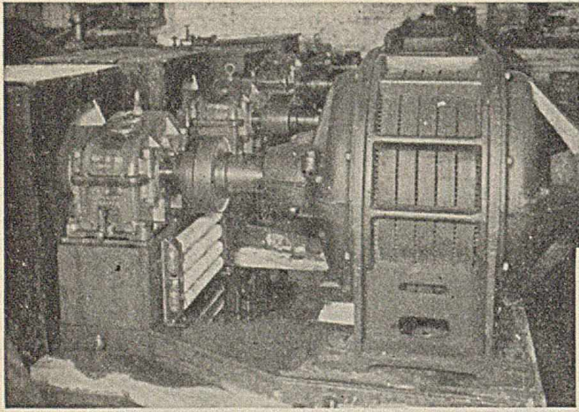


FIGURE 19 (ABOVE). HERRINGBONE SPEED REDUCERS OPERATING JORDAN AND REFINING ENGINES

The reducers are equipped with circulating oil pumps and cooling coils.

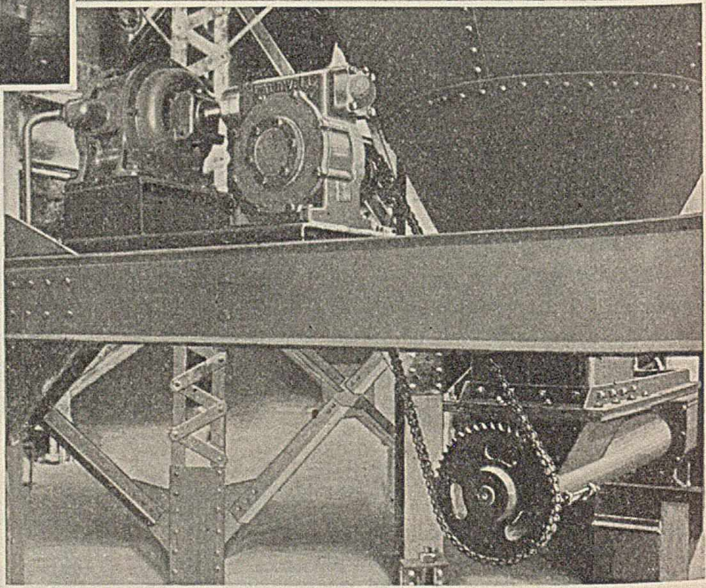


FIGURE 20 (RIGHT). WORM-GEAR REDUCER AND ROLLER CHAIN DRIVING A SCREW FEEDER IN TUBULAR HOUSING FOR HANDLING PULVERIZED LIME

together for a belt, and too far apart for gears." Where an absolutely fixed speed ratio is wanted between the driving and driven shafts, either chains or gears may be used. There can be no slip or creep.

Preferably, chain drives should be horizontal, or nearly so, and the centers should be adjustable so that correct tensions may be maintained. The oblique or horizontal position is always preferable to the vertical, especially if the center distance is fixed. As a chain wears, it elongates. Unless the elongation is cared for, bad chain action results.

Chain and belt drives are similar in that both are at their best when operating horizontally. But because of the fact that belt drives pull better when the top side is slack, many mechanics err in believing that silent chain drives should be operated the same way. If the chain drive is short and if no adjustment can be made for shaft center distances, the tight side should be on top.

Silent chain drives should be kept well lubricated. They are made of hardened steel, but hardened steel is not wearproof. It requires periodic attention. Should the hardened surface once become ruined, it cannot be repaired. Drip lubricators feeding to the inside of the chain close to the pinion are advisable. They should be enclosed wherever practicable to keep out dust, to keep lubricant in, and to protect the operator.

The roller chain is one of the simplest designs for light loads that are not jerky and for speeds averaging about one thousand feet per minute. Two thousand feet per minute is possible but less efficient.

Open-link chains possess the advantage of being self-cleaning. Wood chips, punchings, waste, lint, etc., will not clog them. This type of chain has no right or wrong side. Efficiencies as high as 98 to 99 per cent are claimed for speeds up to 3600 r. p. m. The sprocket ratio should not be greater than 5 to 1. Sprockets should have at least sixteen teeth.

The so-called "block chain" is similar to the roller chain, but less efficient. It is made in widths from $^1/_3$ to 1 inch and pitches of $^1/_2$ to $1^1/_2$ inches. It is seldom operated at a speed greater than seven hundred feet per minute. The sprocket ratio should not be greater than 8 to 1. Sprockets should have at least sixteen teeth.

VARIABLE-SPEED TRANSMISSIONS

There are on the market several successful types of variable-speed transmissions which will convert a given number of pulley revolutions into almost any desired number of revolutions per minute. These devices will vary the speed at will while the machine is in operation. These devices are commonly made of two pairs of cone-faced disks on parallel shafts. The disks are so arranged that they may be moved toward or away from each other on their individual shafts, thereby increasing and reducing the diameter of a V-shaped pulley which is created and which engages a corresponding V-shaped belt. These devices will transmit up to 125 h. p. and will take care of any ratio between 2 to 1 and 16 to 1. Often they are hung from the ceiling out of the way, or they may be incorporated in the machine that is to be regulated. There is also an enclosed design in which the standard internal operating parts are completely enclosed in a cast-iron case. This unit is dust-proof and oil-tight, affording protection in those installations where operating parts must be entirely guarded from water, live steam, chemical fumes, and other destructive elements.

Recently there has been developed a device similar to the above with the exception that a V-chain is used instead of a V-belt. The cone-faced disks are toothed instead of being smooth. This device gives positive transmission; there is no slip. The parts are entirely enclosed and automatically lubricated with oil. Change of oil is necessary but twice a year. This device will transmit up to 10 h. p. and will take care of any ratio between 2 to 1 and 6 to 1.

These variable speed devices are generally employed as countershafts to machines whose shafts are to be operated at variable revolutions per minute. A device of this type cannot be used everywhere economically. With speeds that have to be changed only occasionally, and in machines where the old step cones will do the work satisfactorily, this more expensive device will prove unprofitable.

SPEED REDUCERS

Speed-reducing mechanism of some sort is a necessity today to connect the high-speed driver with the slower speed production machinery. The advent of the electric motor and the steam turbine, both high-speed and economical, has greatly increased the importance of intermediate power transmitting mechanism.

In years gone by, ordinary systems of gearing were used for speed reduction, together with belting. Space was then less expensive than it is today. The modern method is to utilize every square foot of floor space in connection with agitators, mixing vats, pulverizers, grinders, driers, attrition mills, etc. Where the speed of the chemical machine is low and that of the motor high, and where a wrapper-pulley drive or other method of speed reduction would prove impracticable, a suitable reduction gear is necessary. Speed ratios up to 50 to 1 and even higher may be attained by means of belting and pulleys. Higher ratios, such as 100 to 1, 500 to 1, etc., are attained by means of special gear reduction units. Whatever the problem may be, whether the machine is to be driven at high speed or low, whether the requirements are exacting or not, the many designs of speed reducers on the market at the present time make it possible almost invariably to select the reducer that will prove most efficient and economical. Sometimes the speed must be variable, sometimes it must be absolutely constant, and again only a fractional part of a revolution is wanted. If the latter is desired, a special design may be necessary.

For the larger reductions of power, as in steam turbine installations, herringbone gears are commonly used. These are strong and efficient, and make but little noise. Reduction ratios go as high as 8 to 1. Where a greater reduction ratio is desired, it is necessary to use two or more sets of gears and reduce the speed in two or more steps.

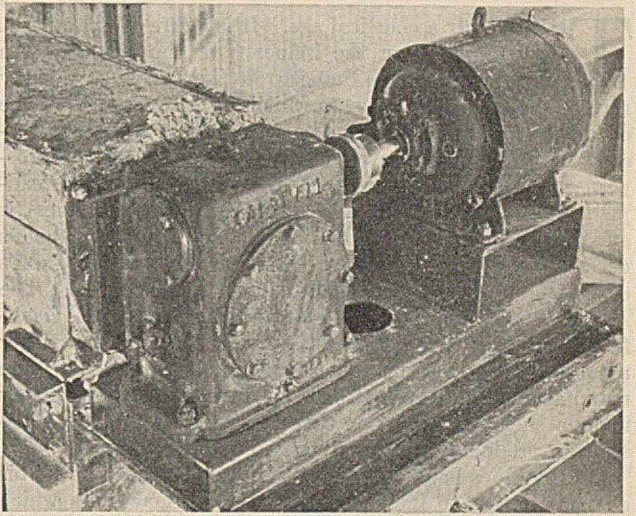


FIGURE 21. A 5 H. P. 1140 R. P. M. BALL-BEARING MOTOR COUPLED THROUGH A WORM-GEAR SPEED REDUCER TO A 12-INCH LIME-HANDLING SCREW CONVEYOR

Cast spur gears were once used for reducing speeds. Thick grease was applied between the teeth to serve as a lubricant and to reduce noise. Today even the most lowly agitator and mixer is equipped with accurately cut tooth spur gears which are entirely enclosed and automatically oiled. The modern drive is much more efficient, long lived, and economical. These spur-gear reducers average less in cost than the herringbone type but are noisier. Single units are made that effect a reduction as high as 500 to 1. Less space is occupied. The ingoing and outgoing shafts are in one straight line, which is a convenience and a space-saving feature. These units are entirely enclosed, keeping out fumes, dirt, and dust, and permitting operation in oil.

The worm-gear type of reducer is perhaps the best known and most common of all reducers. The greater the reduction (as is true of other types), the less the efficiency. The efficiency of worm gearing is dependent largely upon the helix angle. The greater that angle, the greater the efficiency (up to approximately 42°). A single worm-gear reduction unit may be used for ratios up to 80 to 1. For high ratios double worm-gear units may be employed, or various units may be coupled in series. In this way any reduction is possible up to 10,000 to 1 or even higher. There is no limit.

Most of the modern speed reducers are enclosed and are operated in a bath of oil. On drives of importance it is advisable to use flexible couplings on the ingoing and outgoing shafts for reasons that have already been made clear.

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(2) Natl. Safety Council, *Safe Practices Pamphlet* 52 (1927).
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Chemical Securities

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THIS is truly a chemical age. It is a rare company that is divorced from the influence of the chemist. An examination of the stocks on the exchange quickly reveals the tremendous power which lies in the hands of the chemist. By the discovery of new materials and new processes or by great improvements of the old, he brings prosperity to some businesses and obsolesence or radical readjustments to others. Because practically every business is affected by the chemist, it becomes difficult but nevertheless necessary for us to draw some line as to the types or groups of companies which we shall include as chemicals. The *Bulletin of the New York Stock Exchange* includes in its classification: heavy chemical manufacturing companies, fertilizer manufacturers, glass manufacturers, and drug and cosmetic manufacturers. Classifications by other bodies justifiably include such companies as those engaged in producing petroleum products, rubber, rayon, and allied products.

On the other hand, the security analyst usually limits his chemical group to include only those manufacturers which produce chemicals used largely as raw materials by other industries. This includes the alkalies, alcohols, carbon black, explosives, fertilizers, sulfur-manufacturing companies, and a group of the large miscellaneous manufacturers. The author will use this latter type of classification. In the analysis of securities there are at least five well-recognized factors which form the basis for judgment as to their investment merit. These, listed in the order of their importance, are: character or type of the business, management, earnings, financial strength, and dividend policy. A brief review of these important factors will reveal the present strength of the chemical industry as a whole.

If we were in a position to develop an ideal type of business, we would have difficulty in finding one which would more admirably fulfill the requirements than does the chemical industry. Its products are definitely of a repeat nature. The industry is still young and growing, as is shown by all available statistics of production. One evidence of this growth, as well as present status, is revealed in recent employment figures. The index of the Federal Reserve Board for employment in December, 1933, adjusted for seasonal variation, for chemicals and drugs stood at 107.6—that is, 107.6 per cent of the average for that industry for 1923–25. The significant fact is that this is the highest percentage in the entire list, which includes all the principal industries in the United States. This splendid showing of the chemical industry is even more significant when allowance is made for the improvements in technic and processes of manufacturing which have reduced the demands for labor in the industry.

The management of chemical companies is generally characterized by the word "progressive." In addition to those traditional characteristics which are usually thought of in connection with good management, such as absolute honesty with the public and its own organization, humanness, technical ability, etc., this industry is blessed—perhaps not too well, but relatively more than others—with the willingness to spend money on research. The investor is more fully aware than ever before that it is dangerous to put money into industries or companies which despise or ignore research. Research is the advance guard in the procession of progress. Investors are placing their faith in the profession of research work. They are depending upon the management to see to it that this work goes on with undiminished effort. Investors feel there is such a high standard of professional ethics permeating the industry—including the management—that they are not misplacing their confidence in this respect.

The chemicals are receiving praise on every hand for their ability to maintain earnings throughout this depression. A recent calculation shows that eleven chemical companies, which are representative of the industry and whose stocks are included in an index of chemical security prices, were able to earn, for the great depression year 1932, 5.3 per cent on their total stated capital and surplus. It appears from available returns that this will be increased to around 8 per cent or more for the year 1933. This compares with recently published figures[1] of −0.2 per cent as an arithmetic mean of similarly calculated earnings of fifty different manufacturing corporations for 1932. This young, progressive, chemical industry as a whole has shown itself to be depression-resistant if not entirely depression-proof. It has maintained relatively more stable earnings than any other basic industry.

The chemicals are also favorably situated as to the prospects for future earnings. They have the advantages of a rapidly growing industry, abundant raw materials, and a high degree of mechanization with a consequently smaller proportion of labor costs. The recent recommendation to shorten hours and raise wages farther, if carried out, would not be a serious hurdle or handicap to this industry. With further improvement in business, which is certain to come, it is reasonable to expect further acceleration in net incomes.

In considering the fourth factor—financial strength—we are again impressed with the favorable position of this industry. Most of the enterprising companies are blessed with simple capitalizations, with little or no funded debt, and a freedom from bank loans. Furthermore, many of them are amply supplied with funds to provide for further modernization or expansion. This is particularly important at this time when it is generally difficult to secure money from the public through the issuance of new securities.

Little need be said about the dividend policy of the companies in this industry. They have been generally acceptable to the investor and show a willingness on the part of management and directors to act fairly in their positions of trust as between stockholders, the public, and employees. Dividends have been preserved throughout the depression in most cases, and, while mostly earned, there has been an ability and willingness to maintain them by using some of the accumulated surplus on hand.

The conclusion regarding the foregoing five points is that the chemical industry represents a favorable field for the investment of funds. The only difficulty involved is that investors have so generally recognized this fact that security prices of chemical companies have been bid up to high levels. The price index of the eleven chemical stocks, excluding fertilizers, now stands at about 150 per cent of the 1926 average which is relatively higher than any other major group of stocks except for the very new industry—aviation. This is surely a tribute as to how investors look upon the chemical industry and its ability to continue to develop over the next decade or more. In order that we may obtain a somewhat closer view of this field of securities, the prospects of the different groups mentioned earlier will be discussed.

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[1] Epstein, R. C., *Annalist*, **43**, 372 (March 2, 1934).

ALKALIES

Since the ending of the curtailment agreement under the NRA code in January, textile manufacturers have been stepping-up operations which has in turn resulted in increased demand for such chemicals as chlorine, acetic acid, caustic soda, aqua ammonia, and sodium phosphate. The demand from table glassware and liquor bottle manufacturers for soda ash and arsenic is holding steady. Demand from plate glass manufacturers has been increasing in order to supply the increasing call for their product from the automobile industry. It is expected that the total shipments of alkalies for the first quarter of 1934 will exceed the fourth quarter of 1933, but will be somewhat lower than the third quarter of 1933.

The demand for alkalies has remained relatively more firm during the depression than most basic chemicals. This is accounted for by the relative stability of the main consuming outlets. This would generally be regarded as an indication that the group could not look forward to a marked expansion with the return of prosperity. In this case, however, this may hardly hold true because of the opening of new avenues of consumption. For example, we may note the development of the glass container industry and the further marked progress of the rayon industry. An example of the prominent securities in this group are Mathieson Alkali Works and Westvaco Chlorine Products. Mathieson Alkali Works is building a new $7,500,000 plant in Louisiana which may have a great effect upon the industry. It will be completed in 1935 and will produce soda ash, caustic soda, and other chemicals in competition with Allied Chemical Company's subsidiary, the Solvay Process Company. It is likely that this will result in some realignment of the business in this field. It is also possible that both prices and earnings of this group may be affected.

ALCOHOL

The principal consuming industries of solvents which are the chief outlets for alcohol are registering a decided gain in their business over a year ago. Rayon producers, which set all-time high records of production for 1933, are still being pressed for shipments. Lacquer sales are, of course, much improved on the strength of the improvement in automobile production. Also, the general paint and varnish business reports improvement of 50 to 100 per cent over a year ago. Plastics, films, and synthetic resins are also showing gains over a year ago. The unusually cold winter in the northeastern part of the country has resulted in large sales of antifreeze mixtures which consist principally of denatured alcohol. All these demands, coupled with the fully 10 per cent higher rate of output in the chemical industry as a whole, have resulted in the use of considerably greater quantities of alcohol and solvents.

The difficulty in this group lies in the weakness in alcohol prices since the fall of 1933. This has occurred in spite of increasing sales and decreasing warehouse stocks. Since the Government has removed the quotas on manufacture, it is likely that the competitive situation will grow worse. It is also expected that additional competition will come from the producers of liquors when that industry has once caught up with the accumulated inventory demand. Neither the American Commercial Alcohol Corporation nor the U. S. Industrial Alcohol Company has yet engaged in the production of alcohol for beverage purposes. In fact the U. S. Industrial Alcohol Company sold off those properties to National Distillers Products Corporation. Commercial Solvents Corporation, on the other hand, stands in a position to make maximum profits in either field because it can alternate its production between the different kinds as demand dictates. Because of the uncertainties facing this division, other chemical stocks appear more attractive at this time.

CARBON BLACK

The outlook for earnings of the producers of carbon black is brightened materially by a combination of conditions. Tonnage export sales scored sharp advances of more than 50 per cent in 1933 over 1932. Estimated domestic consumption for 1933 is the highest for any year since 1929. Increased production of tires to meet the large original equipment need of the automobile industry has called for larger shipments of carbon black. This demand should continue at a high level. It is expected that there will also be an increased call from tire manufacturers as tires are purchased this spring for replacement. Also demand has arisen from the printing-ink manufacturers as an ultimate result of the increasing need for more advertising and general printing. Another important factor for Columbian Carbon Company and United Carbon Company, the most important producers in this group, was their close to 20 per cent increase in sales of natural gas for 1933 over 1932.

It is expected that the NRA code which went into effect February 19 will assist in maintaining production control. The power to decide on increases in plant capacity in the industry is placed in the hands of the administrator and thus puts a check on additional excess capacity. Price movements of carbon black are also favorable to this group. There was an increase of 0.5 cent a pound on February 15 on less than carload lots of ordinary grade in order to offset the higher operating costs resulting under the NRA code which was going into effect February 19. This followed a rise of approximately 1.25 cents a pound on the new carload schedules of January 1, which were quoted on a delivered basis according to zones, instead of the old prices f. o. b. works. These boosts in prices have brought them up from 2.75 cents a pound to 4 cents, the highest since 1931. The outlook for this division is satisfactory but the equities of the companies have already registered substantial price appreciation, and they would appear more attractive on recessions.

EXPLOSIVES

Revival of large sales by the producers of explosives awaits activity in the construction industry which is the largest type of user of the products of the companies in this group. Actual work on the PWA projects has not yet begun in a big way, and there has been no pick-up in activity in the important copper mining industry. However, CCC work has given rise to some new orders which, together with the increased demand from lumbering, coal mining, and other mining, has resulted in a 16 per cent increase in orders for 1933 over 1932. The gain for December, 1933, over December, 1932, was 29 per cent. Sales of products other than explosives are showing considerable increases since a year ago for the principal specialized manufacturers in this group—Atlas Powder Company and Hercules Powder Company.

Sales of products of these companies other than explosives have been showing decided improvements. Atlas Powder Company reported for 1933 a rise of as much as 43 per cent in the sale of such products as lacquers, leather cloth, and other coated fabrics. The sales of the Hercules Powder Company have been similarly boosted. The price advances, which continue to characterize the naval stores markets, are also favorable factors in this industry. It appears that the equities of the companies in this group have not yet been bid up to discount the long-term prospects. In view of their potential future earnings and the financial condition of the companies, their stocks appear relatively attractive at this time.

SULFUR

The important consuming industries of sulfur—principally fertilizers, textiles, and the paper industries—have been showing very marked trade increases since a year ago. The production of sulfur for the first quarter of 1933, as revealed by Texas tax figures, was 116,500 long tons, while the third-quarter production was 322,200 long tons. The third-quarter figures are nearly double those of the first quarter of 1933 and are 66 per cent more than the third quarter of 1932. Exports of sulfur have also increased sharply since the low point of last February. According to the figures of the Department of Commerce, the total exports in long tons for 1933 were 522,045 or about 50 per cent above the 351,509 for 1932. The 1933 exports are above 1931 and only about 14 per cent below 1930.

It is expected that, as further improvement takes place in practically all business activity, there will be a continuation of the upward trend of this division. However, it should be observed that the earnings of this group are already unusually high. It is estimated that the two largest producers of sulfur—namely, the Texas Gulf Sulphur Company and Freeport Texas Company—earned around 20 per cent on their stated capital and surplus for 1933. The high rate of profit of the units of this group for the present and immediate future gives them a considerable speculative merit, but the uncertainties concerning the life of ore reserves and possible competition from new beds make the longer term values open to question.

FERTILIZERS

For more than a decade the fertilizers have presented the only dark picture among groups usually considered as chemicals. The earnings records of the common stocks of the larger units in this division for the last ten years have not presented an attractive picture. Losses have too frequently predominated. Out of all the important units in this group, which includes American Agricultural Chemical Company, International Agricultural Corporation, Davison Chemical Company (now in receivership), Tennessee Corporation, and Virginia-Carolina Chemical Corporation, only the Tennessee Corporation, which has a relative diversity of products, has been able to pay any dividends since 1926. However, early reports indicate that the fertilizer companies may be able again to show profits by the end of this fiscal year which will end on June 30, 1934.

The prosperity of the fertilizer companies is closely linked with that of the farming industry, and, when the latter ran amuck in 1920, it left the fertilizer industry in bad condition. Excessive plant capacity resulted in intensive competition, persistent price cutting, too liberal credit policies, and wasteful selling practices. It is hoped that operation under the NRA code will bring some degree of order and eliminate many of the past weaknesses. Also, although perhaps temporarily, it seems that the acreage reduction scheme, bringing with it higher prices for agricultural products, will result in increased use of fertilizers by farmers who will try to produce maximum quantities per acre and secure the benefits which accrue from the better price. Based upon this assumption, fertilizer companies should show considerable improvement in their business during the next year.

However, there remains the threat that the Department of Agriculture may take action which will indirectly penalize those farmers who attempt to increase their yield materially with fertilizers. If such a thing develops, it cannot greatly affect 1934 business but would be a longer run factor. In any event, the farm situation and outlook is far from clear, and it is almost impossible to arrive at any sound opinion as to what to expect in this field. However, based purely upon what we see at the present time—that is, improving farm prices, higher fertilizer sales, the possibility of sharp recovery of earnings with continuance of better sales volume—it appears that there is considerable speculative merit to the better situated equities in this group.

MISCELLANEOUS

In addition to the specialized groups considered above, there are many companies such as Air Reduction Company, Allied Chemical and Dye Corporation, E. I. du Pont de Nemours & Company, Dow Chemical Company, Monsanto Chemical Works, Union Carbide and Carbon Corporation, American Cyanamid Company, and others which supply a great variety of chemical products. The du Pont Company has an unusually wide variety of interests. In the order of their importance for the year 1932, the company showed volume of business in the following lines: (1) dyestuffs, etc., (2) pyroxylin and paints, (3) inorganic and heavy chemicals, (4) rayon, (5) Cellophane, (6) explosives, (7) electrochemicals and specialties, (8) du Pont Viscoloid, (9) synthetic ammonia products and methanol, and (10) smokeless powder. In addition to these products, they hold through the General Motors Securities Corporation 10,000,000 shares or 23 per cent of the common stock of General Motors from which it (du Pont) received approximately 30 per cent of its net income for 1933. In other words, it holds about nine-tenths share of General Motors for each share of du Pont outstanding. Du Pont is especially noteworthy for its development of new products, some of the more recent additions of which are Cellophane, Duprene, Dulux, Pyraheel, Doe-Tex, Dynax, Pyralux, and Triclene. All these factors, coupled with capable family management, make du Pont a favorite among investors.

The Allied Chemical and Dye Corporation also has wide diversification of products including coal-tar products, industrial acids, dyestuffs, alkali and soda products, nitrates, and coke. Its plant and laboratory facilities are of the most advanced type, and it is an established policy of the company to make substantial appropriations for research activities and to maintain a highly efficient chemical and engineering staff. The earnings on Allied Chemical common have dropped from a high of $12.60 a share in 1929 to a low of $3.62 in 1932 and were $5.50 for 1933; it is expected that earnings will climb farther as business returns.

Union Carbide and Carbon Corporation is another large unit which falls in the miscellaneous division, although this company is sometimes linked with Air Reduction and treated under the head of welding supplies. The demand for oxygen and acetylene has been relatively well sustained in spite of the inactivity on the part of the railroads and other normally heavy users of these gases. The prospective growth in sales of these companies in answer to greater activity in all metal-working trades should result in relatively greater profit margins for the producers, since the burden of semifixed costs would be distributed over a larger unit base. Union Carbide and Carbon Corporation is especially strong financially and has been able to make many investments during the last few years which should prove of great benefit from an earnings standpoint.

Monsanto Chemical Works has acquitted itself admirably by having earned more on its common stock during 1933 than at any time in its history. It reported a net of $5.14 a share on 432,000 shares outstanding against a previous mark of $4.25 a share on 398,286 shares outstanding in 1929. This has been recognized by the public by having its common shares pushed up to the highest level in its history—that is, after account is taken of the split-up.

American Cyanamid Company has been rather adversely affected because of its heavy interest in fertilizers and chemicals used in the nonferrous mining industries. However, the company is endeavoring to balance its operations by wider diversification, one move of which is the building of the new $7,000,000 alkali plant at Corpus Christi, Texas, jointly with the Pittsburgh Plate Glass Company. The prospects for the company are brighter, and the stock has considerable speculative merit.

Because of their generally wide diversification of products and activities, most of these miscellaneous chemicals may be called the "investment trusts" of the chemical group. These units will benefit from any or all improvements which take place along the business front. As conditions move toward normal, the net earnings of these companies are expected to improve sharply. They have all the advantages of being in a young, growing industry and are not afraid to spend money for research. Who today can predict what may come out of our laboratories as a new development which may create a profitable new branch of business? As a matter of fact, investors, by their attitude toward these stocks, are expecting something like this to happen. It offers a challenge to men who are operating in the laboratories.

CONCLUSIONS

An analysis of the principal factors affecting chemical securities shows that they answer the requirements exceptionally well for the ideal investment, that this fact has become commonly recognized by investors, and they have correspondingly bid the more attractive issues up to high levels. Nevertheless, we are distinctly bullish on good chemical securities for the following three reasons: (1) The chemical industry is the industry which should profit most from new inventions and discoveries. It is where the electrical industry was about twenty years ago. (2) Chemical securities should be one of the groups to benefit most from inflation, when, as, and if it comes. This would be true because of the industry's large holdings of natural resources. (3) The market for chemical securities is in the right sector of the business cycle to profit from the inevitable improvement in business as a whole.

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Formamide

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Formamide is a new chemical to industry. Its freezing point is near that of water, its specific heat is unusually high for an organic liquid, and its dielectric constant is higher than that of water. It has unique solubility characteristics. It is adaptable to novel syntheses and may be used as a solvent in electrolytic deposition.

FORMAMIDE in the past has not been available to the chemical industry but a process has been developed which makes it available in commercial quantities. Here are described some of the properties and reactions discovered incidental to this work. Formamide was early prepared by the dehydration of ammonium formate (*7*) and later by the direct synthesis from carbon monoxide and ammonia (*10, 16*). It was known to condense with formaldehyde in the presence of potassium carbonate to give *n*-hydroxymethylformamide, $HCONHCH_2OH$, and in the presence of acid condensing agents to give methylenebisformamide, $CH_2(NHCOH)_2$ (*9*). With tannin and formaldehyde it reacts to give methylenetanninformamide, $CH_2NHCOHC_{14}H_9O_8$ (*22*). The equilibrium constant (K) of $CO + NH_3 \rightleftarrows HCONH_2$ at several temperatures was found to be as follows:

TEMP.		$K = \frac{P_{CO}P_{NH_3}}{P_{HCONH_2}}$	TEMP.		$K = \frac{P_{CO}P_{NH_3}}{P_{HCONH_2}}$
° C.	*° Abs.*		*° C.*	*° Abs.*	
127	400	20	200	473	960
177	450	321	227	500	3130 (*14*)

PHYSICAL PROPERTIES

Pure formamide is a colorless, odorless, hygroscopic liquid. The commercial product may have a slight odor and a somewhat sour taste. In appearance and feel it resembles glycerol although it has a lower viscosity. Other properties are given in Table I.

Formamide is not unlike water in some respects. The unusually high dielectric constant has made it of interest as an ionizing solvent and as a medium for the electrodeposition of metals. Some binary salts as solutes have a higher coefficient of ionization in formamide than in water; but strong acids, such as tribromoacetic, are little ionized in formamide (*23*). Salts which form hydrates form solvates with formamide (*5*).

TABLE I. PHYSICAL PROPERTIES OF FORMAMIDE

Melting point, ° C.	2.55 (*19*)
Boiling point, ° C.	210 decompn. (*16*)
Dielectric constant (E), CGS units	84 (*24*)
Refractive index	1.44900 (*16*)
Sp. heat at 19° C., joules/gram/° C.	2.306 (*25*)
Heat of combustion (liquid), gram. cal./gram mol.	134,900 (*13*)
Heat of fusion, gram cal./gram	38.47 (*2*)

Vapor pressure:

° C.	*Mm. Hg*	*° C.*	*Mm. Hg*	*° C.*	*Mm. Hg*
129.4	29.7	166.4	170.5	188.4	355.9
143.3	70.4	174.9	231.2	192.4	406.1
153.1	103.4	179.3	265.9	210.7[a]	760.0 (*16*)
160.5	138.7				

Density:

° C.	$d_{4°}^{t°}$	*° C.*	$d_{4°}^{t°}$
18	$1.13510 \pm 2 \times 10^{-5}$ (*19*)	35	$1.12068 \pm 2 \times 10^{-5}$
20	$1.1339 \pm 1 \times 10^{-5}$	50	$1.1078 \pm 2 \times 10^{-4}$
25	$1.12918 \pm 1 \times 10^{-5}$		

Surface tension (air):

° C.	*Dynes/cm.*	*° C.*	*Dynes/cm.*
18	58.53 (*19*)	35	57.11
20	58.35	50	55.72
25	57.91		

Viscosity:

° C.	*Cgs. units*
18	0.03970 (*19*)
20	0.03764
25	0.03302

[a] Extrapolated boiling point.

In a study of the electrodeposition of metals from formamide it was possible to deposit the respective cations from formamide solutions of copper sulfate, copper chloride, lead chloride, zinc chloride, zinc oxide, and tin chloride, while no deposits were obtained from chloride solutions of nickel, cobalt, iron, aluminum, and magnesium (*17*). Deposits of alloys of aluminum with iron and with zinc were obtained although pure aluminum could not be deposited (*1*).

Because of its solvent action (Table II) formamide has been found useful in the determination of absorption spectra and optical rotation. Its convenient freezing point has made it useful in the determination of molecular weights.

Table II. Formamide as a Solvent[a]

Component	Solubility
Albumin	Insoluble
Albumoses	Dissolves
Alcohol	Miscible in all proportions
Alkali metal acetates	Very soluble
Alkali metal carbonates	Practically insoluble
Ammonium acetate	Very soluble
Ammonium chloride	Practically insoluble
Ammonium formate	Miscible in all proportions at temp. above 115° C.
Ammonium sulfate	Very insoluble
Aniline	Completely miscible
Benzene	Slightly soluble
Benzene, chloro-	Insoluble
Benzene, nitro-	Insoluble
Cellulose acetate	Dissolves and gelatinizes
Chloroform	Slightly soluble
Copper acetate	Moderately soluble
Copper carbonates	Slightly soluble
Copper chlorides	Moderately soluble
Copper sulfate	Moderately soluble
Dimethyl sulfate	Completely miscible
Ether	Slightly soluble; forms a miscible, dense liquid
Formaldehyde polymer	Dissolves at 100–150° C.
d-Fructose	Dissolves
Gasoline	Immiscible
Glucose	Equimolar proportion forms clear soln. on heating
Hydrocarbons, aromatic	Insoluble
Insulin	Soluble
Alpha-lactose	Dissolves
Peptone	Dissolves
Petroleum oil	Insoluble in hot formamide
Phenol	Completely miscible
Propionic acid	Completely miscible
Starch	Dissolves
Water	Completely miscible
Zinc acetates	Moderately soluble
Zinc formate	Moderately soluble
Zinc sulfate	Moderately soluble

[a] Data compiled from miscellaneous sources.

Reactions

Formamide may be thermally decomposed according to the following two main reactions:

$$HCONH_2 \longrightarrow HCN + H_2O \qquad (1)$$
$$HCONH_2 \longrightarrow NH_3 + CO \qquad (2)$$

Boiling formamide, at atmospheric pressure, decomposes at the rate of about 0.5 per cent per minute (*16*). In the liquid phase and in the absence of a catalyst, reaction 2 predominates.

Formamide can be vaporized with little decomposition (less than 1 per cent) provided the liquid formamide is contacted in a finely divided condition with surfaces heated to a temperature between 200° and 370° C. and accumulation of liquid formamide is avoided (*3, 11, 16*).

In the presence of suitable catalysts such as coke, thoria, and pumice, reaction 1 may be favored at a temperature between 400° and 600° C. to produce hydrocyanic acid yields in excess of 90 per cent (*6, 8, 12, 15, 16*). In the catalytic dehydration of formamide there is a critical temperature around 650° to 700° C. where a secondary reaction sets in which causes rapid rise in temperature and a very low yield of hydrocyanic acid, probably because of the hydrolysis of the hydrocyanic acid already formed.

Formamide forms numerous addition compounds and substitution products with inorganic salts, for example:

$$SbCl_3 + 3HCONH_2 \longrightarrow Sb(HCONH)_3 + 3HCl$$
$$CuSO_4 + 4HCONH_2 \longrightarrow Cu(HCONH)_2{\cdot}2HCONH_2 + H_2SO_4$$
$$PbCl_2 + HCONH_2 \longrightarrow PbCl_2{\cdot}HCONH_2$$

In the cold, water very slowly hydrolyzes formamide to ammonium formate. Acids or alkalies increase the rate of hydrolysis. A water solution of formamide will react with chlorine to form the explosive compound $HCONCl_2$, according to the equation:

$$HCONH_2 + 2Cl_2 \longrightarrow 2HCl + HCONCl_2$$

In the presence of an inert solvent, sodium will react with formamide according to the following equation:

$$Na + HCONH_2 \longrightarrow HCONHNa + {}^1/_2H_2$$

Formamide acid sulfate possesses an unusually high degree of reactivity. It will readily react with alcohols to form the corresponding formic ester according to the following equation:

$$ROH + HCONH_2H_2SO_4 \longrightarrow HCOOR + NH_4HSO_4$$

In this manner the formic ester of allyl alcohol can be made with yields of 98 per cent without undergoing any of the usual changes encountered in other methods of esterification (*16, 20*).

Ethylene glycol monoformate, which in contact with water readily undergoes hydrolysis, may be made in anhydrous medium using formamide acid sulfate. It might be said that the formamide acid sulfate bears a similar relation in reactivity to formic acid that acetic anhydride does to acetic acid. The amide acid sulfate should react with any compound capable of giving up its hydrogen, for example:

$$PhNH_2 + HCONH_2H_2SO_4 \longrightarrow PhNHCHO + NH_4HSO_4 \qquad (16, 21)$$

This reaction, as well as similar reactions with many of the aliphatic amines, has been shown to take place. In general, this reaction does not take place with those aliphatic amines which are more basic than ammonia.

When formamide is heated with sulfur and a monoaryl amine which may have hydrocarbon substituents in the benzene nucleus, there is obtained a good yield of the mercaptothiazole derivative (*16*). For example, a mixture of one mole of aniline, 1.6 moles of formamide, and 2.66 moles of sulfur was heated in a bomb for 4 hours at 195° C.

The crude mercaptobenzothiazole was extracted with acid, and the thiazole dissolved out with alkali and precipitated with acid, giving 103.8 grams of the purified product, melting at 178° C. The yield based on aniline used was 63.6 per cent. The same procedure was carried out with a number of other aryl amines—e. g., *p*-toluidine gave an 84 per cent yield of the corresponding methyl mercaptobenzothiazole while β-naphthylamine gave 73.7 per cent of mercapto-β-naphthothiazole. Many of the mercaptothiazole derivatives are excellent rubber accelerators.

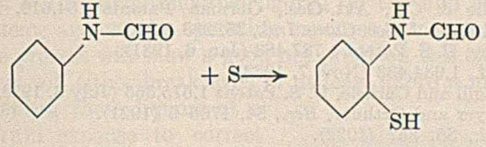
p-Phenylenediamine, *p*-aminophenol, and *o*-aminophenol were heated in a bomb at 195° C. with formamide and sulfur for 4 hours, and the products worked up in the same manner as employed in the case of aniline (*16*). In the case of the diamine, twice the usual amount of formamide and sulfur was employed. All the products were dark-colored amorphous powders, insoluble in water and the usual organic solvents. They dissolved in solutions of sodium hydroxide to give brilliantly colored solutions and were reprecipitated by the action of acids. The *p*-phenylenediamine product gave a green solution in alkaline solution, the *p*-aminophenol product a blue-green solution, and the *o*-aminophenol product gave a brown solution. These alkaline solutions did not give precipitates with iodine as is the case with mercaptobenzothiazoles.

The following is suggested as a possible mechanism for the reaction by which mercaptobenzothiazole is obtained when aniline, formamide, and sulfur are heated under pressure. The first step is the formation of formanilide and ammonia by the action of formamide on aniline:

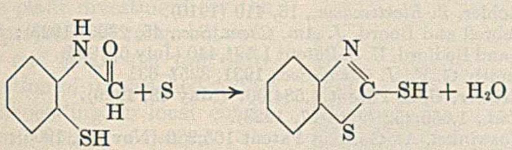
$$C_6H_5NH_2 + NH_2{\cdot}CHO \longrightarrow C_6H_5NH{\cdot}CHO + NH_3$$

Experiments have shown that this takes place at once when the compounds in question are heated gently.

The second step is probably the formation of the *o*-thiophenol of formanilide by the action of hot sulfur on formanilide. This hypothesis is based on the findings of Sebrell and Boord for the mechanism of the formation of mercaptobenzothiazole by the action of sulfur and thiocarbanilide (*18*):



The third step by which mercaptobenzothiazole is formed may then take place as follows:



Preparation

Formamide has been prepared by a great many methods, but only those capable of being readily adapted to laboratory procedure giving relatively high yields are worth mentioning.

Partial Hydrolysis of Hydrogen Cyanide. The earliest approach to the preparation of amides from the nitriles was made when the double compound of formamide and hydrogen chloride was obtained (*4*). This compound can easily be obtained in the following manner which is a modification of the original method (*16*):

> About 300 cc. of dry ether are cooled to −5° C., and into this is passed dry hydrochloric acid gas until approximately 0.5 mole has been taken up. To this is then added 0.5 mole of water. The resultant solution is cooled to −15° to −20° C. One-half mole of hydrogen cyanide is then dropped in while stirring, and the reaction mixture is allowed to stand. The reaction occurs more rapidly at higher temperatures, but, as the reaction is energetic and liberates heat, it is advisable to keep the mixture cool. The ether absorbs the reaction heat and helps to keep the reaction from becoming too violent.

The reaction product, formamide hydrochloride, is insoluble in ether and can be filtered off; it is white and crystallizes in needles. It is very unstable and, upon warming to +15° C., decomposes explosively into carbon monoxide and ammonium chloride according to the equation:

$$HCONH_2{\cdot}HCl \longrightarrow NH_4Cl + CO$$

For this reason its use is limited, as there are few reactions that can be handled with so unstable a compound. The same general characteristics hold for the other halogen acid compounds of formamide.

It is difficult to obtain free formamide from this halogen complex. If an attempt is made to neutralize the halogen acid by means of an alkali, as

$$HCONH_2{\cdot}HCl + NaOH \longrightarrow HCONH_2 + NaCl + H_2O$$

part of the compound is converted to formic acid by the water formed by the above reaction while a considerable portion decomposes into ammonium chloride and carbon monoxide as a result of the heat generated when partial neutralization takes place. A somewhat more satisfactory method is to carry out the neutralization method with a slow stream of dry ammonia. The same scheme to complete a partial hydrolysis of hydrocyanic acid is applicable to sulfuric acid, since a definite hydrate is formed with water, $H_2SO_4{\cdot}H_2O$.

The following method has been used with good success in these laboratories for preparing small quantities of formamide:

> One mole sulfuric acid monohydrate weighing approximately 116.1 grams is cooled to about 0° C., and into this is poured while stirring 1 mole of hydrogen cyanide which likewise has been cooled. The reactants are kept cool to prevent rapid reaction and loss of hydrogen cyanide through evaporation, since the ingredients become warm upon mixing. The resultant product is a clear, colorless liquid. The reactants contained in a 250-cc. flask are kept in a refrigerator at 10° C. After about 2 days, a marked increase in viscosity is noticed, and after the fifth day the contents of the flask may have a consistency of a heavy sirup. Soon after this, white crystals begin to form and after another day the entire reactants become a solid white crystalline mass of formamide acid sulfate, $HCONH_2{\cdot}H_2SO_4$.

This compound is hygroscopic, is stable through a wide range of temperatures, and may be warmed to about 60° C. without noticeable decomposition. At higher temperatures the compound decomposes into carbon monoxide and ammonium acid sulfate.

> To recover formamide from formamide acid sulfate, 1 mole of the latter is placed in a heavy 500-cc. flask and covered with 250 cc. of absolute ether. The crystalline mass is broken up with a glass rod, and a slow stream of ammonia is bubbled through the mixture while it is stirred standing in ice water. As the formamide acid sulfate becomes neutralized, the crystalline component becomes sticky and finally fluid, owing to the liberation of formamide which is only slightly soluble in ether. The neutralization by ammonia is continued until the reaction is complete as shown by the equation:
>
> $$HCONH_2{\cdot}H_2SO_4 + NH_3 \longrightarrow HCONH_2 + NH_4HSO_4$$
>
> The ether is distilled off and absolute alcohol is added to the residue. A little ammonia is bubbled through the alcohol solution to insure neutralization and the ammonium sulfate is separated by filtration. Formamide weighing about 42 grams may be recovered by vacuum distillation. The yield is about 93 per cent.

The time required for the mobile reaction mixture of sulfuric acid monohydrate and hydrogen cyanide to be changed first to a viscous colorless liquid and thence into a white crystalline mass, may be greatly shortened by the introduction of halogen ions which act as catalysts. The reaction rate may be increased to such an extent that it takes place with explosive violence if sufficient catalyst is used. The effect of different halogen compounds is shown in Table III.

Table III. Effect of Halogen Compounds

Amount of Catalyst Equals 0.0000282 Mole of Halide Ion per Mole HCN	Observations	Time for Complete Reaction
Gram		*Days*
0.012 NaF	HF generated did not dissolve in the reaction mixture as readily as did the other halogen acids; change in viscosity was slow	6.5
0.015 NH_4Cl	Change in viscosity was noted after second day, but reaction was slow	5
0.028 NH_4Br	Reaction progressed rapidly; stirring and additional cooling with ice water were required to prevent overheating	20 hr.
0.040 NH_4I	HI produced by reaction of NH_4I with H_2SO_4 was decomposed into iodine; no catalyst action was obtained	7

Purification of Formamide

Formamide can best be purified by high-vacuum distillation, followed by low-temperature crystallization out of contact with moist air (*19*).

It is only with difficulty that a mixture of methanol and formamide can be completely separated. Methanol and formamide react according to the equation:

$$CH_3OH + HCONH_2 \rightleftharpoons NH_3 + HCOOCH_3$$

Both ammonia and methyl formate have higher vapor pressures than either methanol or formamide with the result that, when a distillation of this mixture is attempted, the ammonia and methyl formate pass over with the methanol in considerable quantities in the vapor state and upon condensation recombine with liberation of heat to reform formamide in the distillate.

EFFECT OF FORMAMIDE UPON CONSTRUCTION MATERIALS

Neither oak, cypress, nor redwood unprotected is suitable to have in contact with the formamide, owing to discoloration produced in the formamide. Varnish, Duco paint, Bakelite, shellac, red lead paint, and white lead paint are not satisfactory coatings for wood to be used in contact with formamide.

Allegheny metal subjected to formamide lost approximately 10 times the weight per square inch that aluminum, treated in the same manner, did. Anhydrous and aqueous formamide in contact with air cause a rapid corrosion of brass. Iron rapidly corrodes in the presence of formamide and discolors formamide in contact with it. Lead is relatively little corroded, but the formamide in contact with lead becomes discolored. Aluminum and glass seem to be the most satisfactory materials for storage of the amide. A quantity of several tons of formamide has been in storage over 2 years in glass carboys without any noticeable change in color or melting point. Tests over a shorter period indicate that aluminum is as satisfactory as glass.

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Utilization of Sulfite Liquor

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In so far as is permissible at this time, work is reported which has been conducted during recent years at the Marathon Paper Mills Company, Rothschild, Wis., on the Howard system of treating sulfite liquor.

The work divides into a consideration of main and supplemental processes of treatment. The main process is designed to afford an economical means of treating these liquors to avoid the objections raised to their discharge into streams and to recover products for use at the pulp mill in making fresh cooking acid and as a boiler fuel. The supplemental processes are for making special products.

THE main process for treating sulfite liquor is a precipitation treatment of the liquors with a caustic lime reagent which is carried out in a manner to yield three primary products; (1) a calcium sulfite product for use in making fresh cooking acid, (2) an organic product in solid form constituting the lignin component of the liquor for use as a boiler fuel, and (3) a process effluent containing the carbohydrate constituents of the liquor in altered forms and having a greatly improved character as regards stream pollution. A detailed description of this fractional precipitation has already been published.[1]

The process does not involve evaporation of the liquors and is designed to handle both the strong and dilute liquor drainage from the blow pits. Standard equipment is used throughout the process and consists of raw-liquor storage tanks, reaction tanks, settling tanks, rotary vacuum filter, pumps, piping, and the necessary auxiliary equipment.

This main process results in the removal of about 50 per cent of the organic matter contained in the liquors, and the process effluent will normally show around 85 per cent reduction in oxygen demand as compared with the untreated liquors. The improved character of the effluent as regards stream pollution results: (1) from the removal of the lignin constituent which is the major cause of the oxygen demand and the probable source of whatever toxic effects these liquors may have on fish and fish foods, (2) from the alterations in the carbohydrate constituents taking place under the alkaline treatment of the process, (3) from the treatment having satisfied the lime demand of the raw liquor, and (4) from the effluent being alkaline rather than acid.

If desired, the main process effluent can be given a supplemental heat treatment by which some additional organic matter can be precipitated and removed, thereby yielding a further improved effluent, but ordinarily this additional treatment is not considered necessary.

A number of supplemental processes have been developed for making special products, but the markets for such products are not unlimited and for the present, at least, the main process only should be considered as available to the pulp industry as a means of avoiding objections to discharging these liquors into streams and on the basis of the pulp mill's utiliz-

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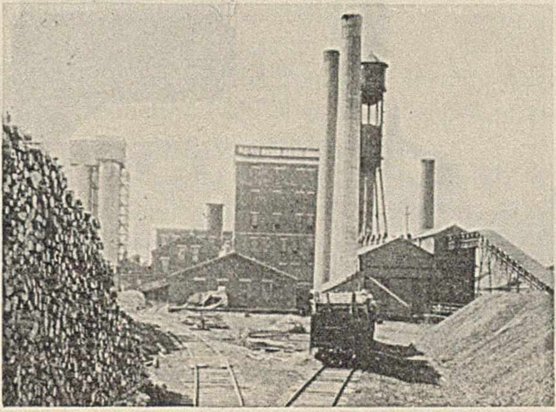
[1] Howard, G. C., IND. ENG. CHEM., 22, 1184–5 (1930).

ing the recovered products for making fresh cooking acid and as a boiler fuel rather than being dependent on outside markets.

The commercial feasibility of the process is generally conceded by independent investigators, and a small commercial unit of the main precipitation process has been in operation for nearly two years in connection with the manufacture of Maratan extract and the development of other special products.

The economics of the process depend on the local conditions at the pulp mill and are determined by the value of the recovered sulfur, lime, and fuel figured on the mill costs for these items against the operating expenses. In some localities the process will show a good net profit on this basis and in others will either break even or at least afford a means of processing these liquors at a minimum expense to correct their stream pollution characteristics.



Pulp Mill and Power House

The plant investment for the main process will range between $1000 and $1500 per ton daily production of unbleached sulfite pulp depending on local conditions and details of design.

Supplemental Processes

The organic matter in sulfite liquor is derived from the noncellulose constituents of the wood and hence consists of a mixture of lignin substance and carbohydrate materials.

The main process makes a separation of the lignin from the carbohydrate constituents and thereby yields more favorable starting materials for the manufacture of refined products.

Research has naturally been directed to the conversion of this lignin material into useful forms and to the recovery of refined carbohydrate products from the main process effluent. This has incidentally necessitated a great deal of work on testing and developing reliable analytical methods for use in sulfite liquor research since in many of the problems the ordinary methods were unsuited to the conditions or lacked sufficient accuracy.

Lignin Material. The lignin product recovered in the main process as a filter cake is a brown, flocculated precipitate which filters readily in its normal alkaline condition above pH = 12.0. This is lignin substance existing in the form of its basic calcium salt of ligninsulfonic acid and constitutes an abundant lignin raw material in relatively pure form. The impurities associated with it are small amounts of calcium and magnesium hydroxides, minor amounts of calcium sulfite and sulfate, and such soluble carbohydrate substances as are contained in the mother liquor of the unwashed cake.

Analysis of the lignin cake with correction for the mother liquor impurities shows a content of organically combined sulfur—i. e., the sulfur over that present as inorganic sulfur compounds—in a ratio of 32 parts of sulfur to around 600 parts of organic matter.

The content of organically combined base—i. e., the base over that present as inorganic compounds—shows a ratio of 84 parts of calcium oxide to 32 parts of organically combined sulfur—in other words, 1.5 CaO to 1 S. Since the sulfonic acid group is monovalent and requires only 0.5 CaO to 1 S, there are other acidic groups present and, as indicated later, of unequal strength but weaker than the sulfonic group.

This lignin material can be dispersed in aqueous solutions by various treatments: for example, (1) by lowering the pH value to below 10.0 through addition of an acid having a strength equal or greater than carbonic acid, which is effective by reaction on the lime component; (2) by addition of salts of weak bases with strong acids which can yield insoluble lime salts such as aluminum sulfate and magnesium sulfate and which are effective through replacement of combined lime and yield solutions which may be either acid or alkaline, depending on the salt used; or (3) by addition of alkali metal compounds such as sodium sulfite, sodium carbonate, sodium sulfate, or sodium hydroxide which render it soluble through conversion from an alkali earth metal to an alkali metal system, and yield solutions of alkaline pH.

Treating the alkaline lignin material with carbonic acid will throw out calcium carbonate and yield a dispersion of ligninsulfonic acid compound containing organically combined base in the ratio between 0.5 and 1.0 CaO to 1 S, thus indicating the removal of calcium from the weakest acid groups.

Lowering the pH of the system further with stronger acids such as sulfurous or sulfuric to a pH around 3.0 yields a dispersion of a ligninsulfonic acid compound having organically combined base in the ratio 0.5 CaO to 1 S, thus indicating the removal of calcium from other weak-acid groups but leaving the sulfonic acid group in its salt form.

Neither disulfite nor sulfurous acid will carry the system beyond this condition as regards the amount of organically combined base present, but sulfuric and other strong acids will carry it to the free ligninsulfonic acid condition.

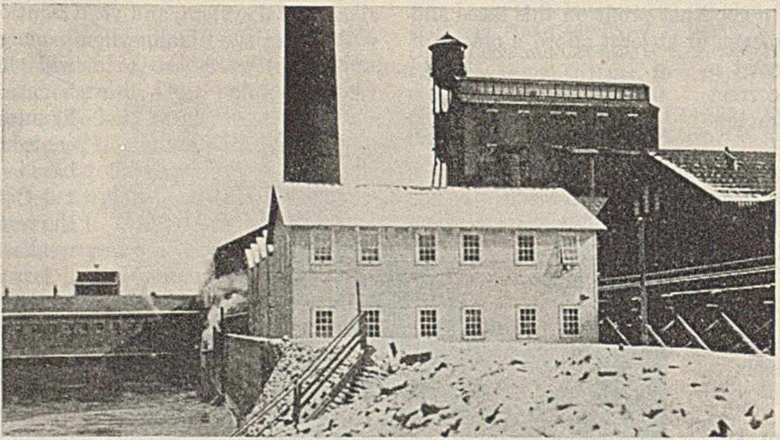
A series of relatively pure calcium salts of ligninsulfonic acid and a free ligninsulfonic acid product can thus be made, and, by double decomposition reactions or starting with the free ligninsulfonic acid, the corresponding ligninsulfonic acid salts of practically all other bases can be prepared, including the salts of toxic bases such as mercury, thallium, copper, zinc, etc.

These salts are noncrystalline and of colloidal character, and in general are soluble in water and are stable so that they can be put out in either dry solid or concentrated solution forms. The lead salt is insoluble as are the salts of some aromatic bases, and some of the bases probably form complex salts.

While this lignin material can be readily solubilized in the sense of forming an aqueous dispersion, the degree of dispersion depends on the procedure employed. Improved dispersions can be prepared by heating at 100° C. or below with disulfite salts during the solubilizing. This normally results in some increase in the organically combined sulfur content but does not represent saturation of the lignin substance with sulfonic groups, since more organically combined sulfur can be incorporated by pressure cooking with disulfite salts.

While the salts of ligninsulfonic acid are relatively stable the free ligninsulfonic acid is not, and tends to go to a gel form. Such gel products can be made by evaporating nearly to dryness a solution of free ligninsulfonic acid which is free from its salts and contains a slight excess of free mineral acid, and then by leaching the residue to obtain the wet gel product. They can also be made by salting out a similar solution of free ligninsulfonic acid with sodium chloride, heating the charge for a period in an open vessel, filtering out the cake, and leaching it to yield the wet gel product.

The physical properties of these gel products can be controlled in the making to range from soft to firm gels with varying water saturation and swelling properties. They are insoluble in acids but are dispersed by alkalies. They can be dried and still retain the property of swelling in water unless overheated or otherwise rendered irreversible. The formation of these gel products is normally accompanied by a loss of organically combined sulfur in comparison with the free ligninsulfonic acid, but whether the gel product is formed as a direct result of the loss of organically combined sulfur or is due to organic changes in the lignin complex is not known with certainty.



Sulfite Liquor Department (Foreground)

When too severe treatment is used in making these gel products, the lignin substance goes to a nonswelling form, and if the salted-out cake mentioned above is dried and heated, reactions take place to yield characteristically black or brown lignin derivatives depending on specific conditions.

When the alkaline lignin product as obtained by the main process is given a steam pressure cook, either with or without the addition of caustic lime, the lignin compound is converted to an acid-insoluble form. This is accompanied by a reduction in its organically combined sulfur content and the formation of calcium monosulfite. There are probably some alterations, but apparently no radical disintegration of the lignin complex.

The properties of the product are controllable by the temperature, time, and other conditions of the treatment and can be made to range from an acid-insoluble lignin derivative (which can be leached to a practically ash-free material of extreme fineness) to an acid-insoluble lignin derivative in gel form which is somewhat analogous to the gel products obtained from the free ligninsulfonic acid.

When stronger alkali conditions are maintained in the pressure cook by the use, for example, of caustic soda, a similar reduction in the organically combined sulfur content takes place, and the lignin complex evidently starts to disintegrate with the formation of an acid-insoluble lignin derivative, and under proper conditions with the formation of material amounts of vanillin and other phenolic derivatives. The process for recovery of such derivatives in refined forms has been worked out and is ready for commercial development.

Carbohydrate Materials. The main process effluent is a complex mixture of organic substances in a solution which is alkaline with caustic lime. These are largely carbohydrate substances originating from the hemicelluloses of the wood, but it contains minor amounts of lignin substance not completely removed by the main process.

Its composition may be roughly classified under the following constituents; (1) residual lignin in the form of its ligninsulfonic acid salt; (2) carbohydrate derivatives of acidic character present as their calcium salt; (3) nonacidic carbohydrate derivatives; and (4) simple organic acids, such as acetic, formic, and lactic, in material amounts and present as their calcium salts.

The residual lignin can be largely removed by a short pressure-cooking treatment of the effluent without using additional reagents, except perhaps the addition of enough caustic lime to sustain the necessary alkalinity throughout the cook. This treatment can be employed when desired to supplement the main process and yield a somewhat improved effluent as regards stream pollution or to remove the residual lignin prior to the recovery of other products. Means are also in the process of development to separate and recover the other constituents of this effluent in purified forms.

Tanning Products

Sulfite liquors are known to have tanning properties, and products made from them have been in use by tanners for many years. These products are ordinarily made from the whole sulfite liquor without apparent endeavor to select the organic constituents possessing the tanning properties and to separate them from useless constituents, with the result that such sulfite liquor tanning products have been handicapped by containing excessive amounts of materials which have little or no tanning value and which tend to accumulate and slow up penetration, cause undesirable fermentation in the yard, and impair the color of the leather.

It is the ligninsulfonic acid constituent of sulfite liquor which possesses tanning properties, and, while its composition is not identical with the natural vegetable tanning, it is well established that it fixes firmly to the hide substance and is very resistant to washing out.

Maratan extract is a tanning product which has been made commercially for nearly two years. It is prepared from the ligninsulfonic acid material obtained in the main process and hence is substantially free from the objectionable constituents of the sulfite liquor. It is natural that a tanning product made from such purified lignin material should possess superior properties, and its successful commercial use in the leather industry has confirmed this.

Its value to the tanner lies not only in its real tanning properties but in its effect on surface conditions of the hide, reduction of astringency, lightening of color, dispersion and stabilization of the vegetable tannings, and hence reduction of yard sediment.

Because it stabilizes other tannings, it is possible to tan with a combination of chrome liquors, Maratan extract, and vegetable tannins in the same bath.

Ligninsulfonic acid compounds have a strong affinity for basic dyes, and Maratan extract can be used as a mordant on textiles and leather.

Conclusion

This research work has laid a broad and sound foundation for making a variety of products from sulfite liquors. These products will find uses in agriculture and in many industries, and their commercial development can be accomplished because of the abundance and relative cheapness of the raw material, the specific properties of both the lignin and the carbohydrate products, and the various marketable forms in which they can be made available.

Maratan extract is the only one of these special products which has arrived at commercial production but others are either under development or are ready for full-scale production. Patents and patent applications have been taken out in the United States and foreign countries.

Acknowledgment

Acknowledgment is due the Marathon Paper Mills Company and particularly D. C. Everest, vice president and general manager, for making it possible to carry on this research work, and to those directly engaged on the work—Carlyle Harmon, Lloyd T. Sandborn, J. Richter Salvesen, and Judson P. Smith.

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Metals and Wines

Corrosion Resistance of Metals in Wine Making and Tolerance of Wines for Metals

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The resistance of metals to wines is studied by exposing specimens of seven metals to wines while they are being processed in commercial equipment; 403 corrosion tests are made. The tolerance of wines for metals is studied by adding metal citrates to three wines and noting the changes; over 125 samples are compared.

The corrosion test data are used in estimating the probable pick-up of metals from equipment made of the metals and this is compared with the tolerance of wines for the metals. Inconel is adequate for all winery uses. Nickel, monel metal, 18-8 alloy, aluminum, and copper are useful in certain equipment. Iron, tin, and tinned metals have limited application.

In studying the effects of metals on wines, brilliance and/or color are found to be affected before any changes of flavor and bouquet are noted. Only small quantities (3 mg. per liter) of iron and tin are required to induce objectionable changes of brilliance. Copper in much larger quantities has a slight effect on the brilliance of sweet red wine. None of the other metals affects brilliance. Aluminum, copper, and chromium have a slight though not serious effect on color. Nickel and zinc have the least effect on color.

THE choice of materials available for the construction of winery equipment has been widened considerably by the development of corrosion-resisting metals which are now available in the form of clad-steel plates (7), as well as in all the usual mill forms.

In the past, wood has been favored for the construction of all winery equipment that could be made conveniently from it. Wood, particularly oak, is held to assist in the aging and processing of wines and spirits. Typical installations of wood tankage are shown in Figures 1 and 2. In more recent years some wineries have used tanks of concrete which are treated in some appropriate way or faced with impervious material. Considerations of economy in cost and space and a desire to improve sanitary standards have been instrumental in the adoption of concrete. Metals are used in pumps, filling machines, etc., as superior physical properties are required of materials used in such equipment.

The corrosion-resisting metals offer important advantages over the older materials of construction. Probably the outstanding advantage is the ease with which such metal equipment can be cleaned and sterilized. Smooth, nonabsorbent metal surfaces lend themselves to rapid cleaning and thorough sterilization. With metal equipment, sterilizing methods involving treatment of the surface only can be substituted for the older practice of burning sulfur to obtain penetration, thereby destroying microörganisms within the body of wood as well as on the surface. The absorbed sulfur dioxide is subsequently assimilated by the wine.

The facility with which metal equipment may be switched from one kind of wine to another is a convenience, particularly when changing from red to white wines. All the colored wine may be quickly washed from metal surfaces. The elimination of losses by leakage and of cooperage expense are also important. The strength of metals permits more efficient utilization of tankage space, as much thinner tank walls may be used.

However, before any widespread application of metals may be undertaken in wineries, it is necessary to know how well the metals resist corrosion by wine and what effect, if any, the metals will have on the product. These two phases of the subject are closely related, as the metal that gets into the product is the result of corrosion. The metal or alloy that best fulfils the requirements will be one that possesses corrosion resistance in high degree and is constituted of a metal or metals that have the least effect on the wine.

The authors investigated the resistance of metals to corrosion by wine by placing metal samples in winery equipment where the metals were exposed to corrosion by wine under the actual operating conditions. In order that the effects of metals on wine might be studied, metal citrates were added to wines and any changes that occurred were noted.

Wine-Making Processes

Figure 3 illustrates a typical process for making sweet wines, such as port and sherry, which are of relatively high alcoholic content (usually over 15 per cent by volume). The grapes received at the plant are crushed in the roller crusher, *A*, and transferred to open fermenters, *B*, where sugar may be introduced to compensate for variations in the natural sugar content of the grapes. Sufficient yeast is added to the batch to induce a rapid fermentation lasting about 72 hours. During this period the batch temperature rises gradually from the original or pitching temperature of about 20° C.

(68° F.) to a higher temperature, but it is not permitted to exceed 32° C. (90° F.). With red grapes the fermentation causes the color that is in the skins to be extracted more or less completely by the juice. In due course of time, the fermented juice is strained from the pulp and run to the new wine receiver, *C*. The pulp which remains behind in the open fermenter is removed to the hydraulic press, *D*. The juice that is pressed out is united with the balance of the juice in the new wine receiver, *C*, and the press cake is burned or disposed of otherwise. The new wine is transferred promptly to the mixer, *E*. Successive batches from the mixer are pumped into the large closed fermenters, *F*, in which a slow fermentation takes place. More yeast may be added to promote fermentation which proceeds for several months in a temperature range of 15° to 32° C. (60° to 90° F.). Precautions are taken to avoid acetic infection. When fermentation has ceased, the young wine is racked from the lees and run to storage tanks, *G*, where the wine is stored for a period of years at cellar temperature—approximately 19° C. (65° F.). Eventually, the matured wine is racked from the lees and pumped to a fortification tank *H*, where grape spirits are added and mixed with the batch by pumping in closed circuit. The fortified wine may be stored in the tank for a further period. Finally, a wine of standard quality is obtained by blending various lots in blending tank *I*. Expert supervision and much experience are required in blending. The blended wine is run to a fining tank, *J*, where it is treated with isinglass or other appropriate substance to induce coagulation of suspended matters. After allowing time for settling, the fined wine is racked from the settlings or finings and pumped through the rough filter, *K*. Then the wine is subjected to a conditioning treatment which varies between wineries. Each wine maker seems to have his own conditioning treatment, and the details are guarded carefully. The conditioned wine is mixed with filter aid and run to the finishing filter, *L*. The wine coming from the finishing filter is brilliant. It flows to the bottling tank, *M*, which supplies finished wine to the bottling machine, *N*. Finally, the bottles are corked, labeled, and cased for shipment.

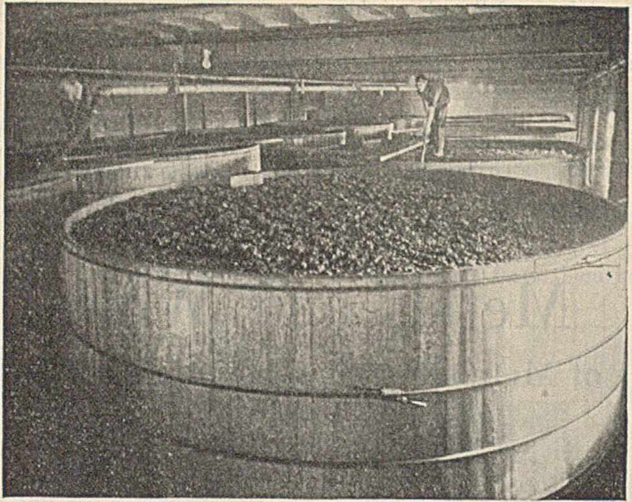
FIGURE 1. OPEN FERMENTERS

The methods used for the production of sweet wines are followed closely in the production of claret, except that no fortification spirit is added. Claret is a dry red wine of relatively low alcoholic content (under 12 per cent by volume) and contains little unfermented sugar.

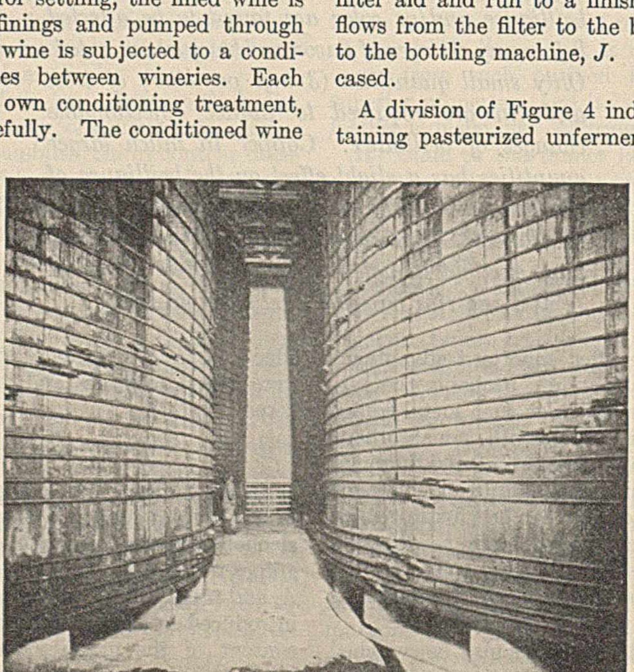
FIGURE 2. TANKS FOR CLOSED FERMENTATION AND STORAGE OF SWEET WINES

Figure 4 shows a typical process for making beverage wines, such as sauternes and Moselle which are of relatively low alcoholic content (usually under 12 per cent by volume). Such wines usually contain moderate amounts of unfermented sugar. As Figure 4 indicates, the use of open fermenters, mixing tank, and rough filter is eliminated. The grapes are crushed in roll crusher *A* and pressed in hydraulic press *B;* the fresh juice or must is run directly through juice receiver *C* to closed fermenters *D* in which fermentation is carried to completion. In some cases the wine maker may depend on the natural yeast in the must to accomplish fermentation. In other cases he may prefer to inoculate the must with his own carefully propagated yeast culture. The propagation of yeast is a highly specialized art and is one of the principal factors determining the character of the finished wine. The fermentation temperature is not permitted to exceed 27° C. (80° F.) and it is preferable to maintain it well below that point. As before, precautions are taken to avoid acetic infection. Upon completion of the fermentation, which requires several months, the wine is racked from the lees to storage tanks, *E*. A lower storage temperature—approximately 3° C. (38° F.)—is required, as these wines are of relatively low alcoholic content and contain moderate amounts of unfermented sugar. In fact, expert care is required at this stage of the process. After blending in tank *F* and fining, the wine is racked from the finings in tank *G* and subjected to such special processing as the wine maker may have found desirable. Then the wine is mixed with filter aid and run to a finishing filter, *H*. A brilliant wine flows from the filter to the bottling tank, *I*, supplying wine to the bottling machine, *J*. The bottled wine is labeled and cased.

A division of Figure 4 indicates the method used for obtaining pasteurized unfermented grape juice. In preparing red grape juice, crushed Concord grapes from crusher *A* are transferred to steam-jacketed kettles *BB*, which heat the batch to 63° C. (145° F.). Heating causes the color in the skins to be assimilated by the juice. The batch is pressed hot in the press, *CC*, which discharges juice to the juice receiver, *DD*. The juice is pasteurized promptly in the pasteurizer, *EE*, and, while still hot, it is run into glass carboys. The juice is stored in these carboys until required for bottling. The storage temperature does not exceed 4° C. (40° F.) and is usually lower.

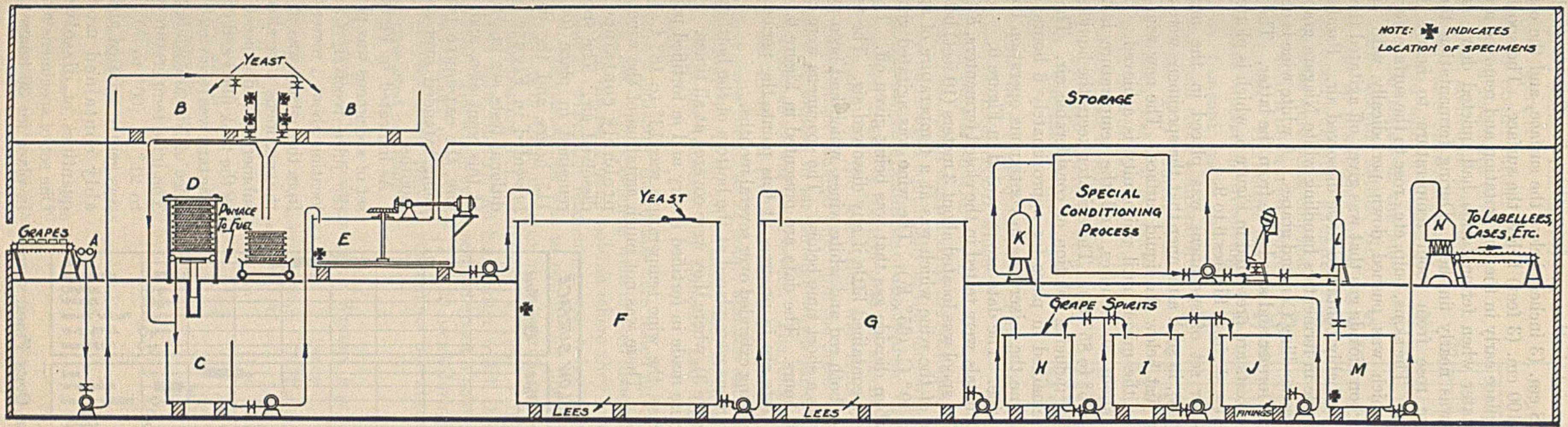

FIGURE 3. TYPICAL PROCESS FOR MAKING SWEET WINES

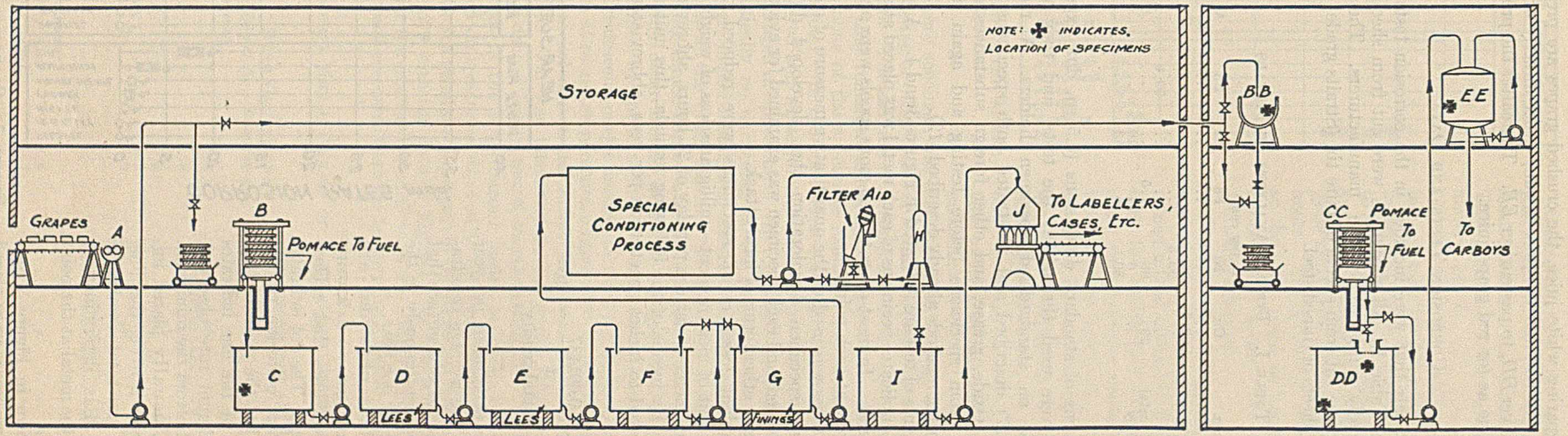

FIGURE 4. TYPICAL PROCESS FOR MAKING BEVERAGE WINES

In preparing white juice, the crushed grapes are pressed cold in press *CC*, and the juice is run, either directly or via juice receiver *DD*, to pasteurizer *EE*. Thereafter the process is the same as for red grape juice.

CORROSION TESTS AND DATA

The metals that were included in the corrosion tests are shown in Table I. All specimens were cut from sheets as commercially supplied by the manufacturers. The tin samples were cut from sheets of pure tin (Straits grade) and not from sheets of tinned steel.

TABLE I. TYPICAL ANALYSES OF METALS

(In per cent)

METAL	Cu	Ni	Fe	Cr	Sn	Al
Aluminum 2S	..	..	..	..	..	99.0
Copper	99.9	..	..	..	..	..
Nickel	..	99.5	..	..	..	..
Tin	..	..	..	..	99.9	..
Monel metal	29	68	1.5	..	..	..
18-8 alloy	..	8	74	18	..	..
Inconel	..	80	6	13	..	..

Specimens of standard dimensions (0.5 sq. dm. exposed surface) were used throughout the tests, and they were supported on standardized specimen holders. A recent article (*17*) described and illustrated both specimens and holders. Oxide, grease, and other foreign substances were removed from specimens before testing and again after testing, using methods already described (*17*).

The points of test are indicated in Figures 3 and 4. A spool carrying duplicate specimens of each metal was placed at each point of test. In most cases two or more spools were placed successively at each point.

Weight loss was used as the quantitative measure of corrosion. Any specimen discoloration that developed during test was noted, and each specimen was examined for evidence of pitting or other forms of local attack.

The weight losses of all specimens were reduced to a common unit of measurement—milligrams loss of weight per square decimeter of surface per day of 24 hours, abbreviated as mdd. By means of the following formula, this unit may be converted to inches penetration per year, abbreviated as ipy.

$$\text{mdd.} \times \frac{0.001437}{d} = \text{ipy.}$$

where d = metal density

By inches penetration per year is meant the average penetration, in inches, of a surface that is exposed continuously to the corrosive for one year.

The data obtained are plotted in Figures 5 to 9, using heavy black lines that enclose white dots. The dot indicates the average corrosion rate of the metal at the point of test. The top of the line indicates the maximum rate observed, and the bottom the minimum. A figure, usually placed immediately above the line, indicates the total number of weight loss determinations made on the metal at the point of test.

As shown in Figure 3, sets of metal specimens were placed at two points in the open fermenters, *B*. One set was located about 8 cm. (3 inches) below the surface, and the other set about 100 cm. (3 feet) below the surface. The spools were put in place early in the fermentation and removed about 50 hours later when fermentation had quieted down and the batch was nearly finished. During fermentation the temperature rose from room temperature to nearly 32° C. (90° F.). The skins, pulp, etc., rose to the surface, forming a crust which was pushed down periodically with paddles. The carbon dioxide gas that was given off agitated the liquid which probably contained little dissolved air. Parallel tests were made in fermenters handling white Niagara grapes and in others handling Concord grapes. A white wine is obtained from the former and a red wine from the latter. The results of these tests are presented in Figure 5, which is plotted on a different scale from Figures 6 to 9.

Another set of specimens was placed in the mixer, *E* (Figure 3), in such a manner that the specimens were always located just below the liquid surface. The new wine is agitated in the mixer until uniformity is achieved. This requires about 30 minutes, and the temperature is 24° to 31° C. (75° to 85° F.). The agitator keeps the liquid stirred, probably inducing solution of considerable air. The specimens remained in place for approximately 6 hours, during which time the mixer was in continuous operation handling white wine. The data are presented in Figure 6.

The metals were tested in the closed fermenters, *F* (Figure 3). The spool was located about 3 meters (10 feet) below the surface of the wine which was at a temperature of approximately 19° C. (65° F.). The wine was agitated gently by the carbon dioxide gas that was being given off. The wine probably contained little if any dissolved air. The test was made in both red and white wines, which had been put into the tanks a short time before. The specimens were exposed for 120 hours. The data are presented in Figure 6. Additional tests are in progress at this point, the period of exposure being extended over several months.

Specimens were placed at the bottom of the bottling tank, *M* (Figure 3), where they were covered at all times. Parallel tests were made in fortified sherry and in fortified port. In each case, the wine temperature was 13° to 18° C. (55° to 65° F.). There was not much agitation of the wine, and it probably contained little dissolved air. The specimens remained in place for 90 to 115 hours, and the data are presented in Figure 7. Additional tests are in progress at this point also, and, as before, the exposure period is being extended over several months.

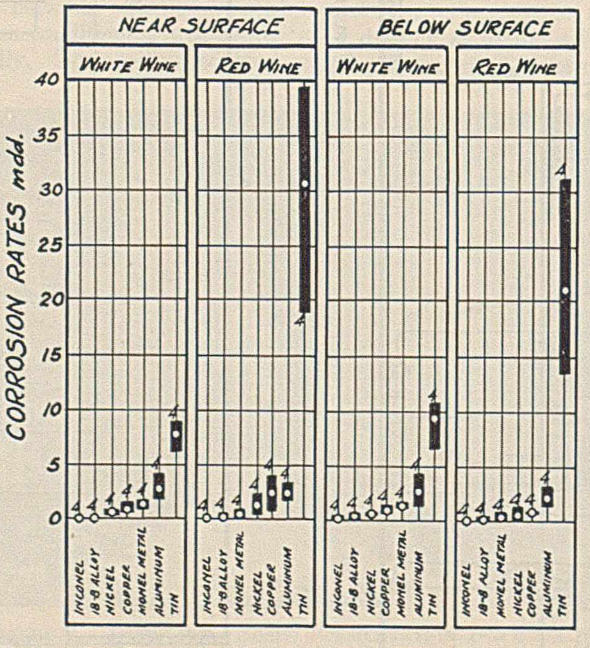

FIGURE 5. CORROSION RATES IN THE OPEN FERMENTERS

As indicated in Figure 4, a set of specimens was placed in the juice receiver, *C*. Their location about 1 meter (3 feet) from the bottom was such that the specimens were alternately submerged and exposed to air as the tank filled and emptied. The tank was receiving the fresh juice of Niagara white grapes. The juice temperature was 16° to 21° C. (60° to 70° F.); it was gently agitated and probably contained moderate quantities of dissolved air. One set of specimens remained in place for 30 hours and the other set for 6 hours. The data are presented in Figure 8.

In order to obtain further information on the resistance of metals to fresh juice, additional tests were made in the juice plant, shown at the right-hand side of Figure 4. Specimens were tested in the aluminum steam-jacketed kettles, *BB*. The spool was so placed as to be below the liquid surface, except when the kettles were being emptied and refilled which occurred about every 30 minutes. The kettles were in continuous operation, receiving only fresh Concord grapes, which were heated from room temperature to 63° C. (145° F.). During heating, each batch was stirred occasionally with a wooden paddle, which probably had a slight aërating effect. The test periods were 20 to 25 hrs. The data are presented in Figure 9.

The metals were tested at two points in the juice receiver, *DD*, which was receiving only fresh Concord juice. One of the spools was placed at the bottom of the tank where it was submerged continually in the juice, which probably contained moderate quantities of dissolved air. The other spool was placed in such a position that the specimens were constantly washed by the juice that was falling from a strainer placed under the feed pipe from the press. As these specimens were located in air through which juice was falling, the aëration effect was quite severe. The juice temperature was 38° to 49° C. (100° to 120° F.). The specimens remained in place for 15 to 22 hours, and the data are presented in Figure 8. It should be noted that there is a temperature difference between the Concord and the white Niagara juice.

As Figure 4 indicates, the metals were tested in the nickel pasteurizer, *EE*. The specimens were located about 1 meter (3 feet) above the pasteurizer bottom where they were submerged except when the pasteurizer was being filled and emptied. The pasteurizer was in continuous operation receiving batches of Concord juice at approximately 43° C. (110° F.) and heating each batch to 82° C. (180° F.). Heating required approximately an hour, after which the batch was emptied. The whole cycle required about 5 hours. The specimens remained in place for 17 to 20 hours during which period the pasteurizer was in continuous operation. The data are presented in Figure 9.

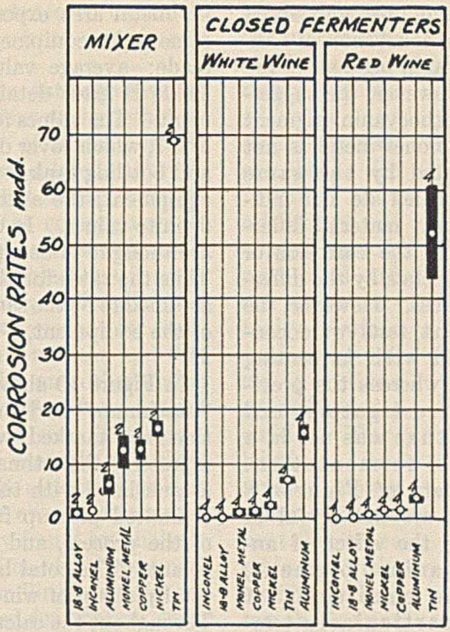

Figure 6. Corrosion Rates in the Mixer and Closed Fermenters

Other tests were made in the nickel pasteurizer when it was handling the fresh juice of white Niagara grapes. This juice was received at approximately 21° C. (70° F.), heated to 74° C. (165° F.), and held at that temperature for 30 minutes. The batch was cooled in the pasteurizer to 38° C. (100° F.) during 30 minutes and then discharged. The complete cycle required approximately 4 hours. The specimens were located at the same point as before for a period of 7 hours. The data are plotted in Figure 9.

None of the wines or juices, against which tests were made, contained added sulfur dioxide. However, the liquids may have contained some sulfur dioxide assimilated from wood storage tanks, etc., which were sterilized by burning sulfur. Thus, in the bottling tank tests the finished sherry and port wines may have contained sulfur dioxide to the extent of 140 mg. per liter maximum.

Every specimen was examined after testing. No evidence of pitting or other forms of localized attack was noted on any metal. The samples of Inconel and 18-8 alloy were the only ones that remained unchanged in appearance in every test, but none of the specimens exhibited any change of serious character. In the open fermenter, tin became blackened by both red and white juices; the other metals were practically unchanged in appearance. In the closed fermenter there was practically no darkening of tin by the white wine, while copper, monel metal, and nickel acquired faint brown tarnishes in the order named. In both the port and sherry bottling tanks, copper and tin were darkened considerably, but the other metals were not noticeably changed in appearance, except in the case of monel metal which acquired an irridescent purple tarnish in sherry. In the fresh white juice at room temperature, copper was darkened appreciably, and nickel and monel metal developed faint mottled tarnishes. Tin was blackened in hot white juice but not in hot Concord juice; monel metal developed a faint mottled tarnish in the hot Concord juice; no other changes were noted on specimens exposed to hot fresh juice.

From a general comparison of the corrosion rates of Figures 8 and 9 with the data of Figures 5 to 7, it is evident that, under the practical conditions of the winery, the fresh juices are more corrosive than the fermenting juices or wines.

Table II. Characteristics of Winery Equipment Influencing Metal Pick-up of Wine Being Processed

Equipment	Capacity	Inside Dimensions Diam.	Inside Dimensions Height	Exposed Metal Area	Ratio Volume:Area		Time of Contact per Batch Max.	Min.	Av.
	U. S. gal.	Ft.	Ft.	Sq. ft.	Gal./sq. ft.	Liters/sq. dm.			
				sweet wine equipment					
Open fermenter	4800	15.3	4.6	350	13.7	5.6	80	48	64 hr.
New wine receiver	1670	6.8	6.4	170	..	..	Flows continuously, 480 gal./hr.		
Mixer	4800	15.3	4.6	350	13.7	5.6	1	0.5	0.75 hr.
Closed fermenter	49000	19.9	20.9	1560	31.4	12.8	6	2	4 mo.
Storage tank	49000	19.9	20.9	1560	31.4	12.8	36	24	30 mo.
Blending tank	2700	8.0	7.3	230	11.7	4.8	90	10	50 days
Fining tank	2700	8.0	7.3	230	11.7	4.8	20	10	15 days
Rough filter	...	..	..	2030	..	..	Flows continuously, 600 gal./hr.		
Finishing filter	...	..	..	830	..	..	Flows continuously, 360 gal./hr.		
Bottling tank	2700	8.0	7.3	230	..	..	Flows continuously, 540 gal./hr.		
				beverage wine equipment					
Closed fermenter	2700	8.0	7.3	230	11.7	4.8	6	2	4 mo.
Storage tank	2700	8.0	7.3	230	11.7	4.8	36	24	30 mo.

Other equipment has same characteristics as for sweet wine.

The data from the corrosion tests on tin in open and closed fermenters (Figures 5 and 6) support the conclusion of Culpepper and Caldwell (*3*) that the anthocyanin pigment of red juice accelerates the corrosion of tin. However, the suggestion of Mrak and Cruess (*13*) that anthocyanin pigment accelerates the corrosion of nickel and monel metal is not supported by the same data which do not indicate any material differences in the corrosion of these metals by the different juices. However, the present tests were concerned with fermenting juices, whereas the previous investigators used juice that was not in a state of fermentation. The data of Figures 8 and 9 are not useful in noting the effect of anthocyanin pigment, as the conditions of test, particularly temperature, were not identical.

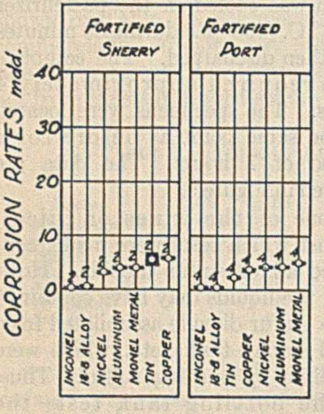

Figure 7. Corrosion Rates in the Bottling Tank

An investigation of this kind is not aimed to show the effects of aëration, temperature, and velocity on corrosion rate, as more than one of these factors is subject to variation in passing from one stage of the process to another. These factors are known to influence corrosion rate, as has been shown by Thompson and McKay (*18*) and others (*5*, *12*, *19*), and undoubtedly they were active in these tests. In the opinion of the authors, the higher rates noted in the mixer (Figure 6) as compared with the same white juice in the open fermenters (Figure 5) results primarily from the higher liquid velocity in the mixer. Higher aëration probably is largely responsible for the differences of corrosion rate noted on the specimens located in falling Concord juice (Figure 8) as compared with the submerged specimens. Higher aëration has a marked effect on nickel, as has been noted in previous investigations (*12*, *19*), whereas tin corrodes more rapidly in grape juice under conditions of lower aëration.

The effect of higher temperature probably accounts for the slightly higher corrosion rates observed on most of the metals in the pasteurizer (Figure 9) as compared to the juice tanks (Figure 8) from which the pasteurizer receives juice. An increase of temperature does not necessarily assure increased corrosion rates, though it usually has that effect at temperatures below 60° to 80° C. (140° to 180° F.). Quam (*15*) has made some interesting observations on this point. The apparent anomaly may be explained by the fact that increased temperature lowers oxygen solubility, and the lowered aëration effect (oxygen) may be more than sufficient to counterbalance the increased temperature effect.

Estimated Metal Pick-up

Having determined the corrosion rates of different metals at various points in the wine-making process, it is possible to estimate the metal pick-up of fresh juice or wine when processed in equipment of these metals. The pick-up from some piece of metal equipment may be estimated by a calculation using known values for the corrosion rate of the metal, the area of metal exposed to the liquid, the time of exposure, and the quantity of liquid in which the metal is distributed.

Some calculations of this kind were made and the data are shown graphically in Figures 10 to 13. The data apply to a sweet white wine made by an average process in typical equipment. In making the calculations, values were selected for metal area exposed and volume of liquid that were the same as for equipment used at the plant where the tests were made; average values for time of exposure were selected; Table II gives detailed information for each piece of equipment. The values for corrosion rate were taken from Figures 5 to 7, which cover open fermenters, mixer, closed fermenters, and bottling tank. In the absence of data for the remaining equipment, the authors have taken the liberty of assigning definite values. In doing this, they have selected values that are thought to be equal to or greater than the actual values. Thus the rates for the new wine receiver, *C* (Figure 3), were assumed to be the same as for the mixer, *E*, and for the balance of the equipment, *G* to *L*, the same as for the bottling tank, *M*.

In Figure 10 above the word "tin" there is a line marked "maximum," and this line is divided horizontally into parts that are marked with numerals. The part marked "5" represents the estimated tin pick-up of wine during storage in a tank lined with tin. Other parts of the line represent the estimated pick-up from tin equipment during other stages of the process, and the footnotes disclose which stages are meant. The total height of the line indicates the estimated total pick-up of wine if processed entirely in tin equipment. Throughout the calculations from which this line was plotted, the maximum corrosion rate values for tin were used. Similar calculations were made using average and minimum corrosion rate values, and corresponding lines show the results obtained. Also, data on nickel, aluminum, and copper are shown in Figure 10.

Figure 11 presents the results of calculations on monel metal. In this graph a group of three lines is marked "maximum;" one represents the combined pick-up of nickel and copper, which are the principal constituents of the alloy; the other two lines represent the nickel and copper pick-ups individually. Otherwise Figure 11 is the same as Figure 10. Figures 12 and 13 present, respectively, the results of calculations on 18-8 alloy and Inconel. They differ from Figure 11 to the extent that lines are shown for three-alloy components instead of two.

These various lines represent the result of three factors acting together. They are: resistance to corrosion, the time the metal is in contact with the wine, and the relation between the liquid volume and exposed metal area. By increasing any one factor, the result is multiplied proportionately. The important effect of changing the relation between liquid volume and exposed metal area is perhaps not as well appreciated as

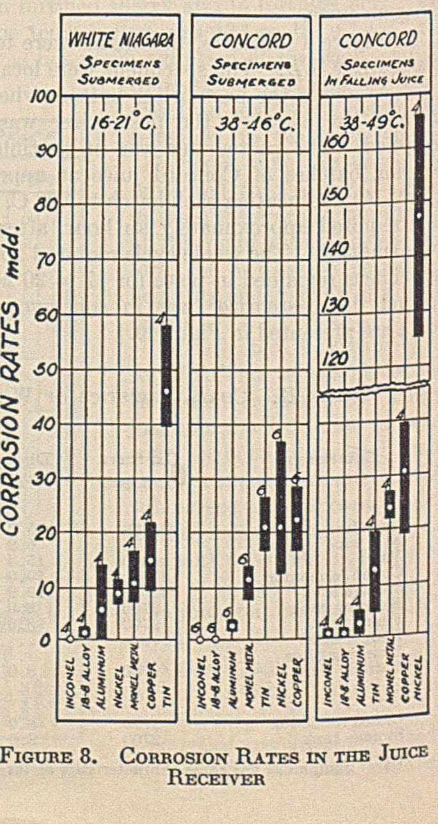

Figure 8. Corrosion Rates in the Juice Receiver

the effect of changes in time or in resistance to corrosion. Table II indicates how this factor varies from one piece of equipment to another.

Technical objection may be taken to the data presented in Figures 10 to 13, inasmuch as the calculations are hypothetical and proof is lacking that the quantity of metal actually entering the wine is the same as that calculated. For instance, the corrosion of the metal may result in the formation of an insoluble adherent coating; thus the corrosion would not add to the metal content of the liquid and the calculated pick-up would be wrong. In spite of such objections, it is the authors' opinion that any erring is in a conservative direction and the method provides the best available means for estimating pick-up. Supporting this contention is the fact that it has been possible, in connection with this and other similar investigations, to check the estimated metal pick-up against the actual pick-up as determined by analyses. The agreement has been good in most cases. An example was given in a previous contribution (*17*) in which the estimated pick-up of copper by condensed milk from copper evaporators was in good agreement with the amount actually found by analysis. In connection with the present investigation, nickel specimens were exposed in a nickel pasteurizer handling a special red juice. Samples of the batch were secured for analysis, both before and after treatment in the nickel pasteurizer. Analyses of these samples showed an increase in nickel content amounting to 4.1 mg. per liter, which may be compared with an estimated nickel pick-up of from 4.9 to 9.9 mg. per liter (average 7.0 mg. per liter) calculated from the corrosion data. Probably the nickel surface of the pasteurizer had acquired, over a period of years, a partially protective film that lowered its rate of corrosion below that indicated by tests on freshly surfaced specimens. However, the important fact is that the actual and calculated metal pick-ups were of the same order of magnitude and that the error of calculation was on the conservative side.

Effect of Metals on Wine

With information already developed as to the estimated metal pick-up from individual pieces of plant equipment, as well as the total pick-up from all equipment, it becomes necessary to determine whether such quantities of metal would be detrimental to the wine.

It has been known for many years that small quantities of iron induce turbidity in white wines and react with tannin compounds in red wines to make them dark (*1, 2, 9, 10, 11, 20, 22*). In fact, methods have been developed and have been used in Europe to remove iron from wine by treating it with potassium ferrocyanide.

There has been some controversy as to the specific mechanism by which turbidity is induced in the presence of iron. In 1909 Baragiola and Huber (*2*) expressed their belief that the turbidity was due to the formation of ferric phosphate which they identified in the sediment from turbid wines. In 1915 Weil (*22*) found that turbidity due to ferric phosphate was influenced by light rays, since turbid samples exposed to the light cleared up, presumably because of the reduction of ferric phosphate to ferrous phosphate. However, when the samples were shielded from the light, turbidity reappeared. On the other hand, Trillat (*20*) believed that the effect of iron was to accelerate the formation of aldehydes, which in turn precipitated the coloring matter in the wine. In 1917 Lopriore (*9*) expressed his belief that the effect of iron was due to the formation of ferric lactate rather than ferric phosphate.

The authors have been able to find comparatively little information in the literature on the effects of other metals on wine. In 1922 Grélot (*6*) studied the effects of several metals on wines containing sulfur dioxide, being especially interested in the influence of sulfur dioxide concentration on the effects of several metals studied. He found that additions of copper, nickel, and lead did not cause turbidity in wines containing 450 mg. per liter of sulfur dioxide. Turbidity developed slowly when these metals were added to wines containing much larger quantities of sulfur dioxide, such as 27,000 mg. per liter. With iron, zinc, aluminum, and tin, turbidity developed in the presence of as little as 25 mg. per liter of sulfur dioxide.

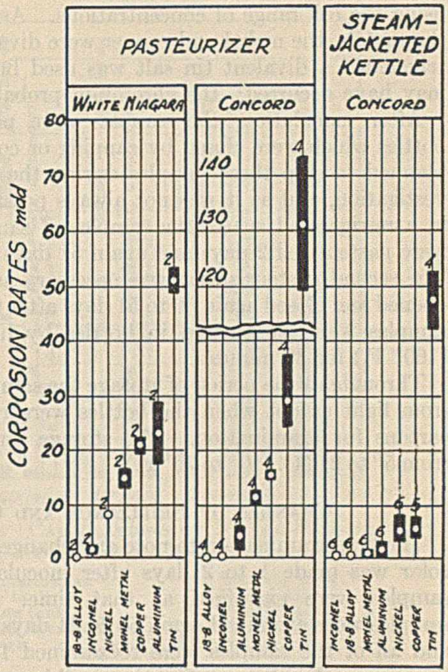

Figure 9. Corrosion Rates in the Pasteurizer and Steam-Jacketed Kettle

Ribéreau-Gayon (*16*) stated in 1929 that as little as 0.5 to 0.8 mg. per liter of copper will induce turbidity in white wines. His findings have not been confirmed by the present authors (Tables III to V) who did not discover any turbidity in sauternes to which were added as much as 200 mg. per liter of copper.

Most investigators have assumed that the metals suspected of inducing turbidity have originated in the winery equipment. However, Dubaquié (*4*) in 1926 and Mummendey (*14*) in 1931 found that the metals dissolved from bottle glass had a noticeable effect on the wine.

None of these investigators attempted to determine the limiting concentration of metal that would induce turbidity. Some experiments along these lines were made by de Waal (*21*) in 1932. He found that, with 8 mg. per liter of iron, turbidity appeared, and above 15 mg. per liter it was objectionable.

As little quantitative information was available on the tolerance of wine for metals, the authors undertook an investigation of this subject. Known quantities of metals were added to three wines, and any changes of brilliance, color, taste, and bouquet were noted. Standard solutions that contained 1 mg. per ml. of metal as citrate were used in making the metal additions, and the quantity of wine selected was such as to result in exactly 500 ml. of inoculated wine. The range of metal concentration was 1 to 200 mg. per liter, through 1, 3, 6, 15, 30, 60, 100, and 200 mg. per liter. In order to detect any differences due solely to dilution, equivalent quantities of distilled water were added to the same wines in the same manner.

The wines used were a dry white wine (sauternes), a sweet red wine (port), and a dry red wine (claret); all of these wines had been aged, conditioned, and filtered by the usual methods followed at the winery. All of the wines were brilliantly clear before the metal citrates were introduced.

The white wine and the sweet red wine were inoculated with citrates of iron, nickel, aluminum, tin, copper, chromium, and zinc, using the full range of concentrations. The claret samples were inoculated only with citrates of iron and nickel, using the full range of concentrations. As to the valence of the metals, the nickel and copper were divalent, and the iron trivalent; a divalent tin salt was used but some oxidation may have occurred; the chromium probably was trivalent.

After inoculation, the samples were placed in separate bottles which were closed by capping or corking. As it was planned to ship these samples during the course of this investigation, and as it was not always possible to keep them in a refrigerated space, the samples of sauternes and claret were pasteurized 2 days and again 51 days after inoculation. The second pasteurization was necessary as the bottles were opened and closed again 50 to 51 days after inoculation. The samples were pasteurized in bottles by holding at 71° C. (160° F.) for 30 minutes.

Throughout the period of storage the samples were shielded from light except when the bottles were removed from the cartons for examination. The storage temperature ranged from 5° to 21° C. (40° to 70° F.).

CHANGES OF BRILLIANCE AND COLOR

The first examination to note any changes of brilliance and color was made 1 to 2 days after inoculation. All of the samples were examined at that time. The white wine samples were examined again 50 to 51 days after inoculation, and all of the samples were reëxamined 105 days after inoculation. Further examinations will be made and reported. At the time the white wine samples were examined for the second time, a 5-ml. portion of every sample was sealed in a glass tube and preserved for future reference.

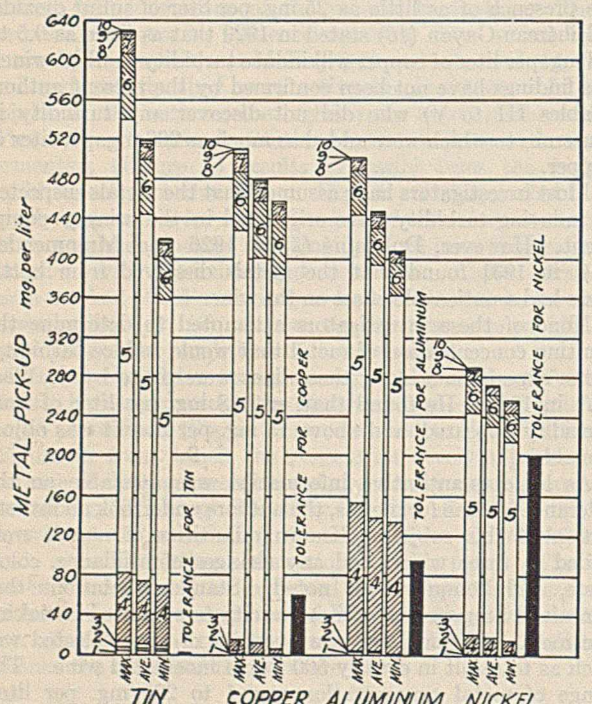

FIGURE 10. CALCULATIONS OF METAL PICK-UP OF TIN, COPPER, ALUMINUM, AND NICKEL

1. Open fermenter
2. Juice tank
3. Mixing tank
4. Closed fermenter
5. Storage
6. Blending tank
7. Fining tank
8. Rough filter
9. Finishing filter
10. Bottling tank

The changes of brilliance and color noted during the first examination are indicated in Table III. A heavy line separates the table into two parts. The metal concentrations to the left of the line either had no effect or so little effect as not to be noticeable during handling or sale of wines. The concentrations to the right of the line have an effect that either is apt to be noticed by discerning eyes or is unmistakable. The location of the line is a matter of opinion, but the authors have striven to be conservative.

TABLE III. CHANGES OF COLOR AND BRILLIANCE OF WINES 1 TO 2 DAYS AFTER ADDING METAL CITRATES

	Metal Concentration (mg. per liter)							
	1	3	6	15	30	60	100	200
				PORT WINE				
Aluminum	.	p	p	p	p	p	p	pp
Chromium	.	..	..	..	..	..	..	dd
Copper	.	..	..	..	..	p	p	p
Iron	.	..	..	..	..	..	..	..
Nickel	.	..	..	..	..	..	..	..
Tin	.	d d	dd tt	*ddd ttt	*dddd tttt	*ddddd ttttt	**ddddd ttttt	**ddddd ttttt
Zinc	.	..	..	..	..	p	p	p
				CLARET				
Iron	d	ddd	dddd	dddd	Q	Q	Q	Q
Nickel	.	..	..	..	..	..	p	pp
				SAUTERNES				
Aluminum	p	pp	pp	pp	ppp	ppp	ppp	pppp
Chromium	.	..	dd	ddd	ddd	dddd	dddd	xxdddd
Copper	p	p	p	p	pp	ppp	pppp	xpppp
Iron	.	t p	ttt ppp	tttt ppp	ttttt ppp	ttttt ppp	ttttt xppp	ttttt xppp
Nickel	.	p	p	p	p	pp	ppp	ppp
Tin	.	p	t pp	ttt pp	tttt pp	ttttt pp	ttttt pp	ttttt pp
Zinc	.	..	..	p	p	p	pp	ppp

p = trace paler
pp = very slightly paler
ppp = slightly paler
pppp = paler
ppppp = much paler
d = trace darker
dd = very slightly darker
ddd = slightly darker
dddd = darker
ddddd = much darker

t = trace of turbidity
tt = very slightly turbid
ttt = slightly turbid
tttt = turbid
ttttt = very turbid
Q = opaque
* = sample had purplish cast
** = sample was purple
x = sample had greenish cast
xx = sample had greenish purple opalescent cast

The changes of brilliance were determined by examining the inoculated wine in bottles. Any turbidity in the white wine could be detected by looking through the bottle from various angles. As light was not as easily transmitted by the red wines, the bottles were turned upside down and the wine in the neck of the bottle was viewed from various angles.

In making observations on color changes, a small portion of some inoculated wine sample was placed in a test tube and compared with a similar portion of the wine sample that had been inoculated with a corresponding quantity of distilled water. A comparator block, such as is used in pH determinations, was employed when making the comparisons. This enabled the detection of slight color differences, which were not as evident when using ordinary methods of examination. The red wines were examined in the conventional manner by looking transversely through the tubes containing wine, but the white wine was examined to better advantage by looking down through the tubes filled to constant depth. Pieces of white paper were placed beneath each tube containing white wine to provide a uniform background.

The changes of brilliance and color noted during the second examination of the white wine samples are shown in Table IV. The same methods of comparison were used as in the first examination.

TABLE IV. CHANGES OF COLOR AND BRILLIANCE OF SAUTERNES 50 TO 51 DAYS AFTER ADDING METAL CITRATES

	Metal Concentration (mg. per liter)							
	1	3	6	15	30	60	100	200
Aluminum	.	..	..	..	p	ppp	ppp	pppp
Chromium	d	dd	dd	ddd	dddd	dddd	ddddd	**ddddd
Copper	.	..	..	lost	..	p	pp	xpppp
Iron	tt	tttt	ppp ttttt	pppp ttttt	pppp ttttt	pppp ttttt	xpppp ttttt	xpppp ttttt
Nickel	.	..	..	..	..	p	ppp	ppp
Tin	.	t	ttt	tttt	ttttt	ttttt pp	ttttt pppp	ttttt ppppp
Zinc	.	..	..	..	..	..	ppp	ppp

The changes noted 105 days after inoculation are shown in Table V. In making this examination, no wine was removed from the bottles. Changes of brilliance were determined as before, but changes of color were noted by looking through the bottles against a white background at a distance of 4 meters (13 feet).

During the last examination, turbidity had developed in some of the port samples to which only water had been added. The sample containing 60 ml. per liter of distilled water showed a trace of turbidity, the sample containing 100 ml. per liter was very slightly turbid, and the sample containing 200 ml. per liter was very turbid. The turbidity of the sample containing 200 ml. per liter of distilled water was comparable with the samples containing 15 mg. per liter of tin and 60 mg. per liter of iron.

TABLE V. CHANGES OF COLOR AND BRILLIANCE OF WINES 105 DAYS AFTER ADDING METAL CITRATES

	Metal Concentration (mg. per liter)							
	1	3	6	15	30	60	100	200
					PORT WINE			
Aluminum	.	p	p	pp	pp	pp	pp	ppp
Chromium	.	..	..	d	d	dd	dd	ddd
Copper		t p	t pp	t pp	tt ppp	tt ppp	tt ppp	ttt pppp
Iron	.	..	t	ttt	tttt p	ttttt p	ttttt pp	ttttt ppp
Nickel	.	..	..	..	..	..	pp	ppp
Tin	.	t dd	ttt ddd	ttttt *dddd	ttttt *ddddd	ttttt *ddddd	ttttt **ddddd	ttttt **ddddd
Zinc	.	..	p	p	pp	pp	ppp	pppp
					CLARET			
Iron	d	d	dd	ddd	ddd	tttt ddddd	ttttt ddddd	ttttt ddddd
Nickel	.	..	..	..	..	p	pp	pp
					SAUTERNES			
Aluminum	.	..	..	..	p	ppp	ppp	pppp
Chromium	d	dd	dd	ddd	dddd	dddd	ddddd	xxddddd
Copper	.	..	..	lost	..	p	pp	xpppp
Iron	tt	tttt	ttttt ppp	ttttt pppp	ttttt pppp	ttttt pppp	ttttt xpppp	ttttt xpppp
Nickel	.	..	..	p	p	pp	ppp	ppp
Tin	tt	tttt	tttt	ttttt	ttttt	ttttt pp	ttttt pppp	ttttt ppppp
Zinc	.	..	..	..	p	pp	ppp	ppp

In comparing samples that contained only added water, it was evident in all examinations that the samples containing 200 ml. per liter of water were slightly paler than the wines to which nothing was added. A trace of paleness was evident in samples containing 60 ml. per liter of water, but no changes were noted in samples containing less water. No changes of importance were noted in successive examinations of these samples.

It is apparent from Tables III to V that changes developed more quickly in the dry wines (sauternes and claret) than in the sweet wine (port). In fact, 2 days were sufficient to indicate which metals had an important effect on the dry wines. With the samples of sauternes the principal effect of an increased storage period was to increase the turbidity induced by iron and tin. With the claret samples the blackness due to iron diminished after the first examination and was replaced with turbidity; probably this change was induced or hastened by the pasteurization. Such other changes as occurred during the storage period did not indicate any important effect induced by the metals. In this connection, it is a matter of some difficulty for an observer to represent consistently the slight variations of color by a system of letters. The difficulty is especially troublesome when it is desired to be consistent not only throughout one examination but throughout successive examinations that are separated by a substantial time interval. For this reason, the slight variations of color, as between no change and a trace paler, noted in successive examinations of the same samples may have resulted from variations of judgment.

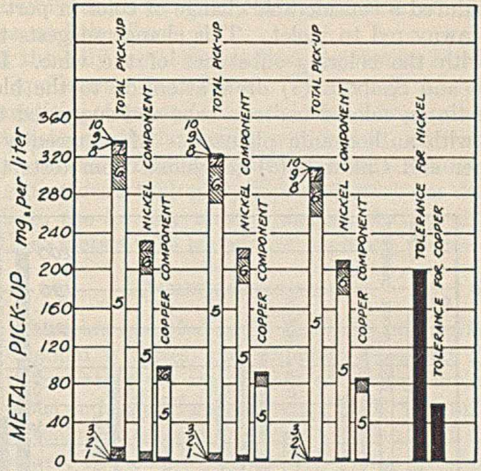

FIGURE 11. CALCULATIONS OF METAL PICK-UP FOR MONEL METAL

1.	Open fermenter	6.	Blending tank
2.	Juice tank	7.	Fining tank
3.	Mixing tank	8.	Rough filter
4.	Closed fermenter	9.	Finishing filter
5.	Storage	10.	Bottling tank

Changes of brilliance are of greater practical importance than changes of color, as consumers are much more critical of brilliance in all wines than of color which varies between types and brands.

Time had a more important influence with the port wine. The turbidity due to tin was the only important change noted after 2 days. As with the dry wine samples, the turbidity of port that was induced by tin increased with time, but, in addition, a definite turbidity due to iron was developed. Also, a slight turbidity due to copper was developed. Whether or not other important changes will develop during further storage remains to be seen. It is to be expected that the metal-wine reactions will reach completion sooner or later, and no further changes will occur. This stage may have been reached within the 105 days that elapsed between inoculation and the last examination.

The turbidity that was induced by tin in sauternes and port tended to settle as a flocculent sediment which was brown in sauternes and purple in port. With iron the tendency to settle was much less; the sediment was brown in sauternes, purplish brown in port, and purple in claret. Such sediment as did separate from the port samples containing copper was of a brownish color.

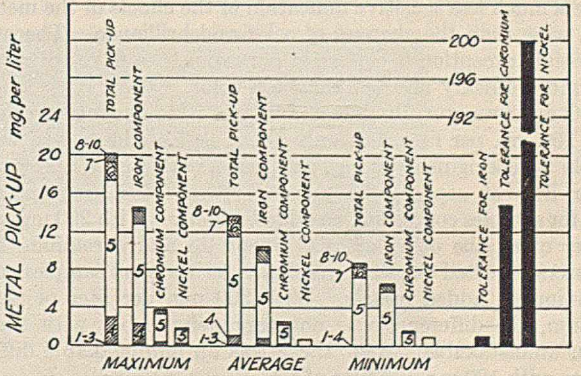

FIGURE 12. CALCULATIONS FOR METAL PICK-UP OF 18-8 ALLOY

1.	Open fermenter	6.	Blending tank
2.	Juice tank	7.	Fining tank
3.	Mixing tank	8.	Rough filter
4.	Closed fermenter	9.	Finishing filter
5.	Storage	10.	Bottling tank

Tin induced a considerable change of color in port wine—from a tawny red to violet. This change suggests that tin reacts with the coloring substance of the wine. In 1924 Kohman and Sanborn (*8*) drew attention to the bleaching effect of tin on colored fruits in cans and suggested that tin reacted with anthocyanin pigments. More recently (1927) Culpepper and Caldwell (*3*) concluded from tests that tin does react with anthocyanin pigments, forming complex metallic compounds of violet color. Possibly the slight bleaching of the port wine by copper, zinc, aluminum, and nickel in the higher concentrations may be due to a similar reaction. The same may be true for the sauternes.

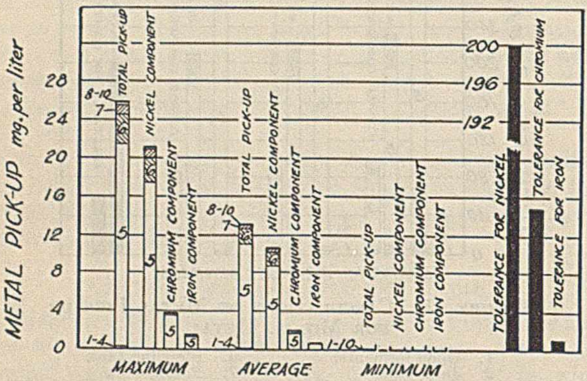

FIGURE 13. CALCULATIONS FOR METAL PICK-UP OF INCONEL

1. Open fermenter
2. Juice tank
3. Mixing tank
4. Closed fermenter
5. Storage
6. Blending tank
7. Fining tank
8. Rough filter
9. Finishing filter
10. Bottling tank

No doubt the pronounced blackening of the claret wine by iron was due to the well-known reaction of iron with tannin substances, which the claret wine is known to have contained. Nickel does not react with the tannin substance to form a black compound.

CHANGES OF FLAVOR AND BOUQUET

A number of the inoculated samples have been examined to note any differences in flavor and bouquet. It has proved a formidable task to compare approximately 150 samples, as the senses of taste and smell are fatigued rapidly by wine, and only a few samples can be compared by any one person at one time. As a result, it is not possible for the authors to present comprehensive information at this time.

However, it is clear that changes of flavor and bouquet are a much less sensitive indication of the effects of the metals on wine than the changes of color and brilliance. The only possible exception is copper in port wine, the flavor of which is more quickly affected than the color.

Copper was readily detected in port wine in concentrations of 200 mg. per liter, but only about half of the tasters were able to distinguish 100 mg. per liter of copper. With 60 mg. per liter of copper, the tasters reported the same results as for samples containing no added metals. With 200 mg. per liter of all the other metals, except tin and chromium, the tasters reported the same results as for the port samples containing no added metals. With 200 mg. per liter of chromium, the difference was not very definite but with tin it was unmistakable. Also, there was an unmistakable difference with 100 mg. per liter of tin.

The tasting tests on the white wine and claret have been less extensive but numerous enough to convince the authors that changes of color and brilliance will be noted at much lower concentrations than changes of flavor and bouquet.

In all of this work it was observed that, when differences of bouquet existed, there was also a difference of flavor. No differences of bouquet have been noted in any samples not exhibiting a difference of flavor.

Both experienced and inexperienced wine tasters participated in these tasting tests, all of which were carried out in such a way as would deprive the taster of any means for distinguishing samples except by flavor, bouquet, and appearance. The appearance factor could not have influenced many of the tests, as nearly all of the tasting that has been done to date has been on samples that do not exhibit noticeable differences in color and/or brilliance. When noticeable differences of color and/or brilliance did exist, the taster was asked to ignore it in making the test.

From information available to the authors on the effect of metals on the flavor of unfermented Concord grape juice, it appears that the flavor of wines is less affected by copper than the flavor of juice. A concentration of copper between 5 and 10 mg. per liter affected the flavor of unfermented Concord juice, which compares with a concentration between 60 and 100 for port wine.

TOLERANCE OF WINES FOR METALS

In deciding upon the tolerance of wines for metals, it is evident from the tests that changes of color and/or brilliance will largely determine the limiting metal concentrations. If the dividing lines of Table III to V are taken as fixing the limit of concentration, and if the minimum is taken for each metal, then the tolerance of wines for metals will fall in the following ranges:

	Mg./liter		*Mg./liter*		*Mg./liter*
Iron	1– 3	Copper	60–100	Zinc	200
Tin	1– 3	Aluminum	200	Nickel	200
Chromium	15–30				

As the precise tolerance is above the lower values shown in this tabulation, it should be reasonably safe to say that neither the color, brilliance, flavor, nor bouquet of wines will be affected noticeably until the metal concentrations exceed the following limits:

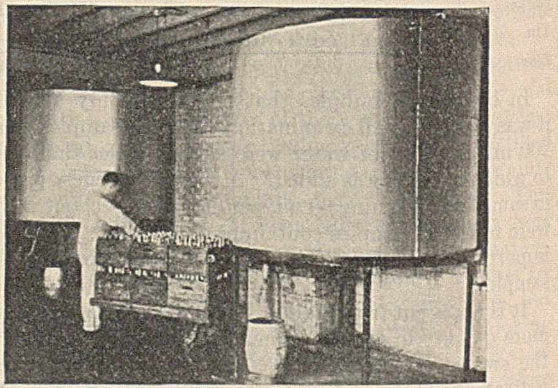
FIGURE 14. NICKEL BOTTLING TANKS

	Mg./liter		*Mg./liter*		*Mg./liter*
Iron	1	Copper	60	Zinc	200
Tin	1	Aluminum	100	Nickel	200
Chromium	15				

These minimum tolerances have been plotted as solid lines in Figures 10 to 13, where they may be compared conveniently with the pick-up calculated from the corrosion tests.

DISCUSSION OF DATA

Two metals (Inconel and 18-8 alloy) included in the corrosion tests were almost perfectly resistant under all the conditions studied. The weight losses noted in Figures 5 to 9 were seldom greater than the errors of measurement, which, in terms of mdd., ranged from 0.1 to 2.0, according to the test.

Figure 13 shows that the pick-up of nickel, chromium, and iron from Inconel may be expected to remain under the tolerance of wine for these metals, even if the wine were processed entirely in equipment of this alloy. This indicates that Inconel is adequate for all winery uses.

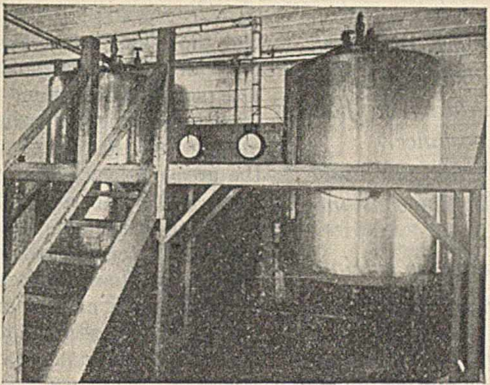

FIGURE 15. GRAPE JUICE PASTEURIZERS OF NICKEL

Figure 12 shows that the pick-up of iron from 18-8 alloy storage tanks probably will exceed the tolerance of wines for iron. In two other stages of the process (closed fermenters and blending tanks) the tolerance for iron may be exceeded. In all other stages of the process the alloy is adequate.

The data for nickel in Figure 10 indicate that, because of the high tolerance of wine for nickel, this metal may be used almost throughout the winery without affecting the color, brilliance, flavor, or bouquet of wine. The data plainly show that nickel may be used for bottling tanks, juice tanks, mixing tanks, and open fermenters. There is proof that these deductions are true, as nickel is in successful service in bottling tanks, pipe lines, juice tanks, and juice pasteurizers. Figure 14 shows two nickel bottling tanks that have been in successful use since 1929 handling a variety of wines. Figure 15 shows nickel equipment in use since 1930 for pasteurizing grape juice.

The data of Figures 10 to 11 indicate that monel metal, aluminum, and copper may be employed in certain winery equipment, such as juice tanks, in which the liquid does not remain for long periods. Wineries now use copper and copper alloys, aluminum, and monel metal in pipe lines, pumps, filling machines, and the like.

Tin is the only metal tested that appears to have a very limited application in wineries. Wine will tolerate only small quantities of tin, and the metal has a comparatively high corrosion rate, particularly when exposed to red wine under conditions of low aëration, which is the usual condition.

It is self-evident that plain iron and steel are dangerous materials to use for any winery purpose that involves contact of these metals with wines that are being processed.

ACKNOWLEDGMENTS

The authors are indebted to K. H. Smith, managing director of Canadian Wineries, Ltd., Niagara Falls and Toronto, Ont., for permitting the installation of testing devices, and for numerous and helpful suggestions. H. B. Barton and H. Reynolds, technical officers on the production staff of Canadian Wineries, Ltd., contributed much to the success of the work, and their assistance is gratefully acknowledged.

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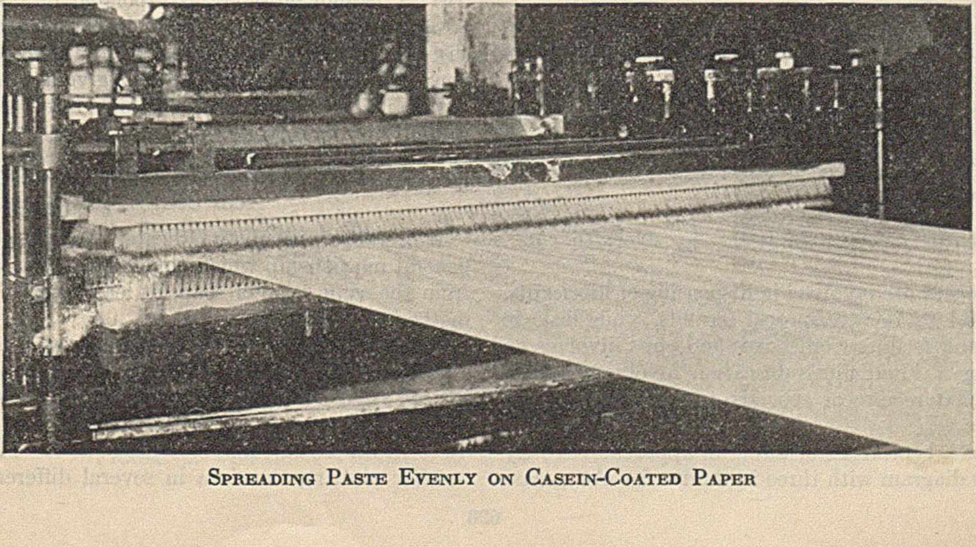

SPREADING PASTE EVENLY ON CASEIN-COATED PAPER

Flow of Petroleum Lubricating Greases

Dependence of Apparent Viscosity on Temperature, Rate of Shear, Oil Viscosity, and Soap Content

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Petroleum lubricating greases are dispensed and used as lubricants under a variety of conditions in which the factors determining the flow characteristics are of primary importance.

Data have been obtained at 77°, 50°, 25°, and 0° F. on a variety of greases using the constant-shear viscometer (1).

All of the data on greases containing calcium mixed-fatty-acid soap have been correlated into one general curve, in which the viscosity of the oil in the grease at the temperature in question, the soap factor K (determined primarily by the soap content), and the rate of shear are the primary factors determining the apparent viscosity of the grease. A relatively small correction is required for the effect of temperature on the soap factor. The agreement between the point data and the general curve is shown in the figures.

A mechanistic conception of grease structure and its behavior during flow is presented. The inability of Bingham's equation to apply to the data is demonstrated.

THE first article in this series (*1*) described the Arveson constant-shear viscometer and presented data obtained on several petroleum lubricating greases at 77° F. (25° C.) in the form of apparent viscosity *vs.* rate of shear diagrams. These diagrams show clearly that: (1) The apparent viscosity of greases decreases with increasing rates of shear in a manner characteristic of the particular soap used, approaching in the limit a value higher than but of the same order of magnitude as the oil in the grease. (2) At any given rate of shear the apparent viscosity increases with increasing soap content.

It is the purpose of this paper to present data, similar to that previously presented, to which has been added another important variable, temperature, and to present a correlation of all the data obtained on commercial greases containing calcium mixed-fatty-acid soap.

As previously stated, the apparent viscosity is that figure calculated from Poiseuille's equation:

$$\eta\alpha = \frac{\pi P R^4}{8LV/t} = \frac{\dfrac{PR}{2L}}{\dfrac{4V/t}{\pi R^3}} = \frac{F}{S}$$

where η = apparent viscosity, poises
P = pressure, dynes/sq. cm.
R = radius of capillary, cm.
L = length of capillary, cm.
V/t = rate of efflux, cc./second
F = stress, dynes/sq. cm.
S = rate of shear, seconds^{-1}

Subscripts α and σ refer to grease, and subscript o refers to the oil in the grease.

There seems to be some disagreement as to what is the true value for rate of shear in capillaries when plastics are involved; therefore, to avoid confusion, the definition of rate of shear will be considered as:

$$S = \frac{4V/t}{\pi R^3} \text{ seconds}^{-1}, \text{ while stress is } F = \frac{PR}{2L} \text{ dynes/sq. cm.}$$

Low rates of shear are involved in dispensing of lubricants, approximately 0.1 to 1000 reciprocal seconds, while leakage from housings and feeding from boxes and cups involves an even lower range. Fluid film lubrication involves rates of shear from 10,000 reciprocal seconds to indefinitely large values.

Figure 1 gives a typical set of data, an apparent viscosity *vs.* rate of shear diagram with three isotherms for the grease and the oil in the grease. The following should be noted: (1) The plot is logarithmic; (2) the most important factor in determining the apparent viscosity of the grease at very high rates of shear is the viscosity of the oil; (3) there is a similarity in the shape of the curves; and (4) the percentage change in apparent viscosity with change in temperature decreases with decreasing rates of shear.

Figure 1 shows that at a rate of shear of 0.1 reciprocal second, the increase in apparent viscosity between 77° and 0° F. is approximately 6 fold; at 300 seconds^{-1} the increase is 64 fold while the oil in the grease increases 132 fold.

The literature contains several references to the improvement in viscosity-temperature characteristics of liquids by the addition of small amounts of certain substances. An example is the addition of 0.1 to 1 per cent of rubber to mineral oil. Instruments commonly used in measuring viscosity operate at variable, but still low rates of shear. It should be apparent from the above data, where the addition of about 4 per cent calcium soap lowered the viscosity change between 77° and 0° F. from 132 to 6 fold, that the addition of very small amounts of certain substances, plastic in themselves, to liquids may cause very marked effects of this sort. Since this addition produces a substance which is no longer a true liquid, extreme caution should be taken when attempting to interpret data obtained with conventional instruments on such mixtures. For example, Saybolt data at 100° and 210° F. cannot be safely extrapolated, on the A. S. T. M. viscosity-temperature chart for hydrocarbon oils, to obtain the viscosity of such mixtures at 0° and 300° F. Further, the conventional instruments will not give a measure of the viscosity of these mixtures at the high rates of shear involved in fluid film lubrication.

GRAPHICAL ANALYSIS OF DATA ON CALCIUM MIXED-FATTY-ACID SOAP GREASES

It has been previously indicated that there should be some general relationship which governs the flow for greases made from the same type of soap, at least when the same general method of manufacture is used.

When the data at three temperatures 77°, 25°, and 0° F. on greases VIII and IX became available, a study was started which will be described in the order of the development. The soap content of both greases was 4.3 per cent and the oil viscosities were 2.61 and 9.69 poises at 77° F.

After plotting the data in several different ways, it was discovered that, if η_G/η_o was plotted as a function of η_oS on logarithmic paper, all points fell in a definite narrow band. Better agreement was obtained, however, if separate isotherms were drawn. The curves (isotherms) required only a slight additional horizontal shift to superimpose. Thus, once the effect of temperature on oil viscosity is taken into account in the manner indicated, only a slight additional correction is required to draw one curve which will probably apply to all greases containing 4.3 per cent of this particular soap.

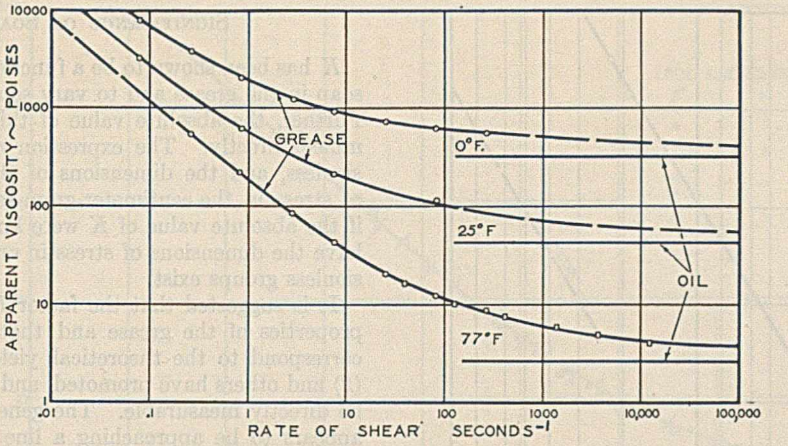

FIGURE 1. ISOTHERMS FOR A TYPICAL CALCIUM SOAP GREASE (IX) AND THE PETROLEUM OIL CONTAINED THEREIN

The data on grease X were treated similarly (soap content 8.5 per cent, oil viscosity 0.25 at 77° F.), and the horizontal shift required to superimpose the curves was found to be the same for the same temperature changes as for greases VIII and IX.

Figure 2 is a plot of apparent viscosity *vs.* rate of shear for a series of greases in which the oil viscosity and the temperature of measurement are constant and the soap content is the parameter. Using the curve for grease I as a reference curve, the horizontal shift required to superimpose each of the curves was determined by averaging the shift required at a series of fixed apparent viscosities. The values obtained were plotted against the soap percentage of various greases. These data are shown in Figure 3, where the actual value of the shift required is plotted against the percentage of soap on logarithmic scales. The symbol, K, has been assigned to this factor. It was interesting that a straight line was obtained as the best curve through these points.

The smooth-curve values of K were read for the various greases from Figure 3. The values of the expressions η_a/η_o and η_oS/K were calculated from the smooth-curve values obtained from Figure 2, and a curve was drawn for these data.

Figure 4 shows the resultant general curve with the points for the original data on greases I to VI. The values of K used were the smooth-curve values of Figure 3. It appears that a fairly satisfactory general curve has been obtained which will fit all of these data. The values of K in Figure 3 are specific to 77° F. for the calcium mixed-fatty-acid soap of greases I to VI.

If the relation is general for grease containing calcium mixed-fatty-acid soap, the data at 77° F. for greases VIII to XII should fall on this curve.

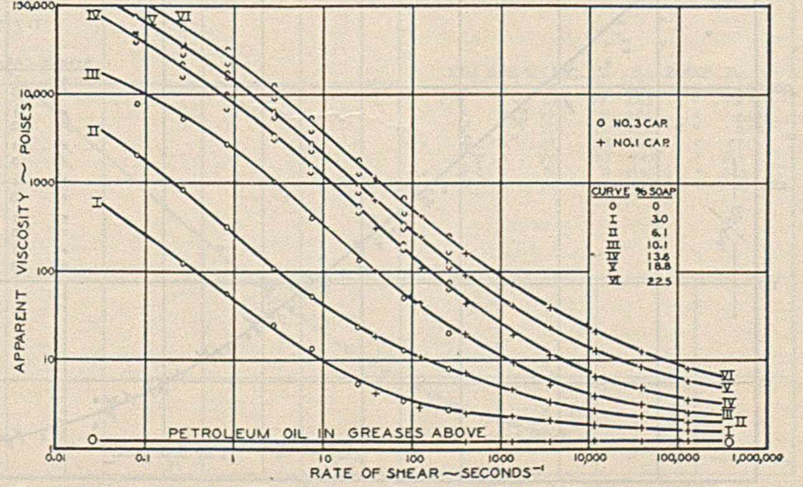

FIGURE 2. APPARENT VISCOSITY *vs.* RATE OF SHEAR DIAGRAM FOR SERIES OF CUP GREASES

Figure 5 shows the agreement that is obtained for greases X and XI when the value for K is obtained from Figure 3, knowing the soap content from analysis. The data for 50° F. also agree satisfactorily with this general curve. It was indicated above that additional shifts would be required to superimpose the curves for 25° and 0° F., upon the 77° F. curve. This shift is the equivalent of multiplying the value of K by 1.5, thus:

$$K_{77} = K_{50} = K \text{ from greases I to VI}$$
$$K_{25} = 1.5 \times K_{77}$$
$$K_0 = 1.5 \times K_{25}$$

This change in the value of K for the lower temperatures was made, and the data for 25° and 0° F. were placed in Figure 5. The values for K and the viscosity of the oil used in the calculations are given in the tabulation on Figure 5.

Exactly the same general curve is reproduced in Figure 6. The data for greases VIII and IX are shown by the points. The best value for K for the 77° F. data was taken arbitrarily, and this value was multiplied by the factors previously given for the lower temperatures. The value of K for 77° F. used was equivalent to 4.4 per cent soap according to Figure 3. (Later precision analyses of these two greases gave check values of 4.3 per cent.)

The data for grease XII were fitted to the general curve in a somewhat different manner and the results are shown in Figure 7. Knowing the value of η_G/η_o for each point, the corresponding value of η_oS/K was read from the general curve. The value of η_oS is known from the original data. By dividing the known value of η_oS by the value of η_oS/K obtained from the general curve, the value of K for each point required to fit the general curve was obtained. The mean value of K for each temperature series (rate of shear being the only variable in each of these series) was determined. Using this value of K, the values of the expression η_oS/K were calculated for each point and the data placed on Figure 7 to show the agreement with the general curve.

The reason for this procedure was that the soap content of this grease was not known exactly but was supposed to be between 10 and 11 per cent. The value of K obtained from these data at 77° F. is equivalent to 11.7 per cent soap according to Figure 3.

Figure 8 shows variation of the ratio, K at the desired temperature to K at 77° F., with temperature.

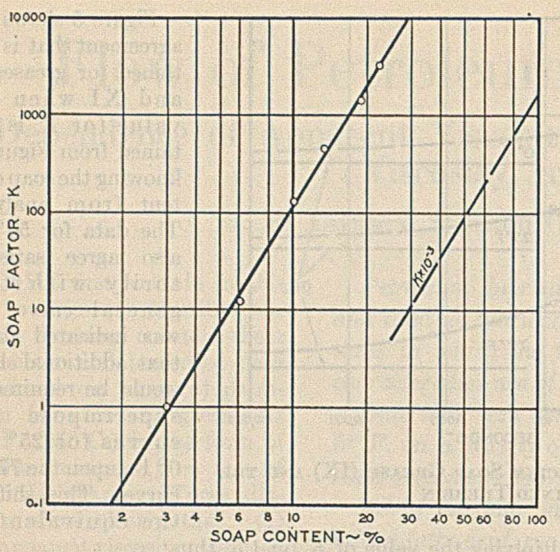

Figure 3. Soap Factor, K, for 77° F. vs. Soap Content for Greases Containing Calcium Mixed-Fatty-Acid Soap

The □ points indicate those calculated from the data on grease XII, and the ○ and + points indicate the values used in plotting greases VIII and IX and grease X, respectively, on the general curve.

The curves of Figures 4 to 7 are identical, and the points indicating the actual data are merely superimposed to show the agreement.

In the case of both Figures 4 and 5 there is a trend away from the curve at low values of $\eta_o S/K$. The general curve has been drawn at the upper end, in the manner indicated, on a more or less arbitrary basis, since the break away from this curve between the various greases is not at all in agreement. Other factors are believed to enter the consideration in this region. These points, which in all cases occur at very low values of the product $\eta_o S$, are in many cases of low precision (pressure, just a few millimeters of mercury). In any event, there is no doubt that at the low values of the expression $\eta_o S/K$ there is a true divergence from the general curve that has been drawn. In this region slippage in the capillary may have occurred. The statement made in the previous paper (*1*) to the effect that no slippage occurred in the capillaries in any region where it was possible to check, still holds.

Slippage is most frequently discussed in the literature in connection with viscosity measurements of rather highly plastic materials where water is the continuous phase. Water has a viscosity of the order of magnitude of one twenty-fifth of the lowest oil viscosity recorded in any of this work. A decrease in the viscosity of the continuous phase and an increase in the concentration of "solid" ingredient both tend to increase the rate of shear at which slippage would be expected to take place.

Significance of Soap Factor K

K has been shown to be a function of the concentration of soap in the grease and to vary somewhat with temperature. Further, the absolute value of this factor cannot be determined directly. The expression η_a/η_o is obviously dimensionless, and the dimensions of the product $\eta_o S$ are those of stress in the centimeter-gram-second system. Therefore, if the absolute value of K were known, it would necessarily have the dimensions of stress in order that only two dimensionless groups exist.

It is suggested that the factor K is related to the elastic properties of the grease and that its absolute value may correspond to the theoretical yield value, which Bingham (*2*) and others have promoted, and which does not appear to be directly measurable. The general curve (Figure 4, etc.) appears to be approaching a line with a slope of -1. If this is assumed to be true, it can be shown that, as the expression $\eta_o S/K$ approaches zero, the stress required approaches the value K, times a constant (the factor for converting the units of K to the centimeter-gram-second system).

Thus as $\eta_o S/K \doteq 0$, $FG \doteq aK$; then by definition aK is the "yield value," and this yield value is determined by the concentration of soap and the temperature, and is independent of the oil viscosity.

Figures 2 and 3 show that, as the soap content increases, the value of K (and therefore the stress required to force the grease through the capillary) increases. K then may be considered as a measure of the resistance of the soap structure to deformation at the particular concentration and temperature in question.

If the straight line through the points shown in Figure 3 is extrapolated, the line intersects the 100 per cent soap ordinate at $K = 1.6 \times 10^6$. If the conversion factor is 10, the value becomes 1.6×10^7 dynes per sq. cm. This extreme extrapolation is not justified because of the dependence of the system on the presence of the oil phase. However, the value obtained is believed to be a fair qualitative indication of the modulus of elasticity of the soap, still in a state of dispersion.

Since completing this work, it has been noted that Poole (*4*), in making measurements of elasticity of gelatin gels, obtained nearly straight lines when log elasticity (Young's modulus) for the gel was plotted against the log concentration (same coördinates as Figure 3) and also found similar variations with temperature.

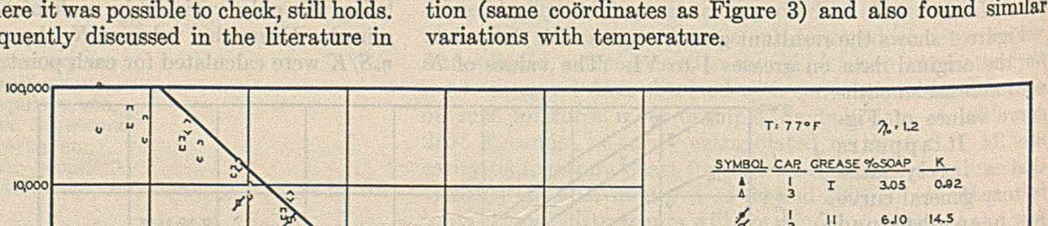

Figure 4. General Curve with Points from Data at 77° F. on Greases I to VI

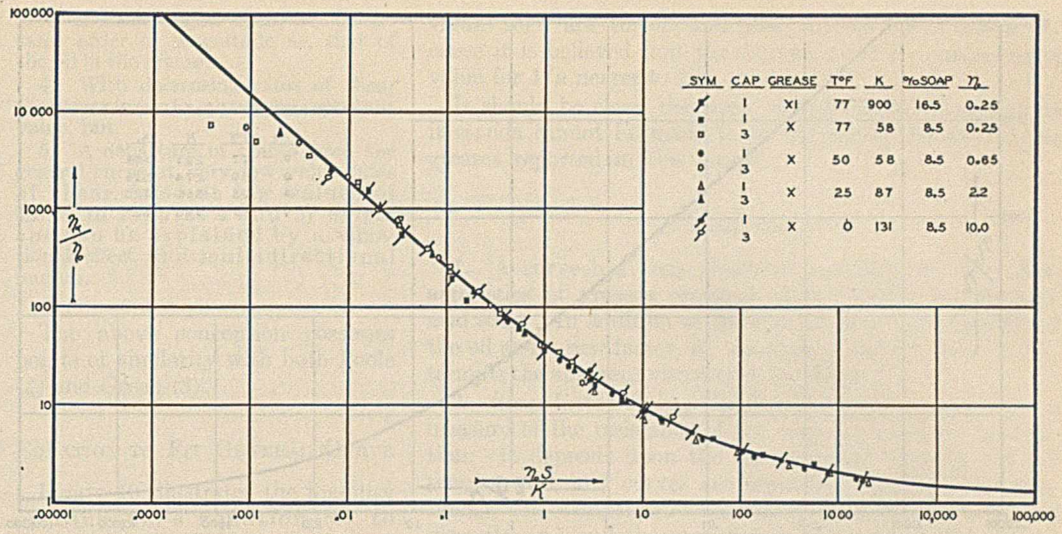

Figure 5. General Curve with Points from Data on Greases X and XI

Application of the General Curve

To illustrate the interrelations of variables, assume that a grease, having an oil viscosity and soap factor of 10 and 10, respectively, is being sheared at a rate of 0.1 (condition A). It may be found from the general curve that η_G/η_o under these conditions is 255; that by arithmetic η_G, the apparent viscosity of the grease, is 2550 poises; and that the stress, F_G, is 255 dynes per sq. cm. It is obvious that decreasing the value of K from 10 to 1, increasing the rate of shear from 0.1 to 1, or increasing the oil viscosity from 10 to 100, will change the value of the expression $\eta_o S/K$ ten fold from 0.1 to the value 1 (condition B).

From the general curve it is learned that the value of η_G/η_o is 40 under condition B ($\eta_o S/K = 1$). Then with other things held constant as in condition A ($\eta_G = 2550$, $F_G = 255$), but with:

η_o increased from 10 to 100, $\eta_G = 4000$, $F_G = 400$ (1)
or S increased from 0.1 to 1, $\eta_G = 400$, $F_G = 400$ (2)
or K decreased from 10 to 1, $\eta_G = 400$, $F_G = 40$ (3)

It is important to understand clearly that changing the rate of shear and changing the viscosity of the oil in a grease, either by temperature change (neglecting effect of temperature on K) or change in oil, by the same ratio result in the same change in stress or pressure required to force the grease through a given capillary. The directions of change are the same.

Grease from Other Soaps

What may be said relative to grease made from other soaps? If two greases containing the same oil, but different soaps, are run at the same temperature, that grease having the flattest viscosity *vs.* rate of shear diagram (log-log) will exhibit the largest percentage change in viscosity with temperature at any given rate of shear, assuming that soap factor K varies with temperature in approximately the same manner in both cases. Since it appears that, in general, soap factor K does not vary markedly with the temperature, the above statement is good to the first approximation, for the following reasons: It was stated that the same oil would be used in both cases and that we would assume that K would vary the same in both cases with temperature. In a logarithmic plot of the data, both greases would appear in the same relative position whether the plot was η_a vs. S diagram or a η_a/η_o vs. $\eta_o S/K$ diagram. Therefore, any decrease in temperature would merely shift the line of constant shear to the right by the same amount for both greases on the latter diagram. The grease having the steeper curve would have the ratio η_a/η_o decrease most and therefore have the least increase in the apparent viscosity of the grease.

It has been previously shown that those greases exhibiting steep logarithmic viscosity-shear diagrams were the most tender. It seems odd that tenderness and change of viscosity with temperature should be so related. It has been known that greases containing soda tallow soap, which are tough and gutty, containing the same oil as a similar calcium mixed-fatty-acid grease, are not nearly as satisfactory as the calcium soap greases for low-temperature use. The prediction from this toughness is that the soda tallow soap transmission grease would have a flat apparent viscosity *vs.* rate of shear diagram and therefore would exhibit larger changes in apparent viscosity with temperature than calcium soap greases. Experimentally this has been found to be true.

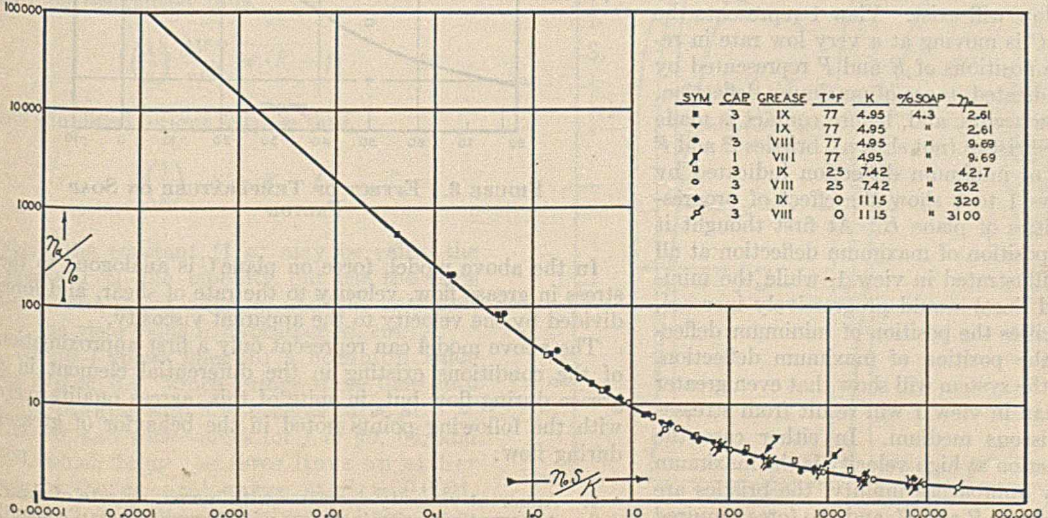

Figure 6. General Curve with Points for Greases VIII and IX

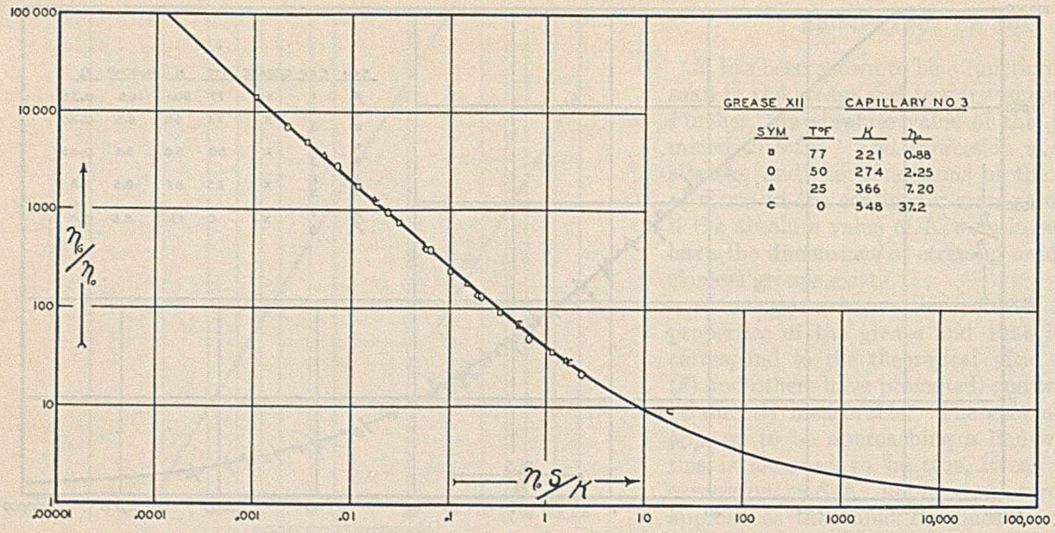

Figure 7. General Curve with Points for Grease XII

Concept of Grease Structure

To augment the views on grease structure presented in the previous paper (*1*), the author wishes to present a highly simplified mechanistic conception of grease structure and its behavior during flow.

The flow of grease, in a capillary for example, consists of the laminar flow of true liquids in which a maze of small solid bodies of various shapes and sizes interferes with the flow. In order that flow exist, these bodies must undergo elastic deformation. The conditions of flow in the differential element may be visualized as similar to two continuous brushes with bristles overlapping, one moving with respect to the other, the space between being filled with a viscous medium. The bristles represent the projections of the maze of soap particles in the grease which interfere with normal viscous flow, and the viscous medium represents the oil.

Figure 9, view 0 represents a finite section through the grease during flow made by a plane normal to the planes of constant velocity and parallel with the direction of flow. Lines *A* to *D* represent several planes of constant velocity wherein *B* is moving in respect to *A*, *C* in respect to *B*, and *D* in respect to *C*. *E* and *F* represent any two bristles associated with planes *B* and *C*, respectively. Views 1 to 8 represent only the small area between planes *B* and *C*, with bristles *E* and *F* only, reproduced. In the absence of any obstructions, normal viscous flow will exist. View 1 represents the conditions when plane *C* is moving at a very low rate in respect to plane *B*. The positions of *E* and *F* represented by the solid lines are, as indicated, those of maximum deflection. The next instant release occurs, and, before contact is made with the next springs or bristles (not shown), bristles *E* and *F* return to the position of minimum deflection indicated by the dotted lines. Views 1 to 8 show the effect of progressively increasing velocities of plane *B*. At first thought it might be felt that the position of maximum deflection at all velocities would be as illustrated in view 1, while the minimum deflection (dotted lines) would progressively increase, until at very high velocities the position of minimum deflection would approach the position of maximum deflection. More careful review of the system will show that even greater maximum deflection than in view 1 will result from stresses transmitted by the viscous medium. In either case the limiting minimum deflection at high velocity is the maximum deflection. As velocity approaches infinity, the bristles are laid down against the planes *B* and *C*, and the force required to give *C* a finite, but very high, velocity is only slightly in excess of that required in the absence of the bristles.

This system would require that a minimum stress be applied before any flow can take place. The derived curve in Figure 10 illustrates how the general curve, as drawn, is approaching a constant stress with decreasing rates of shear, but, as previously indicated, flow exists at still lower stresses. Note the deviation of points at low values of $\eta_0 S/K$ in Figures 4 and 5.

The soap particles are undoubtedly quite irregular in shape, and, therefore, forces perpendicular to the plane of the paper in Figure 9 will exist during flow. This would permit release of the bristles or springs occasionally before the maximum deflection of view 1 is reached. Bombardment of the particles by molecules (Brownian movement) might also aid in the release of the bristles before maximum deflection. Further, it would be expected that the relative frequency of this type of release would decrease as the velocity of plane *C* increases, and that it would be of higher order at low values for the viscosity of the medium. Obviously, increasing the number of bristles in a unit length and/or the degree of overlapping will increase the resistance.

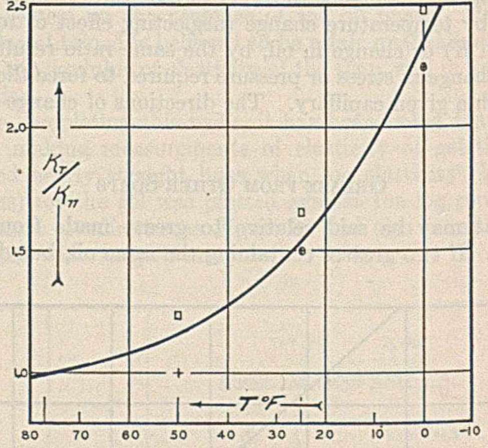

Figure 8. Effect of Temperature on Soap Factor

In the above model, force on plane *C* is analogous to the stress in grease flow, velocity to the rate of shear, and force divided by the velocity to the apparent viscosity.

The above model can represent only a first approximation of the conditions existing in the differential element in a grease during flow but, in spite of this, agrees qualitatively with the following points noted in the behavior of greases during flow:

1. Apparent viscosity decreases with increasing rate of shear.
2. Apparent viscosity increases with increasing soap content.
3. Apparent viscosity approaches a limiting value at high

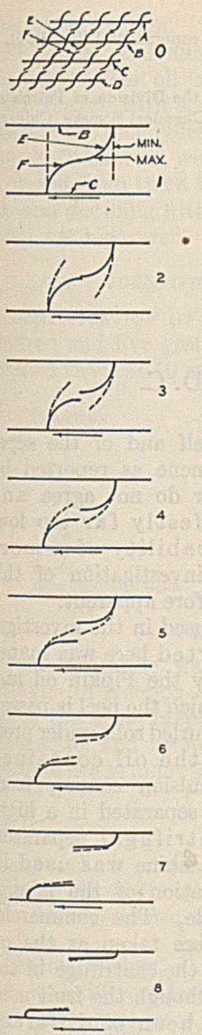

FIGURE 9. GREASE BEHAVIOR DURING FLOW

rates of shear, higher than, but of the same order of magnitude as, that of the oil in the grease.

4. With decreasing rates of shear the stress tends to approach a constant value, but

5. A departure of points from the general curve at very low value rates of shear (also at low values of $\eta_o S/K$ in Figures 4 and 5) exists and can be explained by a vibrational effect and multidirectional motion.

The above conception possesses points of similarity with both Poole (*4*) and Green (*3*).

EQUATION TO FIT GENERAL CURVE

Figure 10 illustrates the inability of Bingham's equation (*2*) to apply to the general curve derived graphically for petroleum lubricating greases containing calcium soap. The conventional variables are used—rate of shear as the ordinate and stress as the abscissa. Logarithmic scales are necessary.

Using the general curve, the S vs. F_G curve for a grease having $\eta_o = 2.6$ and $K = 4.95$ has been calculated. This derived curve and a line for the oil in the grease are shown in both groups of curves. The original data on grease IX are shown in group 2 to illustrate the agreement of direct data with the derived curve.

Bingham's equation (*2*) for capillary tubes,

$$\frac{V}{t} = \frac{\pi \mu R^3}{4} (F - f) \qquad \text{........89}$$

may be rearranged thus,

$$\left(\frac{1}{\mu}\right) \frac{4V/t}{\pi R^3} = (F - f)$$

and simplified for our purpose thus,

$$\left(\frac{1}{\mu}\right) \cdot S = F - f$$

where the constant $(1/\mu)$ may be called the reciprocal of the mobility but has the same dimensions as viscosity, η, and the constant, f, is the yield value in dynes per sq. cm.

Group 1 shows lines for a common value for $1/\mu$ of 3.4, which brings these lines into coincidence with the general curve at S = 100,000, and with values for f of 40, 65, and 100, which bring the three lines on either side of the general curve at S = 0.0001. Group 2 indicates similarly the lines from Bingham's equation when $1/\mu$ = 2.61 and values for f are 40, 65, and 100. Group 2 was drawn because it is believed that the derived curve is approaching a value for $1/\mu$ nearer to 2.61 (η_o) than 3.4.

It should be clear, therefore, that Bingham's equation as it stands cannot be made to fit the curves for any of the greases reported in this paper.

CONCLUSIONS

1. A curve has been presented covering the flow characteristics of greases prepared from calcium mixed-fatty-acid soap. In addition to the rate of shear, the viscosity of the oil and a new factor, K, the soap factor, are found to determine the apparent viscosity of the grease.

2. Soap factor K has the dimensions of stress and is a measure of the resistance of the soap structure to deformation. It depends upon the concentration of soap and the temperature, and curves are presented showing these relations. The temperature determines the values of the oil viscosity (η_o) and the soap factor (K) used in the general curve.

3. The agreement of the general curve with a large number of point data is adequately demonstrated.

4. It is believed that a general curve, using the same variables, exists for each kind of soap.

5. It is shown that Bingham's equation cannot be used to represent the data satisfactorily.

6. A mechanistic conception of grease structure and its behavior during flow, which agrees qualitatively with the data, is presented.

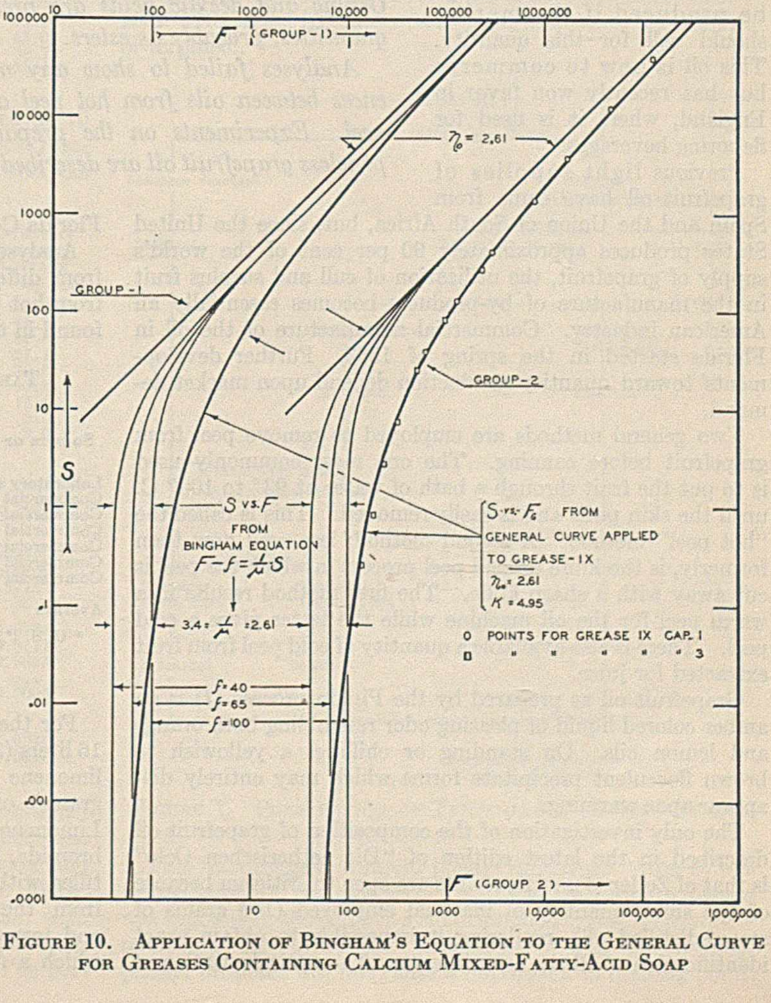

FIGURE 10. APPLICATION OF BINGHAM'S EQUATION TO THE GENERAL CURVE FOR GREASES CONTAINING CALCIUM MIXED-FATTY-ACID SOAP

7. It appears that the relations involved in the general curve cannot be expressed in the form of a simple equation.

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Florida Grapefruit Oil

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Florida grapefruit peel oil, prepared by pressing the peel between rolls and separating the oil in a centrifugal separator, contains approximately 90 per cent limonene, 2 to 3 per cent oxygenated volatile constituents and sesquiterpenes, and 7 to 8 per cent waxy materials. The following other constituents are identified: Octyl and decyl aldehydes, geraniol and octyl alcohol (both free and as acetates), cadinene, and small quantities of citral and methyl anthranilate.

Examination for pinene, terpineol, and decyl alcohol gives negative results, though a small quantity of nonyl alcohol may be present. Octylic and decylic acids are present in small quantities, probably as esters.

Analyses failed to show any marked differences between oils from hot peel and from cold peel. Experiments on the preparation of terpeneless grapefruit oil are described.

The complete utilization of the peel from the grapefruit canned in Florida involves the recovery of grapefruit peel oil.

Approximately 2.5 million boxes or 100,000 tons of grapefruit are processed annually by Florida canners. The industry is sufficiently concentrated so that at least half the peel is readily available for the manufacture of oil. On the basis of a commercial yield of one pound per ton of fruit, 50,000 pounds of oil could readily be produced if the market should call for this quantity. This oil is new to commerce but has recently won favor in England, where it is used for flavoring beverages.

Previous light supplies of grapefruit oil have come from Spain and the Union of South Africa, but, since the United States produces approximately 90 per cent of the world's supply of grapefruit, the utilization of cull and surplus fruit in the manufacture of by-products becomes essentially an American industry. Commercial manufacture of the oil in Florida started in the spring of 1933. Further developments toward quantity production depend upon market demand.

Two general methods are employed to remove peel from grapefruit before canning. The one most commonly used is to put the fruit through a bath of water at 93° to 100° C. until the skin puffs and is easily removed. This is called the "hot peel" method. A second method, less used now than formerly, is the knife or cold peel process in which the peel is cut away with a sharp knife. The first method results in a warm peel for the oil machine while the latter gives a cold peel. There is also available a quantity of cold peel from fruit extracted for juice.

Grapefruit oil as prepared by the Pipkin process (*1*) is an amber colored liquid of pleasing odor resembling both orange and lemon oils. On standing or chilling, a yellowish to brown flocculent precipitate forms which may entirely disappear upon warming.

The only investigation of the composition of grapefruit oil described in the latest edition of "Die aetherischen Oele" is that of Zoller (*5*). His results are open to criticism because of the small quantity of material employed (100 grams of steam-distilled oil), rendering it impossible to obtain exact identification of all the constituents. The optical rotation of the oil itself and of the separated limonene as reported by this author do not agree and are manifestly far too low. The desirability of a more thorough investigation of this oil is therefore apparent.

The oil used in the investigation reported here was manufactured by the Pipkin oil machine in which the peel is passed through knurled rolls under pressure, and the oil contained in the emulsion coming from the rolls is separated in a high-speed centrifugal separator. A small machine was used in the preparation of the laboratory sample. The commercial samples were taken as the oil came from the centrifuge in the plant. Although the fruit used may have been of different varieties, it was principally Florida Common or Duncan type grapefruit.

Analyses were made of seven samples of grapefruit oil from different runs of peel, some of which were extracted from hot peel and some from cold. No great difference was found in the results (Table I).

Table I. Analyses of Florida Grapefruit Oils

Source of Sample	Sp. Gr., d_{20}^{20}	Optical Rotation, α_D^{20} Degrees	Index of Refraction, n_D^{20}	Aldehyde as Octyl and Decyl[a] %
Laboratory cold peel	0.8562	+93.33	1.4758	1.68
Commercial cold peel	0.8563	92.88	1.4753	1.60
Commercial hot peel	0.8579	92.90	1.4760	1.74
Commercial hot peel	0.8572	92.96	1.4758	1.68
Commercial hot peel	0.8558	93.68	1.4758	1.71
Commercial hot peel	0.8561	93.83	1.4760	1.62
Commercial hot peel	0.8543	93.35	1.4760	1.64
Average	0.8563	93.28	1.4758	1.67

[a] U. S. P. method for citral.

Experimental Procedure

For the investigation of the constituents of grapefruit oil, 16 liters (13,700 grams) of the oil were freed from most of the limonene by distilling at 10 mm. Fourteen liters (11,900 grams) of limonene containing aldehydes were obtained. Limonene was characterized by the preparation of the tetrabromide, melting point 104.5° C. The residual oil was distilled with steam in order to separate the volatile ingredients from the fatty and waxy constituents. Seven hundred and twenty grams of volatile material were obtained, from which a further quantity of limonene was removed by distillation at 10 mm. The nonvolatile waxy residue weighed 1020 grams, equivalent to 7.5 per cent of the original oil. The terpeneless oil and the limonene portion were separately shaken with a solution of sodium bisulfite in order to separate the aldehydes. The crystalline bisulfite compounds from both sources were combined, and the aldehydes were recovered from them by mixing with sodium carbonate solution and distilling with steam. A total of 117 grams of aldehydes was recovered.

IDENTIFICATION OF CONSTITUENTS

Identification of Octyl and Decyl Aldehydes. One hundred and five grams of the aldehyde mixture were fractionated twice at 10 mm., affording the following fractions:

Fraction	Boiling Point	Weight
	° *C.*	*Grams*
1	58– 60	33.6
2	60– 70	2.4
3	70– 75	1.0
4	75– 85	7.5
5	85– 93	39.5
6	93–103	0.7
7	103–110	3.7
Residue	.....	1.0
Loss in distillation	.....	15.6
Total		105.0

Octyl aldehyde was identified in fraction 1 and decyl aldehyde in fraction 5 by the melting points of the oximes and of the acids prepared by oxidation with potassium permanganate, and by analysis of the silver salts of the acids. The data are as follows:

	Oxime M. P.	Acid M. P.	Ag in Ag Salt
	° *C.*	° *C.*	%
Fraction 1	58–59	14	42.98
Octyl aldehyde, reported or theory	60	16.5	43.00
Fraction 5	69	27	38.79
Decyl aldehyde, reported or theory	69	31	38.68

The terpeneless, aldehyde-free oil was fractionated at 10 mm., and different fractions were examined as to optical rotation; the esters were calculated as geranyl acetate with the following results:

Fraction	B. P. at 10 mm.	Weight	Optical Rotation, α_D^{20}	Esters as Geranyl Acetate
	° *C.*	*Grams*	*Degrees*	%
1	79– 82	3.7	+15.4	20.9
2	87– 92	4.2	+11.5	44.3
3	92–100	3.9	+17.0	37.6
4	100–105	4.1	+18.0	27.1
5	105–110	17.9	+ 2.0	28.6
6	110–113	4.8	− 0.3	25.8
7	118–121	22.0	+ 1.6	17.5
8	121–125	4.3	+18.0	5.5
9	125–130	13.1	+37.4	3.9

Another portion of terpeneless, aldehyde-free oil was saponified before fractionation at 10 mm., with the following results:

Fraction	B. P. at 10 mm.	Weight	Optical Rotation, α_D^{20}	Specific Gravity 15/15°
	° *C.*	*Grams*	*Degrees*	
1	80– 82	3.92	+ 7.0	0.8778
2	90– 91	1.63	+11.8	0.8711
3	100–102	11.27	+ 9.7	0.9025
4	105–107	1.54	+ 2.9	....
5	107–110	6.45	+ 0.4	0.9005
6	112–115	0.93	− 1.7	....
7	115–118	1.79	− 3.6	....
8	118–119	6.11	− 2.3	0.9066
9	125–129	15.33	+29.7	0.9213

Identification of Acids in Esters. The acids obtained as potassium salts in the saponification of the terpeneless, aldehyde-free oil were separated by steam distillation and divided into water-soluble and water-insoluble acids. Most of the acid is water-soluble. Fractional precipitation with silver and analysis of the silver salts from the various fractions showed it to consist entirely of acetic acid. The percentages of silver found were 64.53, 64.92, 64.55, and 64.08; the silver found in the silver acetate was 64.53 per cent.

The small amount of acid insoluble in water melted at about 0° C., and the silver salt contained 40.28 per cent Ag. Calculated for silver octylate, the Ag content was 43.0, and for silver decylate, 38.66 per cent. The insoluble acids are therefore probably octylic and decylic acids.

Identification of Octyl Alcohol. On treatment with phenyl isocyanate, both fractions 1 and 2 of the saponified oil gave crystalline phenyl urethanes. The crystals were freed from carbanilide by solution in petroleum ether and, when recrystallized twice from dilute alcohol, melted at 73° C. A mixture with *n*-octyl phenyl urethane, melting at 73°, gave no depression in melting point. Optical crystallographic examination confirmed the identity with *n*-octyl phenyl urethane.

Optical - Crystallographic Properties of *n* - Octyl Phenyl Urethane. This substance consists of colorless, micaceous plates and rods. In parallel polarized light (crossed nicols), the extinction is straight and the sign of elongation minus; low-order colors are usually shown; the double refraction is extremely strong ($n_\gamma - n_\alpha = 0.096$). The plates and rods extinguish sharply with crossed nicols; therefore, interference figures were not observable in convergent polarized light. The two refractive indices determinable statistically were as follows: $n_\alpha = 1.560$ (commonly shown lengthwise on rods and also on plates); $n_\gamma = 1.656$ (commonly shown crosswise on rods and also on plates); both, ±0.003.

Examination for Terpineol in Fraction 3. Terpineol, if present, should be found in fraction 3. Accordingly part of this fraction was shaken for a day with 5 per cent sulfuric acid. No terpin hydrate was formed, indicating the absence of terpineol.

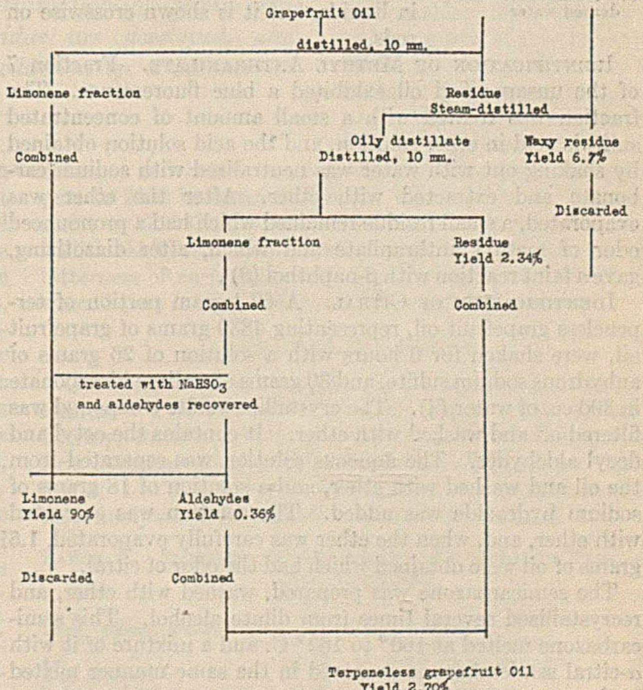

Figure 1. Preparation of Terpeneless Grapefruit Oil

This fraction gave a liquid phenyl urethane. After it was heated with 100 per cent formic acid and the formate formed was saponified, the oil gave a small amount of phenyl urethane melting at 52° to 54° C. Admixture of this with *n*-nonyl phenyl urethane did not cause a depression in melting point.

It is possible that a small quantity of *n*-nonyl alcohol may be present in grapefruit oil.

IDENTIFICATION OF GERANIOL. Fraction 5 (107° to 110° C.) was heated with phthalic anhydride, and the acid geranyl phthalate was converted to the silver salt. The silver geranyl phthalate obtained melted at 135° to 137° C. Admixture with silver geranyl phthalate, prepared from pure geraniol and melting at 132° to 133° C., caused no depression in the melting point. The alcohol was recovered from the silver geranyl phthalate and converted into the diphenyl urethane, which, after recrystallization, melted at 80° to 81° C. and which gave no depression in melting point when it was mixed with pure geranyl diphenyl urethane of 82° C. melting point. Both the geranyl diphenyl urethane and the silver geranyl phthalate had to be carefully recrystallized before proper melting points could be obtained, and therefore the presence of a little citronellol and/or nerol is not excluded.

The geranyl diphenyl urethane was further identified by optical-crystallographic examination. Geranyl diphenyl urethane consists of very fine colorless rods. In parallel polarized light (crossed nicols), the extinction is straight and the sign of elongation plus or minus. The refractive indices are as follows: n_α = 1.550 (crosswise); n_β = 1.665 (lengthwise); both, ±0.003. The maximum index of refraction was not determined, owing to the solubility of the material in liquids, but it is shown crosswise on rods.

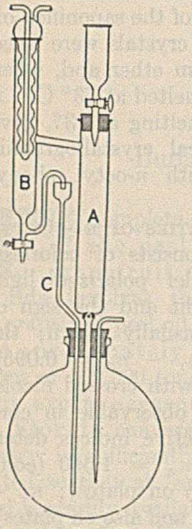

FIGURE 2. APPARATUS FOR PREPARATION OF TERPENELESS OIL

A. Column filled with baffle plates of 8-mesh monel metal gauze
B. Oil trap
C. Return for condensed water

IDENTIFICATION OF METHYL ANTHRANILATE. Fraction 7 of the unsaponified oil exhibited a blue fluorescence. The fraction was treated with a small amount of concentrated sulfuric acid in ether solution, and the acid solution obtained by shaking out with water was neutralized with sodium carbonate and extracted with ether. After the ether was evaporated, a small residue remained which had a pronounced odor of methyl anthranilate and which, after diazotizing, gave a faint reaction with β-naphthol (*3*).

IDENTIFICATION OF CITRAL. A 62.4-gram portion of terpeneless grapefruit oil, representing 4830 grams of grapefruit oil, were shaken for 6 hours with a solution of 26 grams of anhydrous sodium sulfite, and 30 grams of sodium bicarbonate in 300 cc. of water (*4*). The crystalline sulfite compound was filtered off and washed with ether. It contains the octyl and decyl aldehydes. The aqueous solution was separated from the oil and washed with ether, and a solution of 18 grams of sodium hydroxide was added. The solution was extracted with ether, and, when the ether was carefully evaporated, 1.5 grams of oil were obtained which had the odor of citral.

The semicarbazone was prepared, washed with ether, and recrystallized several times from dilute alcohol. This semicarbazone melted at 160° to 162° C. and a mixture of it with α-citral semicarbazone prepared in the same manner melted at the same temperature.

Its identity was further confirmed by optical-crystallographic examination. The refractive indices of α-citral semicarbazone crystallized from methyl alcohol were as follows: n_α = 1.515, n_γ = 1.740; both, ±0.003.[1]

TEST FOR PRESENCE OF PINENE. Fourteen liters of limonene after removal of aldehydes were distilled at 10 mm. pressure until 10 per cent had distilled over. This fraction had an optical rotation of 97.18°. On fractionating this 10 per cent portion at atmospheric pressure, the following fractions were obtained:

FRACTION	B. P.	VOLUME	OPTICAL ROTATION α_D^{20}
	° C.	*Cc.*	*Degrees*
1	172–174	25	+94.5
2	174–175	25	+95.3
3	175	25	+96.4

On redistilling fraction 1, the first 2 cc. showed a rotation of 92°, proving the absence of pinene. This is in disagreement with the results of Zoller (*5*).

IDENTIFICATION OF *d*-CADINENE. The fraction of the saponified oil boiling at 125° to 129° C. at 10 mm. gave the cadinene reaction with acetic and sulfuric acids.

Treatment with gaseous hydrochloric acid in ether solution afforded a good yield of the dihydrochloride which crystallized in needles and melted at 117° to 118.5° C. A mixture with *d*-cadinene dihydrochloride melted at the same temperature.

PREPARATION OF TERPENELESS GRAPEFRUIT OIL

Various procedures were tested in preparing terpeneless grapefruit oil. These included vacuum distillation, extraction with alcohol of various concentrations, and combinations of these two. Limonene can be driven off readily by vacuum distillation, but the waxy residue, which amounts to three or four times the oxygenated flavoring constituents, tends to hold back desirable fractions. In using alcohol extraction methods, alcohol of sufficient strength to extract desirable constituents also extracted an alcohol-soluble portion of the nonvolatile residue. When more dilute alcohol was employed to reduce the solubility of this alcohol-soluble portion, the extraction was long and tedious. The most satisfactory and practical procedure finally developed is illustrated in Figure 1. Limonene was removed from the oil by vacuum distillation, a good fractionating column being used. The residue was then steam-distilled in the specially designed apparatus shown in Figure 2. The residue was admitted dropwise at the top of the packed tower where it met a rising current of steam which deprived the residue of all volatile constituents. The nonvolatile residue settled to the steam generator below, while the volatile fraction and the steam were condensed and caught in the trap. The trap was constructed to return the condensed water to the steam generator via the safety tube. The volatile portion was retained in the trap and drawn off at the end of the distillation.

The volatile portion contained some limonene which was now more easily removed by vacuum distillation in the absence of the waxy residue. The aldehydes were recovered from the combined limonene fractions by means of the aldehyde-bisulfite compound and added to the limonene-free volatile residue to constitute terpeneless oil of grapefruit. The yield by this process was 2.7 per cent, equivalent to a concentration of 37 to 1.

The terpeneless oil prepared as above contains sesquiterpenes. It is soluble in 6 parts of 80 per cent alcohol. The specific rotation is +24° and the index of refraction is 1.4615 at 20° C. Many commercial users do not require an alcohol-soluble flavoring medium and find an emulsion quite satisfactory. This terpeneless oil readily forms a concentrated stable emulsion when used with an emulsifier. The "turpentine taste" caused by the oxidation products of limonene is eliminated.

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[1] These data do not agree with results reported by Wilson and Keenan which were determined on a mixture of α- and β-citral semicarbazones of 132° C. melting point [*J. Assoc. Official Agr. Chem.*, 13, 394 (1930)].

Discussion of Results

From Zoller's work (*5*) it was assumed that citral is the chief aldehyde in grapefruit oil. The present work has shown that citral is a minor constituent and that the predominating aldehydes are octyl and decyl aldehydes. Since the aldehydes of grapefruit oil consist of a mixture of approximately equal quantities of octyl and decyl aldehydes, the factor 0.070 for 0.5 *N* acid, representing the molecular weight of a mixture containing equal parts by weight of these aldehydes, is used in calculating the results reported in Table I. According to Poore (*2*), when decyl aldehyde is determined by the Kleber method, 2 hours should be allowed for the completion of the reaction.

The relatively high percentages of these aldehydes characterize grapefruit oil as aldehydic and emphasize the necessity of protection from oxidation. The admixture of valuable flavoring aldehydes and esters found in this oil should place it in the class with orange and lemon oil as a flavoring oil.

Acknowledgment

Part of the material for this investigation was kindly furnished by W. A. Pipkin of the Citrus Products Manufacturing & Sales Corporation of Tampa, Fla. Optical-crystallographic examinations were made by G. L. Keenan of the Food and Drug Administration.

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Recovery of Naringin and Pectin from Grapefruit Residue

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Complete analyses of grapefruit residues show between 3 and 4.5 per cent of pectin, and about 0.75 per cent of naringin to be present. Methods for the determination of pectin and naringin in the residue are developed, and processes for their production on a commercial scale devised.

The utilization of grapefruit residue from canning plants in Florida, California, and Texas has become of increasing importance in the last few years. This residue, consisting principally of the peel, membrane, and seeds, contains between 3 and 4.5 per cent of pectin and about 0.75 per cent of naringin, the amounts depending mainly upon the ripeness of the fruit. Pectin is a necessary constituent of jellies and marmalades, and, although the market demand is now probably adequately supplied from apple pomace and from lemon and orange residues, it may be profitable at some future time to recover the pectin from grapefruit, as well as the naringin. The latter, which is the bitter substance so characteristic of grapefruit, is a lemon-yellow crystalline glucoside that may possibly have therapeutic value or serve as a compound from which other substances can be obtained when it is chemically treated. Methods for extracting the naringin and pectin have been studied, and commercial processes are outlined.

Many methods (*5–10, 15*), some of them patented, have been proposed for the recovery of pectin from apple and citrus residues. The work of Myers and Baker (*6*) has shown that the most satisfactory extraction of pectin is obtained at a hydrogen-ion concentration of pH 2.15 by boiling for 30 minutes. As naringin is decomposed upon boiling with mineral acids, which are more economical than organic acids, it was necessary to devise a method for recovery of the naringin from the residue before extracting the pectin.

Naringin ($C_{27}H_{32}O_{14}\cdot 2H_2O$), which was discovered by DeVry (*4*) in 1857 in the flowers of grapefruit trees in Java, yields upon hydrolysis with dilute acids, glucose, rhamnose, and naringenin. When boiled with potassium hydroxide, naringenin forms phloroglucin and *p*-coumaric acid. Naringin has not been found in the flowers or fruit of any other variety of citrus. Will (*12, 13, 14*) conducted an extensive research on naringin in 1885–87, and more recently Zoller (*17*) and Asahina and Inubuse (*1*) have studied its properties. When grapefruit is stored, the content of naringin appears to diminish in both the peel and juice. It is soluble in alcohol, acetone, and hot water, but only to the extent of about 1 part in 2000 in water at 20° C. When dried at 110° C., it melts at 171° C.; but when crystallized from water it has an additional 6 molecules of water and melts at 83° C. The bitterness of naringin is quite pronounced; it can be detected when 1 part is dissolved in 50,000 parts of water.

Analysis of Residue

California Marsh Seedless grapefruit picked early in February were halved. The juice, which was removed by burring, contained 12.1 per cent of solids, according to the Brix hydrometer, and 1.87 per cent of acid, giving a ratio of 6.47 to 1. The peel and membrane or rag were ground and then analyzed. The results are given in Table I.

Table I. Analysis of California Grapefruit Peel and Rag Combined

	%		%
Total solids, vacuum at 70° C.	22.02	Crude fiber	2.00
Ash	0.70	Protein (N × 6.25)	1.63
Acid as citric	0.43	Total sugars as invert	8.68
Volatile oil (by steam distn.)	0.56	Pentosans	1.31
Ether extract	0.23	Calcium pectate	3.93
		Naringin	0.63

Determinations of calcium pectate made on other lots of fruit at different times during the investigation showed 3.31, 3.36, and 4.48 per cent in the ground peel and rag. The peel alone in two determinations contained 3.17 and 3.64 per cent. An analysis of the albedo or white portion of the peel showed 6.90 per cent to be present.

One lot of fruit had 0.06 per cent of naringin in the juice, 0.15 in the rag, 0.90 in the peel, and 1.49 in the albedo. Another contained 0.14 per cent in the rag and 0.73 in the peel. Other analyses of the ground rag and peel together showed 0.47, 0.67, 0.69, 0.90, and 1.08 per cent of naringin to be present.

A grapefruit factory in Florida canned some of its residue of peel and rag and shipped it to Los Angeles, where it was analyzed. The results are given in Table II. Separate analyses were made on the peel and rag, and the results show that they contain practically the same amount of pectin and, as in the California fruit, the rag contains much less naringin than the peel.

The results in Table II cannot be accurately compared with those in Table I, as the amounts of moisture in the samples vary, and the canned residue was sterilized and held in the cans some time before analysis. The stage of maturity of the fruit may also have been quite different. The quantity and jellying quality of the pectin especially varies considerably, depending upon the maturity of the fruit from which it is obtained.

TABLE II. ANALYSIS OF FLORIDA GRAPEFRUIT PEEL AND RAG

	PEEL %	RAG %		PEEL %	RAG %
Total solids, vacuum at 70° C.	16.71	15.61	Crude fiber	1.71	1.44
Ash	0.74	0.75	Protein (N × 6.25)	1.13	1.06
Acid as citric	0.74	0.63	Total sugars as invert	6.35	6.30
Volatile oil (by steam distn.)	0.43	..	Pentosans	0.83	0.44
			Calcium pectate	3.19	3.56
Ether extract	0.28	0.16	Naringin	0.40	0.10

The volatile oil was determined by the method of Wilson and Young (*16*) on 200 grams of sample.

The pectin was determined by boiling 100 grams of the ground sample with 300 cc. of 0.4 per cent citric acid for 1 hour and filtering off the extract. This was repeated on the residue until no more pectin was removed, five or six times being sufficient. The calcium pectate was then determined on an aliquot of the combined extracts by the Carré and Haynes method (*3*) with certain modifications. As the extracts generally contained about 0.5 per cent of pectin, a considerable error was encountered if only enough was taken to yield 0.02 or 0.03 gram of calcium pectate according to the Carré and Haynes method. A series of experiments was carried out with various amounts of purified dry pectin and reagents until the following modification of the Carré and Haynes method was adopted:

> Take an amount of extract that will contain about 0.4 gram of pectin, adding water if necessary to bring the volume to 120 cc. If the pectin is to be determined on a powder, dissolve 0.4 gram in 120 cc. water. Add phenolphthalein and neutralize any acid present with 10 per cent sodium hydroxide. Then add 200 cc. 0.2 *N* sodium hydroxide. Let stand at least 1 hour. Add 80 cc. 1 *N* acetic acid. After it has stood for 5 minutes, stir in 50 cc. of 0.1 *M* calcium chloride drop by drop. Then add 100 cc. 2 *M* calcium chloride and boil for 2 minutes. Filter on a 15-cm. paper and wash four times with boiling water. Remove the calcium pectate from the filter and boil for 2 minutes with 300 cc. of hot water. Filter again and wash with boiling water until the filtrate is free of chloride. After washing once with 95 per cent alcohol, transfer the precipitate to a 7-cm. Hirsch filter funnel using a spatula and alcohol. Wash once with ether and remove the calcium pectate with a spatula to a tared dish and dry at 100° C. for 5 hours.

Duplicate determinations checked quite closely, and it was found that the amount of calcium pectate obtained was generally 5 to 10 per cent greater than the amount of moisture- and ash-free pectin taken. It is more rapid than the alcohol precipitate method (*9*) of determining pectin direct. Enough of the 0.1 *M* calcium chloride is slowly added to precipitate practically all the pectin and to give a fine granular precipitate that filters readily after the excess of 2 *M* calcium chloride is added, without the necessity of standing for an hour. When the 2 *M* calcium chloride only was added, the precipitate required several more washings to remove all the chloride.

No quantitative method for determining naringin has been published. It was estimated fairly accurately, however, by weighing the crystals obtained from purified alcoholic extracts of the ground residue. Two hundred grams of the residue were extracted with 300 cc. of 95 per cent alcohol for 30 minutes at 70° C. This amount of alcohol with the water present in the residue gives a final concentration of about 60 per cent, in which the pectin is insoluble. After being extracted, the residue was pressed as dry as possible in a small hand press, and another extraction was made with 200 cc. of 60 per cent alcohol. The two extractions removed all the naringin. After a slight excess of a saturated solution of neutral lead acetate was added and the solution was filtered, the combined extracts were heated nearly to boiling, and hydrogen sulfide was bubbled through until all the lead was precipitated. They were then filtered and evaporated below 70° C. to a sirup, seeded, and allowed to stand until crystallization was completed. After the crystals were removed on a Hirsch filter funnel, they were dissolved in a little hot water and the solution was filtered and allowed to recrystallize. No further crystals were obtained from the mother liquor. After the crystals were dried at 100° C., the percentage of naringin was calculated.

All other determinations given in Tables I and II were made according to methods of the Association of Official Agricultural Chemists (*2*).

EXTRACTION OF THE NARINGIN

The method used for determining the naringin in the residue is not applicable for large-scale production, as the use of alcohol or any other organic solvent in the quantities required is too expensive, even though they were recovered for continuous use upon distillation. If the residue is first dried, a much smaller quantity of solvent is necessary, but drying, as shown by Sucharipa (*11*), brings about detrimental changes in the pectic constituents so that the pectin obtained from such residue has a low jellying quality.

As naringin is very soluble in hot water and only slightly soluble in cold water, a series of experiments was carried out to determine the temperature, time, and quantity of water required to remove it. Because protopectin is slowly hydrolyzed to pectin upon heating with hot water, especially in the presence of the acid contained in the residue, it was necessary to find the point at which practically all the naringin is extracted and a minimum quantity of pectin dissolved. The free pectin present in the residue that is partly dissolved along with the naringin is of low jellying power, as compared with that obtained later upon hydrolysis of the protopectin, so that its loss is of minor importance. It is advisable to heat the residue as soon as possible after the edible portion has been removed from the fruit, in order to destroy the pectinase which gradually converts pectin to pectic acid. The latter is only slightly soluble in water and has no jellying property with acid and sugar.

It was found that, if the ground residue was mixed with 4 parts of water, heated to 90° C., and held for 5 minutes, about two-thirds of the naringin was removed upon pressing. At this temperature, the pectinase is destroyed, and in one test only 0.22 per cent of pectin was removed. The extracted residue, when heated again to 80° C. with 2 parts of water and pressed at once, retained only about one-tenth of the naringin, and only 0.20 per cent more of the pectin was removed, or a total of 0.42 per cent by the two extractions.

The purified naringin finally recovered from the combined extracts from three different lots of residue was 71.5, 78.3, and 87.8 per cent of the total present. Determinations made on the amount of total solids left in the residue after the two extractions showed that 42.8 per cent was removed by the first and 9.1 by the second, or a total of 51.9 per cent of the moisture-free residue was dissolved by the hot water treatments. This consists principally of sugars and acid in addition to the naringin and pectin.

In order to recover the naringin, it was necessary to concentrate the extract to a point where it would not be too viscous and yet where practically all the naringin would crystallize out. This was found to be at about one-ninth of the original volume.

The method finally adopted for the production of naringin is as follows:

To 1 part of the finely ground residue add 4 parts of water, heat to 90° C., and hold at this temperature for 5 minutes. Filter off the water extract, pressing the residue to remove as much of the extract as possible. Again heat the residue, this time to 80° C. with 2 parts of water, and filter at once. Combine the extracts and heat to boiling with one per cent Hyflo Supercel or kieselguhr; filter; and evaporate the clear extract in a vacuum pan to one-ninth the original volume. After cooling, seed the concentrate with a few naringin crystals and set in a cool place, preferably in an ice box. After 2 or 3 days remove the crystals, using suction and a cloth filter. The mother liquor can be heated to 70° C., cooled, and again seeded to obtain another crop of crystals, which however is generally small compared to the first crop. Dissolve the crystals in a small amount of hot water containing about 20 per cent of denatured alcohol, add a slight excess of neutral lead acetate, and filter hot. Remove excess lead by passing hydrogen sulfide into the hot solution until no further test for lead is given when dilute sulfuric acid is added to a few drops of the filtrate. After filtering, evaporate the solution to a small volume to remove the alcohol and hydrogen sulfide. Cool, seed with a few crystals, and after several days remove the naringin, using suction and a cloth filter. Recrystallize twice in small amounts of hot water. Finally break up the nearly dry mass of crystals and set at room temperature to dry further, finally drying in an oven at 100° C. The use of alcohol may be dispensed with, although it aids in holding the naringin in solution while carrying out the lead acetate and hydrogen sulfide treatment. Tests made according to the chromate procedure failed to reveal lead in samples of naringin (11 and 16 grams) prepared by this method.

EXTRACTION OF PECTIN

After the removal of the naringin, the residue is in an excellent condition for the extraction of the pectin, as very little water-soluble material remains and the greater part consists of pectic and cellulosic substances. The method used for the recovery and purification of the pectin is one previously developed by the author (*9*) except that hydrochloric acid is used instead of citric, as it is more economical, much less being required to secure the necessary hydrogen-ion concentration. A series of experiments carried out with various acids, amounts of water, and periods of boiling at different hydrogen-ion concentrations, showed that hydrochloric was the most satisfactory at a pH 2.15, and that it did not adversely affect the pectin when the extracts were evaporated to a paste at 60° C. Because of the buffering salts in the residue 0.04 N (equals 0.15 per cent) hydrochloric acid was required to give a pH of 2.15 during extraction. Upon boiling 1 part of residue for 30 minutes with 5 parts of 0.04 N hydrochloric acid and pressing, 3.20 per cent of good-jellying-quality pectin of 220 grade was obtained on one lot of original residue weighing 4.4 kg. Boiled again for 10 minutes with 2.5 parts of 0.025 N (equals 0.09 per cent) hydrochloric acid which gave a pH of 2.2, only 0.24 per cent of a poor-jellying-quality pectin of 51 grade was extracted. Hence one extraction removed practically all the pectin; that remaining was of an inferior quality. The grade of a pectin is the figure indicating the number of parts by weight of sugar that can be made into a good jelly with 1 part by weight of the pectin. The jellies were made according to the test used by the author in some earlier work (*9*), and the grade was determined by comparison with a standard 160-grade pectin. The extract was clarified by adding 1.5 per cent of Hyflo Supercel direct to the acid solution at the end of the boiling period and filtering hot on a large Büchner funnel. In order to determine the effect of hydrochloric acid on the pectin while evaporating the extract to a paste at 60° C., a series of experiments was made in which part or all of the acid was neutralized with calcium carbonate, calcium oxide, sodium hydroxide, or ammonia. It was found that the addition of these substances, which changed the pH to near the neutral point, affected the resulting pectins so that they were of poor jellying quality and of high ash content. Part of one lot of extract was precipitated directly in the cold with alcohol, the remainder being evaporated to a paste with all the acid present. Comparison of the two pectins obtained showed that both were of the same jellying quality of 165 grade, so there was no destruction of the jellying quality at the evaporation temperature of 60° C. when the acid was present.

The process developed for the recovery of the pectin after removal of the naringin from the residue is as follows:

Boil gently 1 part of residue with 5 parts 0.04 N (0.15 per cent) hydrochloric acid for 30 minutes. Add 1.5 per cent of Hyflo Supercel and filter while hot, coating the filter also with Supercel. Evaporate the extract at 60° C. or lower to a paste containing between 25 and 50 per cent solids. On a large scale the evaporation can be carried out in a vacuum pan or, probably better, on a revolving drum or some similar arrangement where a little solution is rapidly evaporated to a paste. By means of a countercurrent washing device, use the minimum quantity of 95 per cent denatured alcohol at 60° C. required to unite with the water in the paste to form a 60 per cent alcoholic solution in which the pectin is insoluble. The alcohol removes the acid and most of the nonpectin constituents of the paste, forming a granular nongelatinous mass from which the solvent can be removed by pressure. Break up the pectin cake, dry below 70° C. (preferably under a vacuum), and grind to a fine powder.

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TRANSPARENT CELLULOSE SHEETING FOR PRESERVING RECORDS. The Bureau of Standards has found that the acetate type of transparent cellulose sheeting offers considerable promise as a protective covering for preserving valuable written or printed records. The high degree of transparency, tensile strength, and smoothness of cellulose sheetings are attractive features for this use. The cellulose acetate sheeting appears to be particularly well adapted, since it is apparently very stable if made from high-grade cellulose, can be secured in sheets only one-thousandth of an inch thick, and is thermoplastic.

Decrease of Salts in Whey Protein by Electrodialysis

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The objective of the work reported here was the design of an apparatus suitable for quantity production of whey protein (lactalbumin) of a reduced ash content sufficient to permit of the use of the purified product in infant foods and thus to make their lactalbumin content comparable to human milk. Such a modification of cow's milk involving the adjustment of casein and lactalbumin to the proper percentages and protective ratio is considered necessary by infant food specialists in order to obtain the proper physical characteristics and hence the digestibility normal to human milk.

The distinctive features of the apparatus are an easily regulated device for control of the pH of the colloidal solution and rigid siliceous diaphragms or membranes used without preliminary infiltration of a foreign substance, such as colloidion, the partitions being made impermeable to colloidal substances by the hydration or gelatinization of the silica within the walls.

The apparatus has been found to be efficient and practical of operation and is recommended for general use in the purification of protein and other colloidal solutions.

According to Freundlich and Loeb (*8*) electrodialysis is a combination of electrolysis and dialysis—the separation of electrolytes under the influence of an electric potential from a colloidal system through semipermeable membranes. The literature dealing with electrodialysis is extensive. Dhere (*5*), Rheinböldt (*15*), Reiner (*13*), Reitstötter (*14*), and Spiegel-Adolf (*17*) have reviewed the work done with electrodialysis in biological and colloidal chemistry. Pauli (*12*), Ettish (*6*), Bradfield and Bradfield (*4*), and many others have published original researches on the subject.

As early as 1896 Winkler (*19*) described a process for the purification of protein degradation products by means of electricity. Schwerin (*16*) obtained in 1900 his first patent for a method of purification of proteins by means of the electric current.

The three-chambered glass cell of Pauli, equipped with electrodes of platinum, silver gauze, or graphite, is probably the most widely used apparatus for electrodialysis. Although a review of the literature indicates an increased interest in the subject, the process is still among the group of neglected methods, if the wide field of its possible uses is considered.

Theoretical Factors

Three factors of major importance in the practical operation of an electrodialytic process are: (1) the nature and permeability of the membranes used, (2) the phenomena of electroendosmosis, and (3) the causes, extent, and prevention of the changes in hydrogen-ion concentration in the colloidal system. A discussion of cataphoresis, layering phenomena, and other phases of the process may be found in the work of Freundlich and Loeb (*8*), Pauli (*12*), and Spiegel-Adolf (*17*).

In electrodialysis the colloid to be purified is placed in the central compartment of a three-compartment cell between two dialyzing membranes, and a suitable electrode is placed in each of the outer compartments. The outer compartments are filled with water which is changed continuously or intermittently in order to facilitate the removal of the electrolytes. Membranes consist of various materials such as collodion, Cellophane, parchment, and parchment impregnated with gelatin, albumin, hemoglobin, and other proteins.

Negatively charged membranes such as parchment and collodion are satisfactory for use as cathode membranes. No strictly positive membranes are known. However, membranes which are positive when used next to the anode may be prepared from amphoteric substances like proteins. A recent investigation has indicated that an alumina plate is a suitable positive diaphragm for electrodialysis on a commercial scale (*10*). Various investigators recommend the use of a negative membrane next to the cathode and a positive membrane next to the anode.

The passage of water through the diaphragm under the action of the electric current during electrodialysis is termed "electroendosmosis." The flow is commonly from anode to cathode, and the volume of flow is proportional to the electrokinetic potential. Hepburn's work (*9*) indicated that there was a constant electrolytic water transport per farad for solutions up to 1 *N* concentration, modified by a specific action of the diaphragm. Fairbrother and Balkin (*7*) found that the relation between the voltage and the velocity of endosmosis was linear up to 150 volts, but at higher voltages the velocity increased more rapidly than the voltage. Löddesöl (*11*) found that the extent to which water passes through the membranes depends partly upon the type used and was able partially to control the flow by the use of one type of membrane at the anode and another type at the cathode.

It is known that in the process of electrodialysis the cation is removed more rapidly than the anion, and consequently an acid reaction is produced in the dialyzing chamber. Bradfield (*3*) has found that the rate of removal of the cation is influenced by the nature of the anion with which it is combined, while the rate of removal of the anions is in the order $Cl^- > SO_4^{--} > H_2\,PO_4^-$. It is usually considered that the increased hydrogen-ion concentration is due to differences in permeability with respect to cations and anions, most membranes being more permeable to the former. From experiments made in this investigation, however, it seems probable that the more rapid back-migration of hydrogen ions than of hydroxyl ions, and the electroösmotic flow from the anode to the cathode are accountable in a larger measure for these changes in reaction. In support of this view it has been observed that the transfer of alkali from the cathode compartment to the anode compartment in a small dialysis cell by means of an adjustable siphon device resulted in regulation of the pH even to an alkaline reaction if desired, not only with porcelain or alundum membranes but also when these

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[1] The preliminary investigation concerning the diaphragms and the development of a small-scale electrodialysis apparatus was completed by Philip N. Peter, who died on December 11, 1930.

materials were heavily coated with infiltered collodion or when parchment was used.

Where no controlling device is utilized, the rate and intensity of the change in reaction in the dialyzing chamber will depend upon the current density and upon the nature and quantity of electrolyte present. It is obvious that, as the electrodialysis nears completion, the direction of the change in reaction will be towards neutrality.

Methods for controlling the hydrogen-ion concentration of the solution in the dialyzing compartment have been devised by several investigators, and a detailed account and criticism of such procedures may be found in the excellent review by Spiegel-Adolf (*17*). Briefly, these methods consist of a preliminary dialysis or the employment of small current strengths until the electrolytic content is reduced to a low value (Pauli); the use of a positively charged membrane at the anode and a negatively charged one at the cathode (Ruppel, Freundlich); the addition of such electrolytes as will by precipitation or other means change the valence of the anions to be removed (Stern); and the continuous addition of sufficient alkali to maintain the colloidal solution at neutrality (Fricke). In addition, Baer (*1*) maintains an approximately neutral reaction in the middle cell of an electrodialysis apparatus by means of a membrane combination which tends to establish an alkaline reaction therein and carbon dioxide is led through the middle cell to neutralize the alkali.

It is believed that the adjustable siphon device mentioned previously affords a more advantageous and practical procedure for regulating the hydrogen-ion concentration of the colloidal solution undergoing electrodialysis than any of the methods mentioned above.

DIAPHRAGMS

In a preliminary investigation, membranes of collodion, of parchment, or of thin sheets of a light, porous wood (basswood) were used. It was found that, while these materials permitted a satisfactory separation of electrolytes, they possessed certain undesirable properties which unfitted them for industrial use.

Rigid siliceous or alundum membranes are durable and may be made a part of a more permanent apparatus. They possess the particularly desirable advantage of permitting rapid and thorough cleaning and hence may be used repeatedly. With respect to impermeability to protein, such membranes when properly prepared have given very satisfactory results. It is believed that the adsorption of protein which naturally occurs in the capillary spaces of the rigid membranes is a favorable influence with respect to impermeability of the partitions to colloidal materials.

FOUR-CELL PLANT-SCALE APPARATUS

DESIGN. Before the large-scale apparatus was designed, a preliminary study was made with a small model having a dialyzing chamber capacity about one-fourteenth that of the large unit. This model was essentially the same in material and design as the large unit described below, except that it was possible to use small alundum diaphragms with about half the thickness necessary in the large apparatus.

In some preliminary experiments with a large stock size Coors porcelain cell of 7.5 liters capacity, it was found that the material was suitable for large-scale equipment if the cell was frequently cleaned with fairly strong hydrochloric acid and if the polarity of the current was reversed occasionally during operation. However, alundum cells were chosen in preference to porcelain cells mainly because they were obtainable with the least delay in the required size and had less tendency to excessive electroendosmotic expansion in volume of contents during operation.

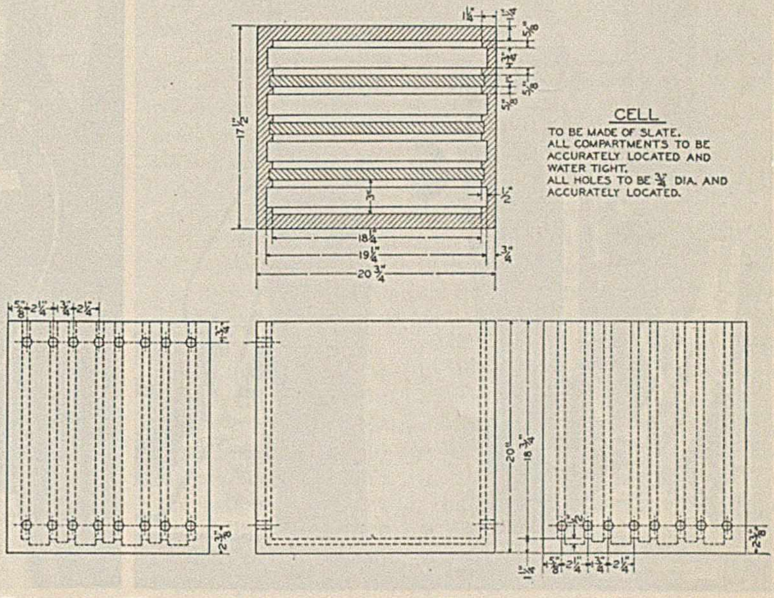

FIGURE 1. WORKING DRAWING OF SLATE TANK FOR THE FOUR-UNIT CELL

In order to provide for a satisfactory rate of salt removal, it is necessary that the design of the apparatus should provide for the requisite current concentration:

$$\text{C. C. (current concentration)} = \frac{\text{amperes}}{\text{cell volume in liters}}$$

$$\text{C. C. of original small cell} = \frac{3}{0.42} = 7.1$$

$$\text{C. C. of a large cell} = \frac{40}{6} = 6.7$$

It was concluded that, neglecting the factor of the difference in the wall thickness and consequent difference in electrical resistance, a cell of 6 liters capacity carrying a current of about 40 amperes would approximate the small cell in efficiency. Accordingly, a new unit containing four such cells was designed and constructed. Several of these large units could be connected to a suitable power line to handle whey liquor on an industrial scale.

The common electrode system was not employed, but each cell was installed in a separate water-tight compartment in a newly designed slate box. Provision was made to connect the cells in series with a 220-volt direct-current power line, thus affording a potential of about 55 volts for each cell. This system was thought to be more trouble-proof and flexible than the common electrode system in view of the narrow width of the electrode chambers and the necessity of connections for the automatic siphons. The use of rubber tubing facilitated the speedy change of the water connections when a reversal of the flow in the siphons was desirable.

On account of the narrowness of the new cells and the heating effect of high amperage, the design provided for the cooling and stirring of the liquid by means of its continuous circulation from cell to cell and through a long cooling coil, and also for the stirring within the cells by means of slowly moving paddles.

DESCRIPTION. In Figure 1 are shown the details of the slate tank in which four alundum (Norton RA 84 mixture)

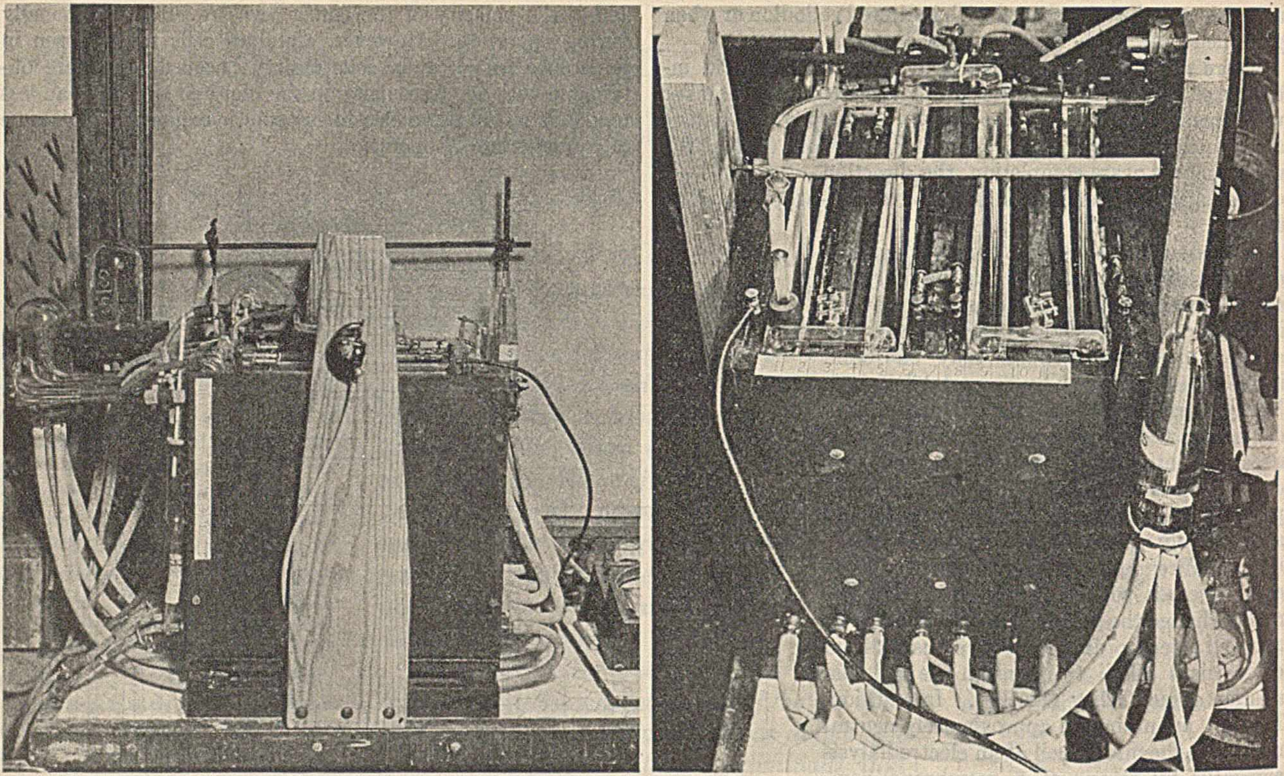

FIGURE 2. LARGE ELECTRODIALYSIS UNIT: LEFT, FRONT VIEW; RIGHT, TOP AND SIDE VIEW

cells were installed. Views of the complete apparatus are shown in Figure 2.

The manufacturers had difficulty in preventing the cells from warping during their heat treatment; consequently, they varied somewhat from the correct dimensions which caused some irregularity in the width of the electrode chambers.

Each graphite electrode (Acheson) consisted of three pieces, each measuring 46.4 × 15.2 × 1.27 cm. ($18\frac{1}{4} \times 6 \times \frac{1}{2}$ inches), the edges resting one upon the other. The electrical connections were brass rods which extended a short distance into the upper edge of each electrode. Heavy copper wire was connected to binding posts on each rod and the whole covered with rubber tubing and rubber cement in order to reduce the corrosion. The ends of the electrodes which partially obstructed the water outlets and inlets in the slate tank were beveled off so that a free flow was obtained. The electrodes were held firmly in place against the walls of the tank by means of Bakelite strips which were wedged between the electrode and the alundum cells at the ends of the electrode chambers.

The alundum cells were sealed in place in their respective slots by means of felt strips impregnated with hot paraffin. Two long strips 0.5 cm. in thickness and 2 cm. in width were used for each cell.

Pyrex glass tubes 14 mm. in internal diameter were cemented into the holes in the slate box to carry the water flow through the compartments. Heavy rubber tubes of 13 mm. internal diameter were slipped over the outside ends of the glass tubes to carry the water between the electrode chambers and the adjustable glass stand pipes, which regulated the rate of inflow and difference in level between the anode and cathode chambers.

Figure 3 shows the principle employed for the siphon arrangement and water circulation in the compartments of a single unit:

> *D* is the dialyzing chamber. *A* and *C* are the anode and cathode compartments, respectively. If the siphon, *S*, and the tap water inlet, *E*, are placed near the top of the compartments, then tap water inlet *I* and outlet for all or part of *A* and *C* effluent, *O*, must be placed near the bottom of the compartments or vice versa in order to provide the proper circulation of wash water. By means of an adjustable outlet, *F*, to the drain on the siphon tube it is possible to control the amount of alkali transferred to the anode chamber, thus permitting regulation of the hydrogen-ion concentration in the dialyzing chamber, *D*.

The siphon device was arranged so that all or part of the cathode wash water could be siphoned from an outlet near the top of the cathode chamber through a U-tube into the top of the anode chamber. After dilution with the anode wash water, the mixture flowed out of the opposite end of this compartment near the bottom. In addition the drainage tubes at the bottom of the compartments were converted into additional siphons by means of glass Y-tubes, and provided better circulation in the narrow chambers. The combined anodic and cathodic flow on its way to the drain passed through a standpipe which was adjusted so that the level of water in the anode chamber was slightly lower than that in the cathode chamber, thus operating the siphon continuously. In order to insure, if desired, dilution of the alkaline cathode flow with fresh tap water upon its discharge from the siphons near the top of each anode chamber, the inlets for the inflowing anode water supply were placed directly above the siphon discharge openings. All or part of the cathodic discharge could be diverted directly to the drain if desired by means of an opening in the U-tube siphons at the top and the Y-tube siphons at the bottom of the apparatus. The openings in the U-tube siphons at the top of the apparatus were adjusted so as to serve as a constant-level overflow device in the event of accidental stoppage of the outlet tubes.

Provision was made to draw the whey from the top of the front cell of the apparatus down through a large tube which contained a thermometer and up through a cooling coil by means of a pump which delivered the whey to the bottom of the rear cell, but part of the flow of the cold liquor could be diverted directly to the front cell, thereby lowering the temperature and raising the level therein. The liquor was circulated continuously from cell to cell through Pyrex glass siphons of 16 mm. inside diameter. When the by-pass was not in use, the contents of each cell could be changed every 2 minutes, and the rapid circulation in addition to the paddles provided effective stirring. The paddles were made of Pyrex glass and one was mounted above the center of each cell upon a wooden shaft powered by a vacuum-operated windshield-wiper mechanism.

The bronze gear pump was plated with chromium on the interior and pumped the liquor at the rate of 3.3 liters per minute at a speed of 486 r. p. m.

The cooling coil was made of block tin tubing with a 9.5 mm. ($\frac{3}{8}$ inch) inside diameter and a length of 9.1 meters (30 feet), which was bent into twenty-four coils about 12.7 cm. (5 inches) in diameter. The coil was enclosed in a cylindrical galvanized tank through which cool tap water flowed.

The sizes of various parts of the apparatus are as follows:

Distance between electrodes	5.1 cm. (2 in.)
Effective cross-sectional area of each graphite electrode 46.4 × 45.7 cm. ($18\frac{1}{4}$ × 18 in.)	2122 sq. cm. (329 sq. in.)
Operating capacity:	
Each alundum cell	6 liters (1.6 gal.)
Total for apparatus (4 cells)	24 liters (6.3 gal.)
Capacity of cooling coil, pump and tubes	1 liter (0.26 gal.)
Width of electrode compartments (approx.)	6.4 mm. ($\frac{1}{4}$ in.)
Dimension of alundum cells (over-all)	47.6 × 47.6 × 3.8 cm. ($18\frac{3}{4}$ × $18\frac{3}{4}$ × $1\frac{1}{2}$ in.)
Interior width	2.54 cm. (1 in.)
Thickness of alundum side walls (approx.)	5.6 mm. (7/32 in.)

The cost of the main items comprising the apparatus was as follows:

4 alundum cells at $23.20 each, plus $15.00 mfg. cost	$107.80
Slate tank with 4 compartments, slotted and drilled	25.00
24 Acheson graphite plates, 61 × 15.2 × 1.3 cm. (24 × 6 × $\frac{1}{2}$ in.)	18.74
Westinghouse motor, $\frac{1}{6}$ h. p., 220 a. c., 60 cycles, 1725 r. p. m.	16.47
Block tin cooling coil and galvanized tank	19.18
Metal tank base with wooden supports for motor and paddles	20.00
Oberdorfer No. 2 bronze single-shaft gear pump (chromium plated)	12.10
Total	$219.29

OPERATION. In some preliminary experiments it was found that the current rose to 40 amperes or more with the use of approximately 55 volts across each cell and not over 7 per cent concentration of salts in the liquor. However, upon continued use, the resistance of the cells apparently increased and the current ranged lower, averaging about 20 to 25 amperes over the duration of some experiments. It is thought that excessive amperage is sometimes due to the concentration or shorting of the current through deposits of coagulated protein on the walls and bottom of the cells.

In order to build up the current concentration at the beginning of each run, no water, or very little water, was circulated through the compartments for the first half-hour or until the whey was warmed. The maximum amperage was not generally attained until the run had progressed for over an hour. Toward the end of the process the current gradually fell from about 30 to about 12 to 15 amperes.

The cells carried about 8 amperes greater current with the bottom siphons open than when closed. This was due, presumably, to the fact that in the first instance part of the fresh water flowed across the bottom of the cathode chamber and out without diluting the more concentrated salt solution above, which had somewhat the same effect as the use of less wash water.

The temperature of the tap water used in the electrode compartments and also to cool the tin coil was about 8° C. The temperature of the water after passing around the coil in the galvanized tank at the rate of 5 liters per minute was 12.5° C. The efficiency of the process would be lessened by the use of water warmer than 8° C., as this temperature made it possible to hold the temperature of the whey liquor below 30° C. with about 30 amperes of current passing. The temperature of the whey as measured just after leaving the front cell farthest from the pump was about 30° C. with about 30 amperes of current. However, the whey remained at this temperature for only a short time inasmuch as the temperature of the whey in the rear cell just after leaving the cooling coil and pump was about 20° C.

Before some of the experiments the alundum cells were pretreated with fairly strong hydrochloric acid (50 to 75 per cent concentrated acid plus water) to which a little hydrofluoric acid was sometimes added. This treatment was found to be necessary to clean the cell pores efficiently and to keep the conductivity of the cell walls at a high level. Occasionally it was also necessary to reverse the potentials and water flow in the electrode chambers because of the tendency of the cathode wall of the cell to become clogged. Some protein was deposited on the walls of the cells during the runs, mostly on the cathode side. Putrefaction of traces of protein which had been adsorbed in the cell pores was retarded when the apparatus was not in use, by filling the cells with a solution of sodium chloride.

The current concentration and temperature of liquor was regulated somewhat by the rate of water flowing through the electrode chambers, and this was varied from time to time. The rate of water flow for the four-cell unit was varied from 2 to 13 liters per minute, but generally the total flow was about 5 or 8 liters per minute. When the flow was regulated at 2 to 5 liters per minute, the tap water entered the bottom of the cathode chambers, and all of it was siphoned to the top of the anode chambers at the opposite ends of the cells without dilution with any additional tap water. In case the total flow entering the system was 8 or more liters per minute, it was divided between the cathode and anode chambers in proportions which were varied, but the total cathodic effluent was siphoned as before to the top of the anode chamber where it was mixed with a fresh supply of tap water. The above figures represent the total amount of water which entered the system and must be divided by four to obtain the flow for each separate cell.

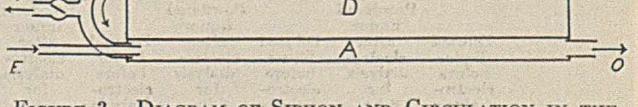

FIGURE 3. DIAGRAM OF SIPHON AND CIRCULATION IN THE ELECTRODE COMPARTMENTS OF A SINGLE UNIT

The transfer of all the cathode effluent to the anode chamber was necessary to regulate the acidity of the liquor in the central compartments, and the variations which were made in the rates of flow mentioned above appeared to be of little effect in this respect. The condition of the cell walls as a result of acid treatment and reversal of the polarity seemed to be of importance in controlling the acidity of the liquor.

If the cells were operated without reversal of polarity and especially if strong acid was not used in pretreatment between runs, then the cell walls appeared to become progressively denser, especially the walls on the cathode side. Inasmuch as the electrolytic water transport takes place from the anode to the cathode, there was as a consequence of this difference in density a tendency for the hydrogen-ion concentration and the volume of liquid in the cells to increase. Therefore, the reversal of polarity after every few experiments tended to facilitate the control of acidity in the liquor and any tendency to volume increase.

Except in the case of one experiment, it was necessary to add water (0.5 to 6 liters) to the liquor in order to maintain constant volume during electrodialysis. The shrinkage was greatest in the runs made after the cells had been treated with strong acid and the polarity had been reversed.

The concentrated whey used in the experiments was diluted with water before dialysis so that the percentage of concentrated liquor in the total volume varied from 33¹/₃ to 50 per cent. This was necessary because the concentrated whey became viscous while being held in storage at a low temperature prior to the experiments. Then, too, the salt concentrations of the undiluted whey were sometimes too great to allow for its sufficient reduction in an 8-hour run.

Results. After making a number of preliminary experiments, seven runs were carried out with the large apparatus, and the dialyzed whey protein liquor was powdered in a spray drier. These results will be briefly summarized in the following paragraphs.

The largest amount of powder obtained per run was 1.6 kg. (3.5 pounds). The loss in drying this small amount of powder in a spray drier about one-fourth the size of a commercial unit was excessive and was estimated to be approximately 25 per cent. It is thought that the actual yield would be about 1.8 kg. (4 pounds) for the four-cell apparatus, using 11.4 liters (3 gallons) of concentrated liquor which had been diluted with an equal amount of water, making a total volume of 22.7 liters (6 gallons) with a total solids content of about 30 per cent. The ash content of the powders varied from 3.85 to 6.81 per cent, the average being 5.50. The moisture content of the powders varied from 1.28 to 3.38 per cent, the average being 2.12. The length of the runs varied from 6 to 10 hours, the average being 8. The liquor for five of these experiments was analyzed before dialysis, and percentage reduction in ash during the process, based on the ratio of the total solids to ash in the liquor as compared to the powder, ranged from 44.2 to 61.6 per cent, the average being 55.9.

In most of the experiments it was possible to maintain the pH of the liquor above 4 during the process by means of the siphon arrangement, and in these instances the powder was not excessively acid to the taste.

Table I. Results of Typical Experiments with Semi-plant-Scale Apparatus

	Experiment A		Experiment B		Experiment C	
	Diluted liquor before electrodialysis	Powdered liquor after electrodialysis for 6 hr.	Diluted liquor before electrodialysis	Powdered liquor after electrodialysis for 8 hr.	Diluted liquor before electrodialysis	Powdered liquor after electrodialysis for 8 hr.
	%	%	%	%	%	%
Total solids	25.29	98.70	25.62	97.45	30.85	98.13
Ash	3.68	5.55	2.66	3.85	4.46	6.81
Protein	...	...	4.18	19.20	7.25	20.74
Lactose (by difference)	...	...	18.78	74.40	19.14	70.58
Reduction of ash in total solids	...	61.4	...	61.9	...	52.0

The powder from five runs was thoroughly mixed, and the distribution of nitrogen in the samples was determined. The casein was precipitated by the acetic acid method, and the protein precipitated by Almen's tannic acid reagent was estimated as lactalbumin and albumoses. The percentage of nonprotein nitrogen was found to be 31, and there were about 4 parts of lactalbumin and albumoses to 1 part of casein in the sample as compared to 2 parts of albumin and albumoses to 1 part of casein in undialyzed whey protein. This change in ratio is presumably due to coagulation and loss of a portion of the casein during the electrodialysis and is not undesirable, inasmuch as the proportion of albumin in the product is thereby increased.

The analyses were carried out according to official A. O. A. C. methods, but the nitrogen was determined by the gasometric micro-Kjeldahl method of Van Slyke (*18*).

The results on three of the experiments described in the group above are presented in some detail in Table I.

Discussion of Results

A study of the various data obtained in the experiments indicated that the electroendosmotic volume changes and the course of the reaction in the liquor may be partially regulated by the simultaneous reversal occasionally of the polarity and water connections of the system between the experiments. It was also evident that, as the cell walls grew progressively denser and less conductive with use, it was necessary that they be cleaned frequently by allowing fairly concentrated hydrochloric acid solution to remain in them for several hours or a day. It is thought that these changes in the permeability of the diaphragms resulted from the adsorption of protein and the dehydration or formation of silica gel in the pores.

The actual efficiency of the salt removal in the large apparatus was somewhat lower than expected in the last group of experiments described above. This is considered to be due to the fact that the cells were not pretreated with strong hydrochloric acid often enough, with the result that the average amperage was nearer 20 than 30. However, the percentage reduction in salts as figured on the total solids basis compares favorably with that obtained with the small apparatus. It is presumed that the greater relative electrical resistance and the less efficient functioning of the siphon device of the large cell as compared to the original small alundum cell model was the result of the difference in the wall thickness of the two cells, the large-size cell necessitating a wall thickness about twice that of the small model.

It was noted in the preliminary experiments that the percentage decrease of ash in the solids (actual efficiency) was approximately 20 per cent less than the percentage decrease of ash in the liquor (electrodialytic efficiency). This difference was due to the decrease in the total solids during the process, resulting from coagulation of protein, loss of lactose, and reduction in salts.

It was observed in this investigation that sometimes large amounts of denatured protein were deposited on the cathode side and bottom of the dialyzing cell. This difficulty seems to be due to certain poor batches of liquor with a yellow gelatinous appearance in which the protein was apparently denatured to some extent. Filtration or clarification of the whey liquor before use to rid it of lumps and easily coagulable protein was helpful. Much of the liquor available for these experiments was variable in composition and high in lactose. High lactose content and excessive coagulation of protein resulted in a low protein content in the dialyzed product. Ordinarily, the lactose content of the powder should not be over 50 per cent. It was also evident from the experiments that grain-curd casein whey was not very suitable for electrodialysis on account of the relatively large amount of ash present as compared to the protein.

It was apparent from these experiments and some preliminary work in which higher voltages were used, that it would be feasible to increase the speed of electrodialysis by raising the voltage per cell to about 70 during part of the time in order to maintain the amperage above 30 for a longer period during the process. This would necessitate the use of colder water than was available for the experiments described in order to prevent overheating of the liquor.

Ordinary whey protein powder, which is obtained by drying the concentrated Swiss cheese or rennet casein whey after partial separation of lactose, contains about 17 per cent salts and would cost about 10 cents per pound (*2*). However, the dialyzed powder would be a high-cost product which would limit its uses. Estimates, based on the operating results of the large semiplant-scale unit, indicate that the power consumption for an 8-hour run in which the ash content was reduced by about two-thirds would be about 40 kilowatt-hours. With a yield of about 1.8 kg. (4 pounds) of powder and a cost of one cent per kilowatt-hour the electrical costs would average about 10 cents per pound of powder. It is thought that the addition of other manufacturing costs would make the total cost of the dialyzed product somewhat less than 50 cents per pound, and that its chief value would be as an ingredient of modified infant foods which retail at about one dollar per pound.

The addition of the powder would serve to correct the deficiency of lactalbumin in cow's milk and would aid in the formation of a finely divided, easily digestible curd in the infant's stomach. Actual tests have shown that cow's milk modified with 5 per cent of this powder will yield a finely divided curd upon acidification with dilute hydrochloric acid to the pH range of infant digestion. Then, too, lactalbumin is held to be an essential protein for the support of growth and for the correction of deficiencies in other proteins. It is possible by the proper dilution of cow's milk with water and the addition of fat, lactose, and the dialyzed powder, to adjust the amount of albumin and other substances to approximately that of breast milk without appreciably increasing the total protein content, or increasing the buffer value excessively. The presence of lactose in the powder makes it possible to reduce the amount of this sugar which it would be otherwise necessary to add. In making up such a modified milk, the amount of the dialyzed whey protein necessary in the mixture would be less than 30 per cent on the dry basis.

ACKNOWLEDGMENT

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The Raman Effect

Applications and Present Limitations in Petroleum Chemistry

JAMES H. HIBBEN, Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.

A brief discussion of the nature of the Raman effect and of its application to the study of various systems is given. It is to be particularly emphasized that the applications and limitations mentioned pertain not only to the petroleum industry but also to any other industry or scientific research which seeks to utilize this new research tool. The Raman spectra method of investigation is one which may prove particularly useful under conditions where other methods of approach are not applicable. There are, however, certain limitations such as the complexity of the system to be examined, color, and lack of Raman lines of sufficient intensity.

THE utility of the Raman effect as a means of obtaining fundamental information in regard to petroleum hydrocarbons bears the same relation to the petroleum industry as it does to any other industry or special branch of science where fundamental information is per se of advantage.

The particular efficacy of the Raman effect lies in the fact that it is a physical method which neither shifts an equilibrium nor causes chemical change, and is independent of the state of aggregation of the material to be examined and, within wide limits, its chemical constitution. It can, in certain cases, by empirical analysis give a picture of the constitution of certain complex liquids which are otherwise so complex as to defy other methods of approach. It provides information in regard to the frequency of vibration of the atoms within the molecule, the strength of the bond between atoms in their normal states, their amplitude of vibration and, in simple cases, their spacial configuration. From this information it has been possible to calculate the specific heats of certain compounds and their normal stability, and to gain an insight into the complexity of solutions both organic and inorganic (*8*).

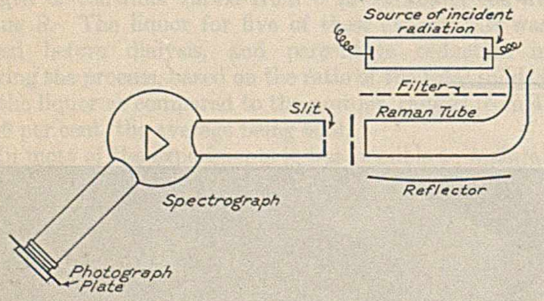


FIGURE 1. EXPERIMENTAL ARRANGEMENT FOR RECORDING RAMAN SPECTRA

That this is a popular method of approach to the study of many of the complex problems of organic and inorganic chemistry is evidenced by the fact that in the five years since C. V. Raman discovered this effect there have been more than a thousand publications on this subject.

This phenomenon is most simply explained on the basis of a collision between a light quantum and a molecule. A certain analogy can be drawn between the mechanism for eliciting Raman spectra and ordinary collisions. In the case of collision between two molecules it is quite conceivable that one molecule may bounce off after an inelastic impact with less velocity and consequently less energy than it possessed previously, imparting some of its energy to the other molecule as kinetic or as potential energy. As a result of this impact, all or part of the atoms making up the molecule may be set into vibration.

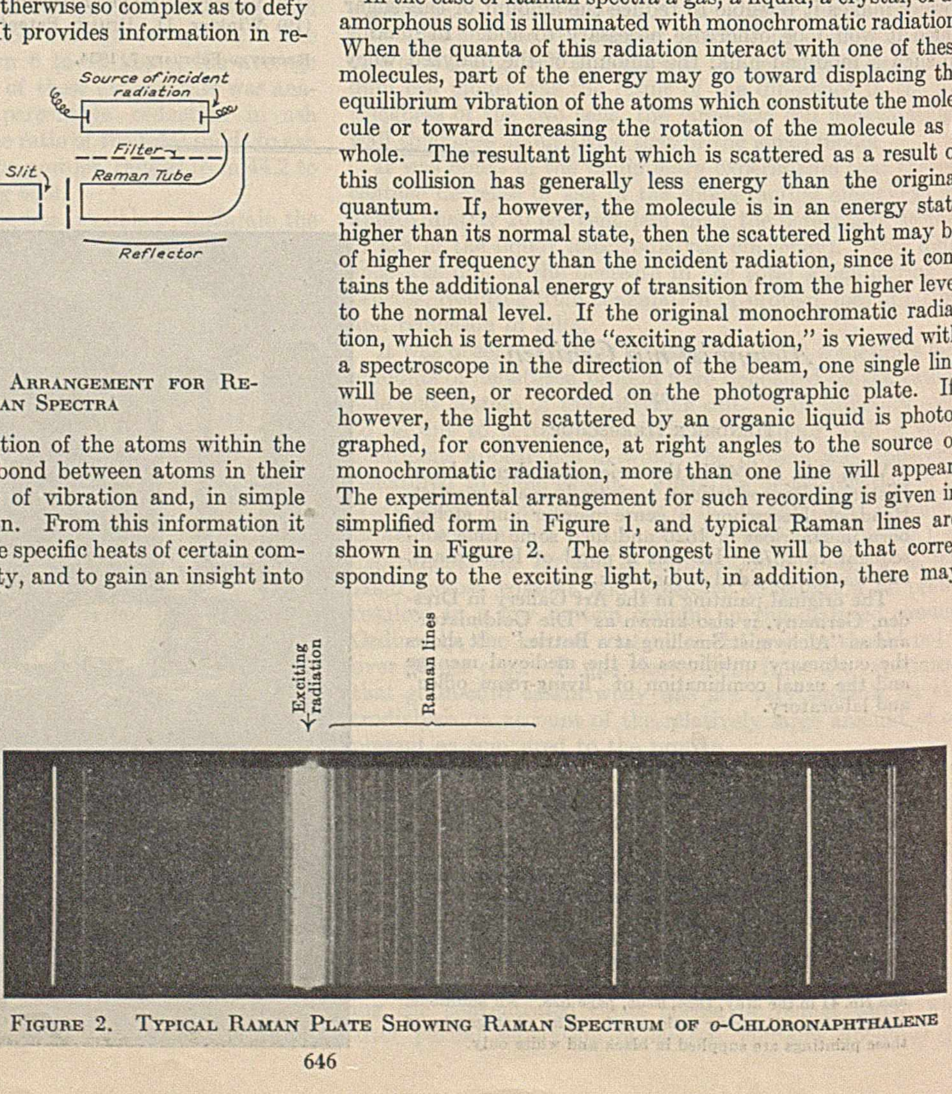


FIGURE 2. TYPICAL RAMAN PLATE SHOWING RAMAN SPECTRUM OF *o*-CHLORONAPHTHALENE

RAMAN SPECTRA

In the case of Raman spectra a gas, a liquid, a crystal, or an amorphous solid is illuminated with monochromatic radiation. When the quanta of this radiation interact with one of these molecules, part of the energy may go toward displacing the equilibrium vibration of the atoms which constitute the molecule or toward increasing the rotation of the molecule as a whole. The resultant light which is scattered as a result of this collision has generally less energy than the original quantum. If, however, the molecule is in an energy state higher than its normal state, then the scattered light may be of higher frequency than the incident radiation, since it contains the additional energy of transition from the higher level to the normal level. If the original monochromatic radiation, which is termed the "exciting radiation," is viewed with a spectroscope in the direction of the beam, one single line will be seen, or recorded on the photographic plate. If, however, the light scattered by an organic liquid is photographed, for convenience, at right angles to the source of monochromatic radiation, more than one line will appear. The experimental arrangement for such recording is given in simplified form in Figure 1, and typical Raman lines are shown in Figure 2. The strongest line will be that corresponding to the exciting light, but, in addition, there may be one or more lines corresponding to light scattered by those molecules which have taken up a certain amount of energy from the incident radiation. These lines, consequently, represent smaller frequencies than the exciting radiation and appear shifted to the longer wave-length side, depending on how much of this energy has been removed. For example, if the exciting radiation is the blue 4358 Å. mercury line, the scattered lines appearing on a photographic plate will consist of the 4358 Å. mercury line plus lines of a greenish blue or green, or in exceptional cases perhaps even yellow. If a molecule is in one of its higher energy states, a corresponding shift in the opposite direction is possible but comparatively rare. These shifted lines are Raman lines. The term "shift" is used to indicate the fact that the Raman line is a weaker part of the original exciting radiation which has been degraded, and consequently the modified radiation generally appears at a lower frequency; that is, part of the exciting radiation, as stated above, has apparently been shifted to a longer wave length. The magnitude of this shift is expressed as a difference between the frequency of the exciting radiation and the frequency of the Raman line. By more or less common consent this difference is expressed in wave numbers or the number of vibrations per centimeter, but it may also be expressed in wave length, in which case the differences will usually fall between 1μ and 75μ. The difference between the frequencies of the exciting radiation and the Raman lines may correspond to the characteristic infra-red absorption of the molecule. Pure rotational Raman spectra have been observed in a few instances.

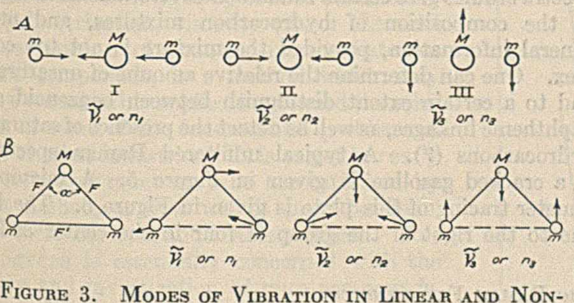


Figure 3. Modes of Vibration in Linear and Nonlinear Triatomic Systems

The frequency of either the exciting radiation or the Raman radiation is given by the expression:

$$\tilde\nu = 10^8/\lambda_{\text{Å}}. \qquad (1)$$

where $\tilde\nu$ is expressed in wave numbers and the spectral lines in Ångström units. The Raman shifts are obtained from the following relation:

$$\tilde\nu_1 - \tilde\nu_2 = \pm\Delta\tilde\nu \qquad (2)$$

It is a demonstrable fact that, as a first approximation, the frequencies of some of these Raman lines are related to the atomic constitution of the molecule by the equation for a simple atomic harmonic oscillator—namely,

$$\tilde\nu_m = 4.25\sqrt{F/\bar\mu} \qquad (3)$$

where $\tilde\nu_{mechanical} \cong \Delta\tilde\nu_{radiation}$
F = the force constant and is a function of the binding strength between the atoms
$\bar\mu$ = the reduced mass—i. e., $1/\bar\mu = 1/M + 1/m$
M, m = atomic weights of the vibrating masses

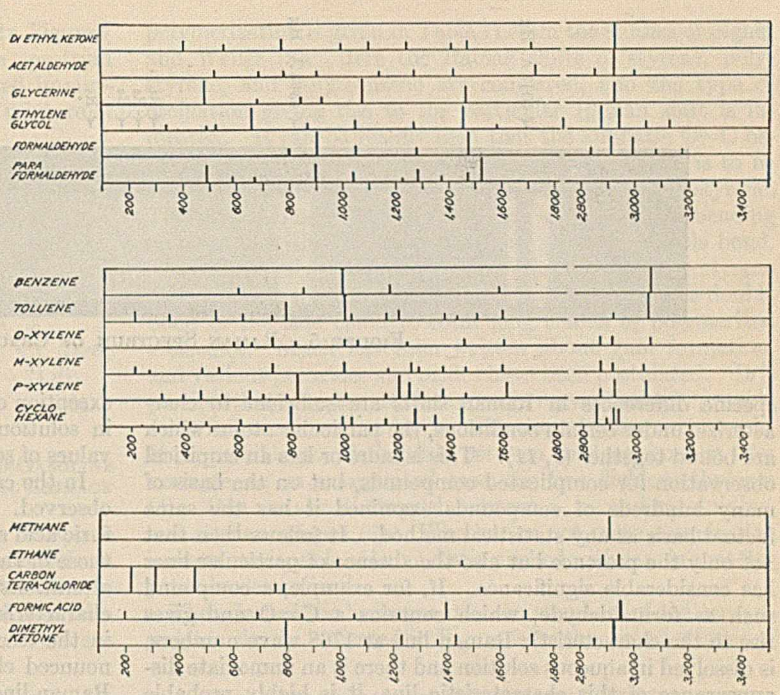


Figure 4. Typical Raman Shifts of Organic Compounds

The reason such a simple equation will approximately hold is that the shift in the amplitude of vibration of the atoms on absorption of the exciting radiation corresponds to only a few hundredths of an Ångström unit. From this it has been shown, for example, by Andrews and others, that the force constant for a double bond is roughly twice that of a single bond, and the constant for a triple bond is approximately three times that for a single bond (*1*). If one knows the approximate force constant (which for a single bond is usually of the order of 5 dynes per cm. for carbon-to-carbon or carbon-to-hydrogen linkages), then one can calculate what the frequency for specific linkages should be, or the reduced mass in a case of an unknown. This is for simple oscillatory motion. If the motion described by the atom is not of this type or if the atom is acted upon by more than one force, this equation no longer holds true and the prediction of Raman lines becomes more complicated. The same two atoms may give rise to a number of different lines, depending upon the possible types of vibration. The different modes of vibration for linear and nonlinear triatomic systems are illustrated in Figure 3. While it is generally true that the force constant for simple oscillators is of the same order of magnitude or multiples of it, this naturally varies slightly from compound to compound, depending somewhat on the nature of the other constituents. These variations serve to identify not only the type of linkage—that is, whether it is single, double, or triple bond—but may also serve to identify the particular compound, since it is highly improbable that two compounds will give precisely the same Raman spectrum (*3*).

Differences in Raman Shifts

This means of identification may be carried a step further. While it is true that double bonds, for example, are readily recognizable by the fact that the lines which correspond to them fall in the region of the spectrum which is generally free from the presence of other lines, it is also true that the frequency shifts corresponding to C═O are not identical with C═C. This is because of slightly different values of F and $\bar\mu$ in Equation 3. The characteristic frequency shift for C═C is from 1550 to 1660 wave numbers, while the shift for C═O is from 1650 to 1770 wave numbers per cm. These

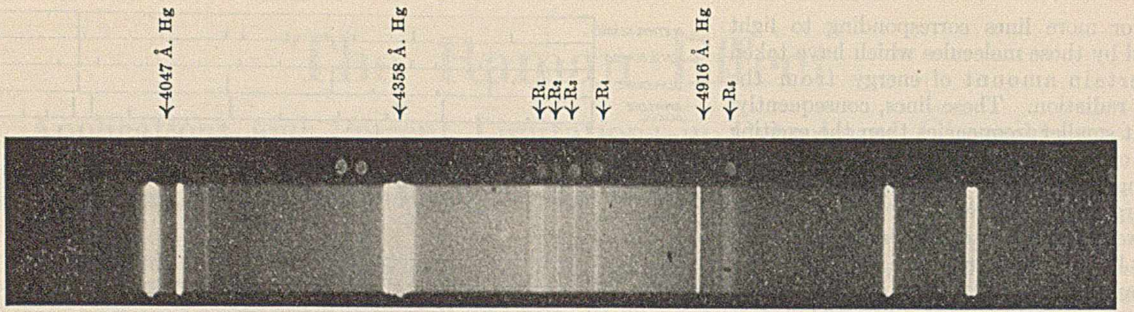


FIGURE 5. RAMAN SPECTRUM OF CRACKED GASOLINE

specific differences in Raman shifts are sufficient to characterize, under certain conditions, the particular atoms which are bound together (*5*, *11*). This is more or less an empirical observation for complicated compounds, but on the basis of many hundreds of compounds examined it has the same factual basis as any statistical method. It follows then that not only the presence but also the absence of particular lines has considerable significance. If, for example, a compound such as formaldehyde, which contains a C═O and gives rise to the characteristic Raman line at 1768 wave numbers, is dissolved in aqueous solution and there is an immediate disappearance of this characteristic line, it is highly probable that this type of linkage is no longer present and the compound is no longer formaldehyde in the sense in which it has usually been considered, but becomes most probably methylene glycol (*9*).

Typical Raman shifts for some organic compounds are shown in Figure 4, where the relative intensities are roughly given by the height of the lines, indicating the Raman shifts. As is to be expected, methane has only one strong line, corresponding to a carbon-hydrogen oscillation. Ethane, however, has several lines. Those appearing near $\Delta\bar{\nu}$ 2900 corresponded to the carbon-hydrogen oscillations and the one near $\Delta\bar{\nu}$ 1000 corresponds to the carbon-carbon oscillation. The shift between $\Delta\bar{\nu}$ 1400 and 1500 is due to the transverse oscillation of the hydrogen atom. It is notable that in carbon tetrachloride one naturally finds no lines corresponding to the carbon-hydrogen oscillation. The lines appearing near $\Delta\bar{\nu}$ 1600 correspond to the C═C vibration in cyclic hydrocarbons and are absent, as is to be expected, in cyclohexane. The shifts corresponding to C═O in the ketones, aldehydes, and acids are visible near $\Delta\bar{\nu}$ 1700 with the exception of the spectrum for formaldehyde, which was taken in solution. In Table I are given the average numerical values of some typical characteristic wave-number shifts.

In the case of inorganic substances similar behavior also is observed. Concentrated nitric acid and concentrated sulfuric acid show Raman spectra which are quite different from those of the dilute acids (*12*). In addition to these profound alterations there may also exist slight displacements of the characteristic Raman lines when there is a pronounced change in the electric environment. Concomitant with this, pronounced changes in the relative intensities of characteristic Raman lines may occur as a result of an interaction of atoms with the solution or with each other.

These modifications and suppressions are all quite characteristic of the particular compound and its environment, and are as much a specific physical property from the broader aspects of the problem as are the boiling point and melting point, or any other so-called physical properties.

APPLICATION TO PETROLEUM INDUSTRY

From the point of view of the petroleum industry, Raman spectra studies give certain fundamental information in regard to the composition of hydrocarbon mixtures, and other general information, provided the mixture is not too complex. One can determine the relative amount of unsaturates and to a certain extent distinguish between benzenoid and naphthenic linkages, as well as detect the presence of saturated hydrocarbons (*7*). A typical unfiltered Raman spectrum of a cracked gasoline is given in Figure 5. A microphotometer tracing of this plate is given in Figure 6. The last line to the right of the group of four in the center of Fig-

TABLE I. SOME CHARACTERISTIC RAMAN FREQUENCIES[a]

(In wave numbers per cm.)

						C═C			C—H					
Ethylene						1620						3000	3080	
Butadiene						1634						3000	3090	
Amylene						1667				2863	2936	2967		
		C—C												
Methane											2915			
Ethane		990								2890	2950			
Hexane		897							2731	2862	2941			
			C—O											
Methyl alcohol			1034							2835	2943			
Ethyl alcohol			1046	1094						2876	2928	2974		
	C—S							H—S						
Methyl mercaptan	704							2537			2932	2975		
							C═O							
Formic acid							1647				2951			
Acetic acid							1666				2942			
Acetaldehyde							1716				2914			
Formaldehyde							1768				2945			
					C═C									
Benzene					1584								3060	3185
Toluene					1604						2933		3052	
Cyclohexane					..				2858	2887	2920	2935		

[a] Only some of the strongest lines are given.

ure 6 owes its origin to the C=C oscillation. In Figure 7 are given microphotometer curves of the Raman spectrum of a cyclopropane containing traces of unsaturated impurities (*11*). The Raman spectrum resulting from a mixture of

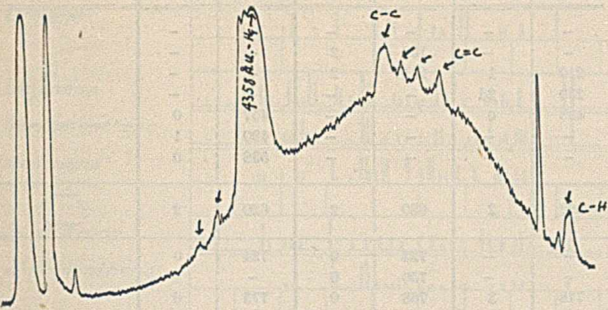


FIGURE 6. MICROPHOTOMETER TRACING OF CRACKED-GASOLINE SPECTRUM, SHOWING LINE ATTRIBUTABLE TO OLEFINIC LINKAGE

several cyclic hydrocarbons is shown in Figure 8. It is true that most of this type of information can be obtained from other sources, by more convenient means, but it is not so easy by ordinary chemical procedure to distinguish the relative strength with which the various hydrogen atoms are bound to carbon in their normal state, or in the case of compounds involving oxygen to demonstrate, for example, that the polymerization of acetaldehyde (*13*) or formaldehyde (*9*) is brought about through the formation of a ring structure with the oxygen atoms as part of the ring. The application of the Raman effect to complicated systems, such as one finds in the petroleum industry, is yet in its infancy; it should be borne in mind that, while there apparently are certain limitations in so complicated a system, any method which may throw light upon such phenomena as polymerization, viscosity (*2*), or chemical constitution of doubtful intermediate organic compounds, is a method which may have considerable application toward the solution of some of the fundamental problems of this or other industries. It is as yet too early to state how much may be accomplished by this method, or how well it may be done, but there has been undeniable progress. This progress is essentially concerned with the study and investigation of pure compounds, a mandatory preliminary to the interpretation of complicated mixtures.

It is of interest not only to the petroleum industry but to other industries as well to know why aluminum chloride and zinc chloride act as catalytic agents in producing polymerization. This problem has not been solved but it has been demonstrated that aluminum chloride will profoundly modify the characteristic Raman spectra of solutions in which it is dissolved, that aluminum chloride hydrate probably consists of an arrangement wherein the molecules of water are more nearly adjacent to the aluminum than are the chlorine atoms, that the characteristic Raman spectrum of zinc chloride is profoundly altered on solution in methanol, and that its aqueous solutions remain unaltered until diluted to such an extent that the molecular species themselves are probably changed (*10*). A typical example of the demonstration of polymerization is given in Table II from the studies of Signer and Weiler (*2*). Here the Raman shifts of styrene, polystyrene, and ethylbenzene are compared, and the type of oscillation giving rise to the particular Raman shift is indicated. It can be readily seen that the aliphatic C=C oscillation, for example, is present in styrene, but, as is to be expected, is absent in both ethylbenzene and polystyrene. This may also be said of the frequency assigned to the bending moment of hydrogens attached to an aliphatic double bond. The entire analysis is consistent with the view that the styrene molecules are coupled through a breaking down of the double bond in the side chain to form long chains of polymerized molecules. Much has been written about gum formation, and various peroxides and oxides have been postulated. It is possible that here, too, Raman spectra may ultimately provide some information as to the constitution of these compounds. It is possible to distinguish between various isomers—for example, as an exaggerated case, the two dichloroethylenes (*4*). One can also distinguish between *o*-, *p*-, and *m*-toluidine, and similar xylenes (*6*). Whether or not more complicated isomers are capable of being distinguished with ease is a matter yet to be determined.

The effect of the hydrogenation on members of the terpene series is clearly indicated in Figure 9 by the disappearance of

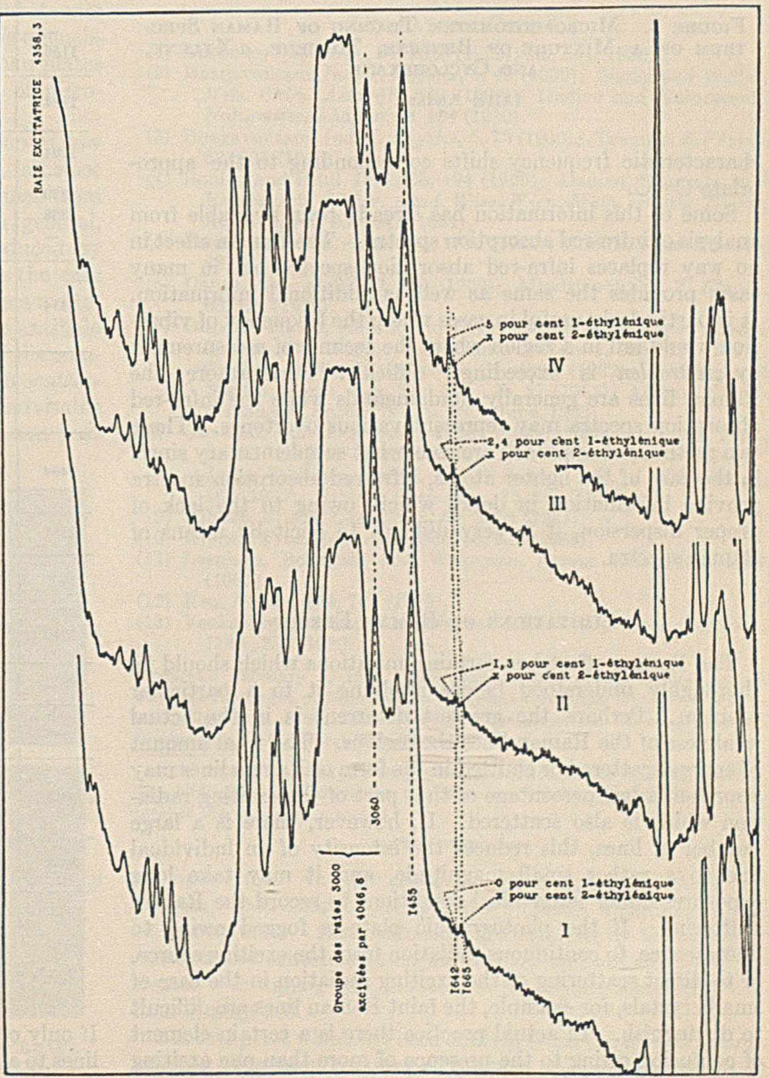


FIGURE 7. MICROPHOTOMETER TRACING OF RAMAN PLATE OF CYCLOPROPANE, SHOWING PRESENCE OF OLEFINS AS IMPURITIES

(After Lespieau, Bourguel, and Wakeman, *11*)

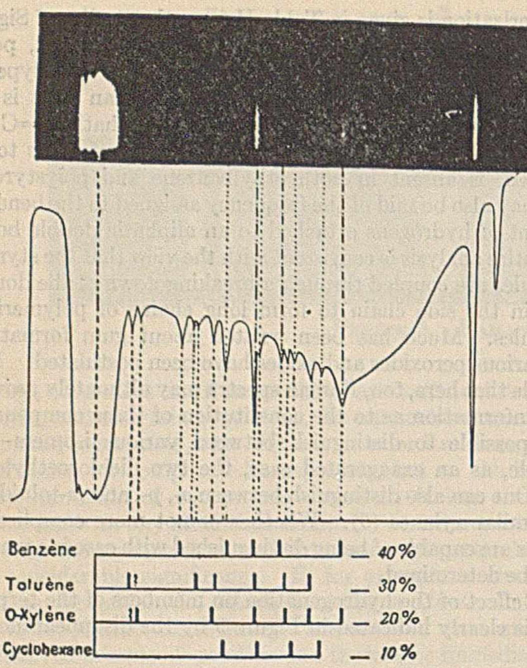


FIGURE 8. MICROPHOTOMETER TRACING OF RAMAN SPECTRUM OF A MIXTURE OF BENZENE, TOLUENE, *o*-XYLENE, AND CYCLOHEXANE

(After Andant, 7)

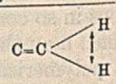
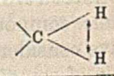
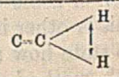
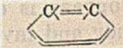
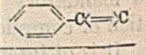
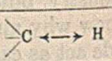
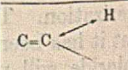
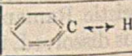
characteristic frequency shifts corresponding to the appropriate C=C.

Some of this information has already been available from analysis of infra-red absorption spectra. The Raman effect in no way replaces infra-red absorption spectra but in many cases provides the same as well as additional information. It is particularly useful in cases where the frequency of vibration would fall in a region where the technic of measurement by *restrahlen* is exceedingly difficult. Furthermore, the Raman lines are generally fundamentals while the infra-red absorption spectra may represent various overtones. These two methods of approach are somewhat supplementary since, in the case of the lighter atoms, infra-red absorption spectra provide information in detail which, owing to the lack of proper dispersion, it is very difficult to elicit by means of Raman spectra.

LIMITATIONS OF RAMAN EFFECT

The Raman effect has certain limitations which should be thoroughly understood before applying it to a particular problem. Perhaps the greatest deterrent is in the actual weakness of the Raman lines themselves. The total amount of energy scattered or emitted in the form of Raman lines may approach a fair percentage of that part of the exciting radiation which is also scattered. If, however, there is a large number of lines, this reduces the intensity of an individual line to a rather small magnitude, and it may take long exposures under fairly ideal conditions to record the Raman scattering. If the photographic plate is fogged owing to fluorescence, to continuous radiation from the exciting source, or to direct scattering of the exciting radiation in the case of small crystals, for example, the faint Raman lines are difficult to distinguish. In actual practice there is a certain element of confusion owing to the presence of more than one exciting line, as each exciting wave length gives rise to its own individual set of Raman lines. A further such element is introduced in the overlapping of Raman lines themselves.

TABLE II

STYRENE [a]		POLYSTYRENE		ETHYLBENZENE		MODES OF VIBRATION
$\Delta\bar{\nu}$	I	$\Delta\bar{\nu}$	I	$\Delta\bar{\nu}$	I	
–	–	–	–	–	–	
–	–	196	2	–	–	
210	1	211	2	–	–	
239	2d	–	–	–	–	
438	0	–	–	457	0	
–	–	–	–	490	1	
–	–	–	–	538	0	
622	2	620	2	620	2	
–	–	722	0	724	0	
–	–	750	0	–	–	
778	3	788	0	773	0	
–	–	831	0	–	–	
–	–	–	–	962	0	
988	1	–	–	–	–	
999	6	998	4	1000	4	
1028	1	1032	2	1032	2	
1039	2	–	–	–	–	C ←→ C
–	–	1058	0	1057	0	
–	–	1094	0d	–	–	
–	–	1110	2	1106	0	
1156	2	–	–	1156	1	
1184	3	1177	1	1176	1	
1204	4	1204	2	1204	3	C ←→ C
–	–	1269	0	1260	1	
1320	1	1326	0d	–	–	
1339	2	–	–	–	–	
–	–	–	–	1381	0	
1414	3d	–	–	–	–	
–	–	1447	1	1448	1dd	
–	–	1470	0	1465	1dd	
1494	1	–	–	–	–	
1581	1	1588	1	1587	1	
1606	5	1608	3	1608	3	
1640	6	–	–	–	–	
2922	1	–	–	–	–	
–	–	2936	2d	2936	2d	
3015	1	–	–	–	–	
3058	1	3056	2	3053	2	
–	–	3066	1	3066	2	

[a] $\Delta\bar{\nu}$ = wave-number shift; I = intensity.

If only one plate is taken in a given study, the attributing of lines to a given source of excitation may be entirely erroneous. It is necessary, therefore, that the illumination be reduced to as near a monochromatic source as possible by choosing a proper source of light and by the interposition of proper filters.

If a series of spectrograms is taken, it is possible, by diminishing the intensity of various exciting lines, to diminish also the concomitant Raman lines and so attribute each Raman line to its proper source of excitation. In a similar manner fluorescence may be reduced by eliminating the light of higher frequency and by quenching the fluorescence—through collisions of the second kind—by the addition of proper substances to the solution under examination. Examples of this quenching process are given in Figure 10. These are Raman plates of water-white oil; *B* contains one per cent or less of nitrobenzene. Actual Raman lines are discernible in *B*.

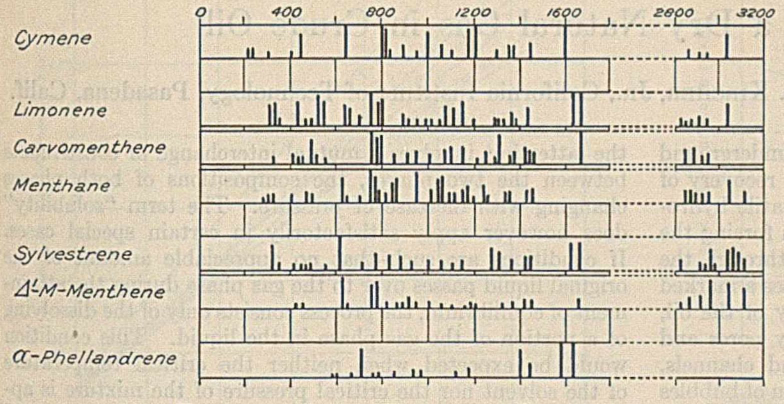


FIGURE 9. RAMAN SPECTRA OF TERPENES

(After Dupont, Daure, Allard, and Lévy, 7)

Raman lines corresponding to an atomic vibration of low frequency, of the order of 200 wave numbers or less, fall close to the exciting radiation and are difficult to distinguish from slit ghosts and halation of the exciting line. In general, scattering from the source of the light may be reduced by operating at a sufficiently low temperature and, in the case of small crystals, by using great precautions to obtain a monochromatic radiation and by using plates which are antihalo in the extreme. Another deterrent is in the color of the solutions themselves. Since the intensity of the Raman scattering varies as a fourth power of the wave length, it is advisable to use as short a wave length as possible for excitation purposes. If the solutions are colored, this is not possible, since there will be an absorption of both the exciting radiation and of the Raman lines themselves. Consequently it is necessary to use, in this case, as a source of excitation a monochromatic radiation in the green, yellow, or even red. This reduces the intensity of the Raman scattering and diminishes the actual distance between the Raman lines and the incident line on the photographic plate because of the lower dispersion in the red or yellow of the average prism, and makes the measurement of the Raman lines more difficult. Last of all in this connection, there are few practical sources of monochromatic radiation in the yellow and red parts of the spectrum. In the case of studying the Raman spectra of compounds having a highly complex constitution, the Raman lines are so numerous that it becomes next to impossible always to assign a particular vibration to its proper source.

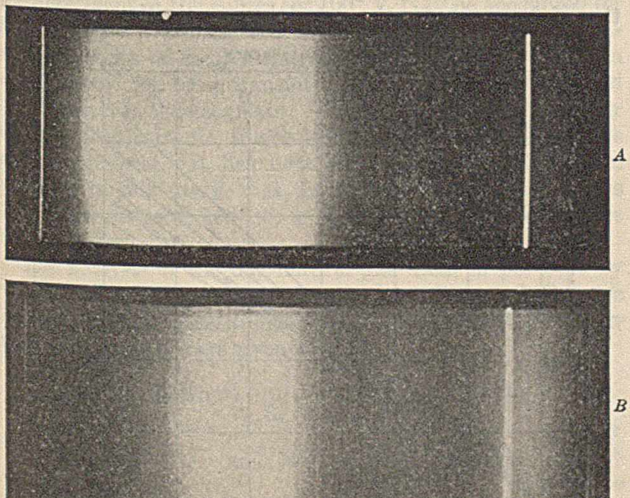


FIGURE 10. RAMAN SPECTRA OF OILS, SHOWING DECREASE IN FLUORESCENCE RESULTING FROM THE ADDITION OF A SMALL QUANTITY OF NITROBENZENE

A, above; *B*, below.

Some Raman lines are visible on the original negative of *B*.

Nevertheless, in spite of these limitations, as has been stated previously, much progress has been made and many of these limitations may be reduced with the development of improved technic.

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RECEIVED February 8, 1934. Presented as part of the Symposium on Physical Properties of Hydrocarbon Mixtures before the Division of Petroleum Chemistry at the 85th Meeting of the American Chemical Society, Washington, D. C., March 26 to 31, 1933.

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[1] The references cited are only a small fraction of the published works. The bibliographies included in the references cited under (*8*) cover a fair total of the published material.

CORRECTION. In the paper on "Sulfonic Acids from Petroleum," IND. ENG. CHEM., 26, 395–6 (1934), we should like to correct an error. Beta sulfonates are obtained by the action of concentrated sulfuric acid on mineral oils and not when oils are treated with fuming acid, as stated in the tabular material in column 1, page 395.

Another point which has been omitted is that alpha and gamma sulfonic acids form, contrary to common opinion, some 25 to 40 per cent of the bulk of the acid sludge resulting from the treatment of lubricating oils with concentrated sulfuric acid. This fact seems to be of commercial interest. E. NEYMAN AND S. PILAT

Phase Equilibria in Hydrocarbon Systems

III. Solubility of a Dry Natural Gas in Crude Oil[1]

W. N. Lacey, B. H. Sage, and Charles E. Kircher, Jr., California Institute of Technology, Pasadena, Calif.

GASES dissolved in the crude petroleum in underground formations play an important part in the recovery of the oil. The presence of these more volatile hydrocarbons in solution contributes energy to help in forcing the oil through the porous sands to the well and through the tubing to the surface of the ground. It also causes a marked lowering of the surface tension and the viscosity of the oil, thus favoring better drainage from the capillary pores and greater freedom of movement through the sand channels. It is true that, if the gas leaves solution in the form of bubbles suspended in the oil, it may impede flow through the capillaries; but, if formation pressures are maintained, this difficulty may be minimized and benefit obtained from the advantages resulting from the dissolved material.

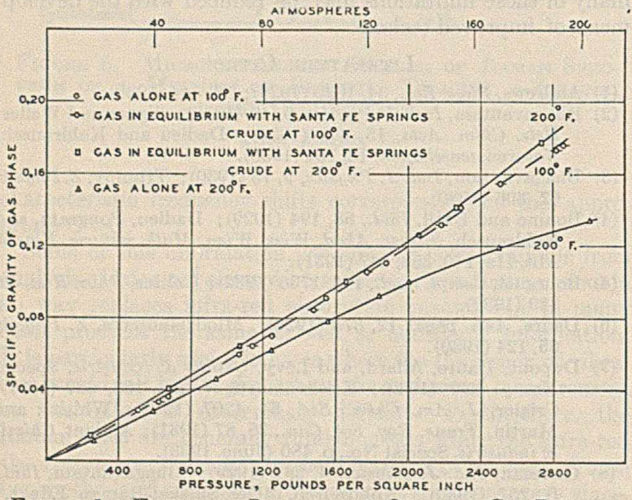

Figure 1. Effect of Presence of Oil upon Gas Density

A knowledge of the solubility of natural gases in crude petroleum and of the changes in properties resulting from their presence is of importance in learning the mechanics of the processes taking place in underground formations, in estimating underground reserves, and in arriving at rational methods of prorating petroleum production within a given pool. The present paper presents values for the solubility of one "dry" natural gas in several different representative crude oils at 100.0° F. (37.8° C.) and for pressures from atmospheric to 3000 pounds per square inch (204 atmospheres). In addition, data are presented showing the corresponding changes of the volumes and densities of the liquid phases present at equilibrium. The apparatus and methods used in this investigation have been described in Part I of this series.[1] The measurements presented here were made prior to certain minor improvements in apparatus and method included in the description. These additions have improved the accuracy of subsequent measurements.

When dealing with hydrocarbon systems involving volatile constituents in the original liquid phase, the term "solubility" in its strict sense cannot be applied. The process whereby equilibrium is attained between the liquid and the added gas does not consist merely of a partial dissolving of the latter but involves a mutual interchange of constituents between the two phases, the compositions of both phases changing with increase of pressure. The term "solubility" does however apply satisfactorily in certain special cases. If conditions are such that no appreciable amount of the original liquid passes over to the gas phase during the attainment of equilibrium, the process consists only of the dissolving of a portion of the gas phase in the liquid. This condition would be expected when neither the critical temperature of the solvent nor the critical pressure of the mixture is approached. Another case where the process consists only in the solution of a given gas in the liquid is found in a procedure consisting of a gradual compression of given amounts of gas and liquid until the gas phase just disappears and only liquid is left. The absence of gas phase at final equilibrium thus prevents loss of volatile constituents by the liquid.

It would seem probable that the case of a dry natural gas dissolving in a crude oil at 100° F. (37.8° C.) might be accompanied by a negligible transfer from liquid to gas. If this were true, the experimental procedure and the calculations to determine and describe equilibrium conditions would be much simplified. To determine whether such an assumption would be justified, an experiment was carried out in the density balance unit described in Part I.[1] First, the change in density of a dry natural gas sample upon compression at 100° F. and throughout the pressure range was determined. Then the gas was brought to equilibrium, at various pressures and the same temperature, with one of the crude oil samples, the variations in the gas density again being determined as a function of equilibrium pressure. A similar pair of runs was made at 200° F. (93.3° C.). The resulting gas density curves are shown in Figure 1. The results are expressed in terms of specific gravity, referred to water at its maximum density. The composition of the gas was only slightly different from that of the gas used in the rest of the investigation.

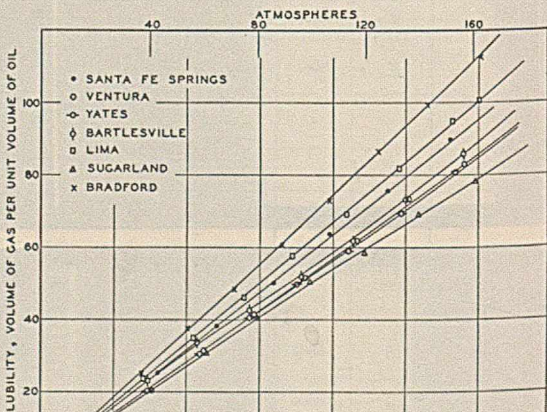

Figure 2. Solubility of Dry Natural Gas in Crude Oils at 100° F.

The assumption of simple solubility holds reasonably well at 100° F., but at 200° F. the divergence of the density curves is too great for such an assumption. It is possible that

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[1] Part I appeared on pages 103–6, January, 1934; Part II, pages 214–17, February, 1934.

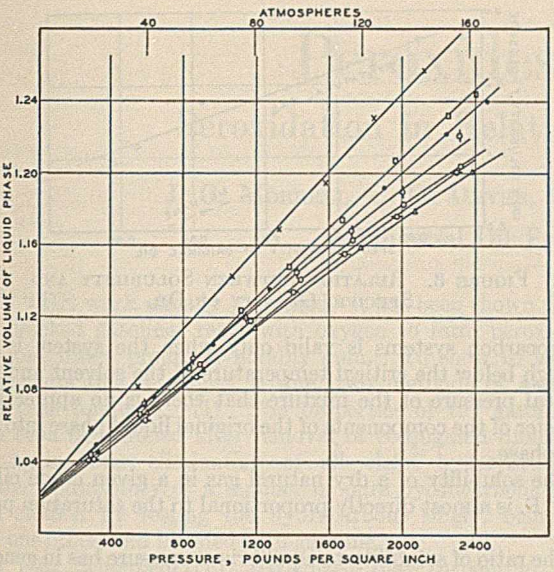

Figure 3. Changes in Liquid Volume Due to Solution of Gas at 100° F.

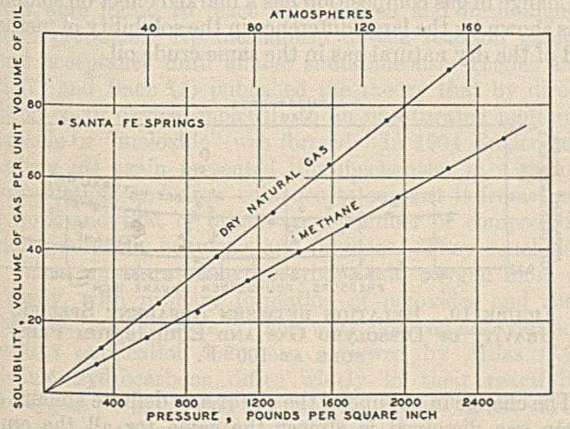

Figure 5. Effect of Gas Composition upon Solubility at 100° F.

the agreement of the curves for 100° F. may be accounted for by a decrease in density of the gas phase due to greater relative solubility of its heavier constituents, which has been compensated for by a transfer of some of the lighter liquid constituents to the gas phase. However, within the accuracy of such measurements, this would be equivalent to the simple solution process. It has been assumed, therefore, for the purposes of this study, that the transfer from the crude oils to the gas phase at 100° F. is negligible within the pressure range studied.

The analysis of the dry natural gas used, in per cent by volume, was as follows: methane 84.4, ethane 8.6, propane 6.6, and heavier constituents 0.4. The sources and properties of the crude oils are given in Table I.

Table I. Sources and Properties of Crude Oil Samples

Source	Av. Mol. Wt.	Gravity	Sp. Gr. (100°/40°)	Viscosity at 86° F. (30° C.)
		° A. P. I.		*Millipoises*
Bradford, Pa.	186	45.8	0.781	26.5
Santa Fe Springs, Calif.	199	33.4	0.842	50.1
Lima, Ohio	226	38.2	0.818	46.8
Bartlesville, Okla.	232	32.8	0.845	70.6
Ventura, Calif.	236	29.5	0.863	125.6
Yates, Texas	243	29.9	0.861	103.8
Sugarland, Texas	244	27.1	0.876	112.8

Figure 2 shows the relations between solubility of the dry natural gas in each of the seven crude oils at 100.0° F. as a function of the equilibrium pressure. The solubility is expressed in volumes of gas, measured at 60° F. (15.6° C.) and 14.73 pounds per square inch (30 inches of mercury, or 1 atmosphere) dissolved in unit volume of original oil, measured at 60° F. These values may be converted to cubic feet of gas per barrel of oil by multiplying by 5.615.

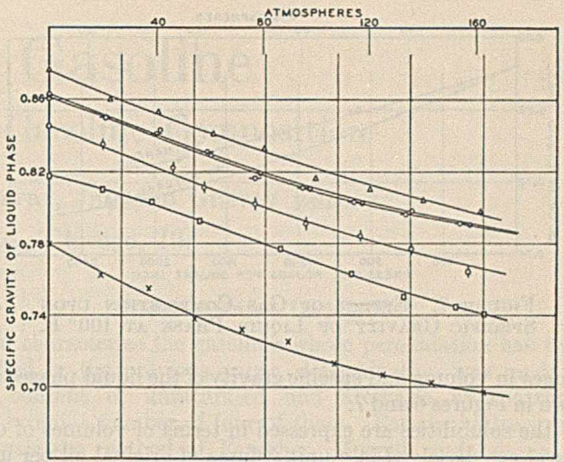

Figure 4. Changes in Specific Gravity of Liquid Phase Due to Solution of Gas

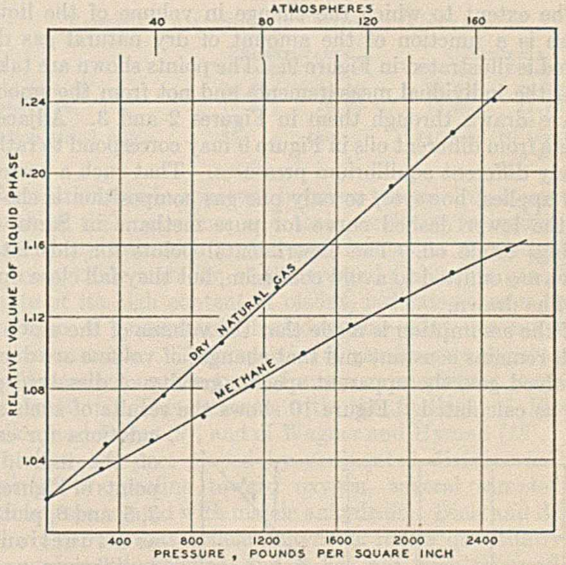

Figure 6. Effect of Gas Composition upon Change in Volume of Liquid Phase at 100° F.

The corresponding increases in volume of the liquid phases due to solution of the gas are depicted in Figure 3. The increase in volume is expressed as the ratio of the volume of the liquid phase existing at a given equilibrium pressure and temperature to the original liquid volume as measured at 60° F. before any gas was dissolved. The changes in specific gravity of the liquid phases due to dissolved gas are shown in Figure 4. The specific gravities are given as the ratio of the weight of a unit volume of the existing liquid phase to the weight of an equal volume of water at its maximum density.

Figure 5 gives an indication of the effect of the composition of the gas upon its solubility in Santa Fe Springs crude oil at 100° F. The solubility for the dry natural gas is compared to that for pure methane. The absence of the ethane and heavier hydrocarbons in the latter case is seen to result in a much lower solubility. Comparisons of the resulting

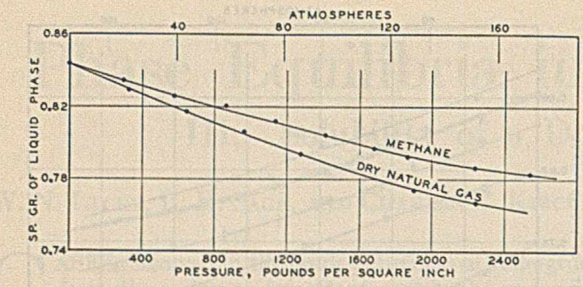

Figure 7. Effect of Gas Composition upon Specific Gravity of Liquid Phase at 100° F.

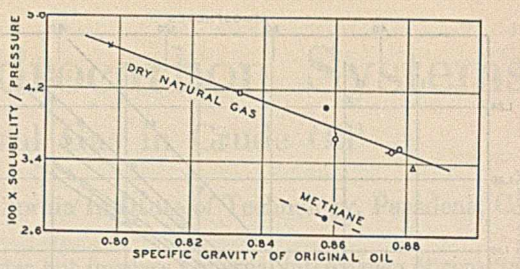

Figure 8. Relation between Solubility and Specific Gravity of Oil

changes in volume and specific gravity of the liquid phases are shown in Figures 6 and 7.

If the solubilities are expressed in terms of volumes of dry natural gas dissolved in a unit volume of original oil per unit of pressure [100 pounds per square inch (6.8 atmospheres) is taken here as a convenient unit of pressure], they may be roughly correlated with the specific gravities of the original oils as shown in Figure 8.

The extent to which the change in volume of the liquid phase is a function of the amount of dry natural gas dissolved is illustrated in Figure 9. The points shown are taken from the individual measurements and not from the smooth curves drawn through them in Figures 2 and 3. Adjacent points from different oils in Figure 9 may correspond to rather widely different equilibrium pressures. That such a correlation applies, however, to only one gas composition is shown by the lower dashed curve for pure methane in Santa Fe Springs crude oil. The experimental points for this latter curve are omitted to avoid confusion, but they fall close upon the line drawn.

If the assumption is made that the volume of the crude oil itself remains constant and that changes of volume are due to dissolved gas, the apparent specific gravity of dissolved gas can be calculated. Figure 10 shows the results of such calculations for each of the individual points of Figures 2, 3, 5, and 6, plotted as a function of equilibrium pressure. The apparent specific gravity appears to be nearly independent of pressure, although a slight increase is indicated at the higher pressures. The divergence of the points is somewhat increased by the sensitiveness of the apparent specific gravity values to small errors in the measurement of the volume of the liquid phase. The apparent specific gravity of methane, as would be expected, is found to be somewhat lower than that for the dry natural gas.

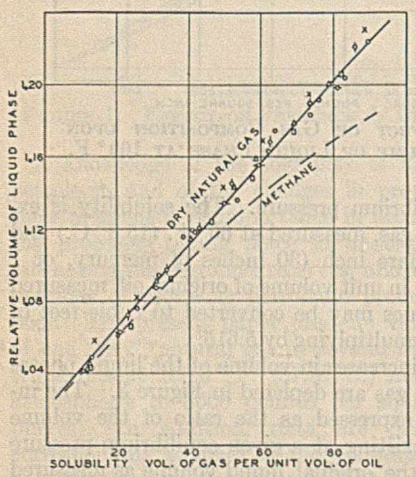

Figure 9. Relation between Changes in Volume of Liquid Phase and Amount of Gas Dissolved at 100° F.

Conclusions

The assumption that a simple dissolving process occurs when a gas is brought to equilibrium with a liquid in complex hydrocarbon systems is valid only when the system is far enough below the critical temperature of the solvent and the critical pressure of the mixture that there is no appreciable transfer of the components of the original liquid phase into the gas phase.

The solubility of a dry natural gas in a given crude oil at 100° F. is almost directly proportional to the saturation pressure.

The ratio of solubility to equilibrium pressure has in general a roughly linear relation to the specific gravity of the crude oil.

Change in gas composition has a marked effect on solubility as is shown by the large difference in the solubility of methane and of the dry natural gas in the same crude oil.

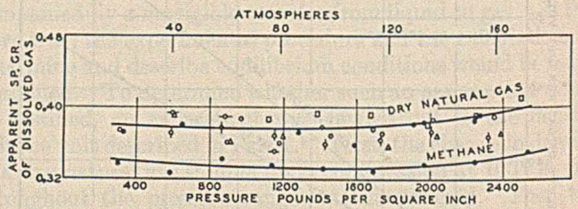

Figure 10. Relation between Apparent Specific Gravity of Dissolved Gas and Equilibrium Pressure at 100° F.

The change in volume of the oil for any definite amount of a given gas dissolved is almost the same for all the crudes studied. However, the pressure at which this solubility would be obtained would vary for each crude oil.

The apparent specific gravity of a given dry natural gas dissolved in crude oil at 100° F. is nearly independent of the pressure and of the solvent.

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German 1933 Dye Trade. The receding trend in German dye exports in 1932 was arrested in 1933. Total exports of all types of dyestuffs amounted to 26,818 metric tons valued at 133,738,000 marks in 1933, compared with 29,142 tons valued at 133,662,000 marks in 1932.

Peroxides in Gasoline

Peroxidation in Relation to Gasoline Composition

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In THE work already presented,[1] it has been shown that cracked gasolines react with oxygen to form peroxides and other products, notably gum. To show to what components this reactivity is due, two methods of attack have been followed: (1) The properties of the gasolines have been determined after removal of conjugated diolefins and again after elimination of all olefin hydrocarbons; (2) the oxidizability of a number of pure hydrocarbons has been studied by testing the hydrocarbons singly, blended with one other, and blended with gasoline.

In 1852 Schönbein (*15*) recognized that turpentine, on exposure to oxygen, formed some compound of strong oxidizing power. In succeeding years, other unsaturated substances were found to react with oxygen and form highly reactive products. No mechanism of the reaction gained general acceptance until almost simultaneously Engler and Wild (*7*) and Bach (*1*) published the theory that by direct addition of an oxygen molecule to an unsaturated molecule a peroxide or "moloxide" was formed. In 1904 Engler and Weissberg (*6*) again presented this mechanism in a review of autoxidation, and drew evidence to support it from their own work and that of others on a number of compounds, including amylene, hexylene, and fulvenes. They concluded that "most unsaturated hydrocarbons add oxygen more or less easily, with primary formation of peroxides and then further reaction products." The work done on autoxidation since this publication has been reviewed by Milas (*14*).

Olefinic hydrocarbons differ widely in their reactivity with oxygen. Wagner and Hyman (*18*) showed great variation in the rates of oxidation of the isomeric amylenes by air in the presence of an oxidation catalyst.

A number of investigators have found that diolefins containing conjugated double bonds oxidize and produce peroxides much more readily than olefins of other types. Thiele (*16*) showed that fulvenes absorb oxygen and resinify with extraordinary rapidity. Brooks (*3*) stated that conjugated diolefins oxidize much more readily than simple olefins. Cassar (*4*) reported that his accelerated oxidation test "did not affect simple olefins, but only diolefins." Flood, Hladky, and Edgar (*9*) found that "Diolefins as a class are markedly less stable than monoölefins, but the position of the double bonds is important in determining stability. Conjugated double bonds introduce extreme instability, while a compound containing double bonds widely separated is almost as stable as an average olefin." Kogerman (*11*) arrived at similar conclusions in a study of the hexadienes. Those with separated double bonds did not absorb a measurable amount of oxygen during several months' exposure at room temperature. The isomeric conjugated compounds began to absorb oxygen immediately on exposure, and oxidation continued at a rapid rate. Analysis indicated that in two cases his products were peroxides and in one case a "monoxide," which he believed had formed from a peroxide.

The opinion is quite general that the ready autoxidation and gumming of some cracked gasolines is due to their content of diolefins [Brooks (*3*), Flood, Hladky, and Edgar (*9*)].

Analysis of Gasolines

To characterize the gasolines whose peroxidation has been studied in the previous paper, determination was made of the content of unsaturated and aromatic hydrocarbons and bromine number of four of them. For the hydrocarbon analysis the method of Faragher, Morrell, and Levine (*8*) was used. Bromine numbers were determined according to Francis (*10*), slightly modifying the method by adding the bromate solution at 0° C. as fast as taken up, rather than all at one time.

Table I. Analysis of Cracked Gasoline

	Pennsylvania		California	
	Untreated	Treated	Untreated	Treated
Unsaturates, %	36.89	24.50	38.94	29.77
Aromatics, %	19.81	16.90	13.06	17.83
Bromine No.	64	43	61	54
Induction period, min.	65	120	445	No break in 40 hr.

No relationship is apparent between the total unsaturated content of these gasolines and their tendency to oxidize as measured by induction period and formation of peroxides. The remarkable stability of the treated California gasoline, in spite of its high content of olefins, indicates that a large proportion of unsaturated hydrocarbons need not make a gasoline unstable. The properties of gasoline are apparently more dependent on the type of unsaturates present than on their amount. This accords with the findings of Flood, Hladky, and Edgar (*9*), and of Wagner and Hyman (*18*).

To show the part played by conjugated diolefins in the reactivity of gasoline toward oxygen, several samples of gasoline were treated with maleic anhydride. Diels and Adler (*5*) have shown that maleic anhydride reacts quantitatively with conjugated diolefins, and it has not been reported to react under mild conditions with any substances of other types which are likely to be present in cracked gasoline. Birch and Scott (*2*) used this reagent to remove specific diolefins from fractions of cracked gasolines.

To the Pennyslvania gasoline, 3 per cent of the reagent dissolved in benzene was added, and the solution was heated in the bombs under nitrogen for 4 hours. It was then washed with slightly more than an equivalent amount of an aqueous-alcoholic solution of caustic potash made up as follows: potassium hydroxide, 100 grams; alcohol,[2] 400 cc.; and water to 1300 cc.

This solution reacts quickly with maleic anhydride and its addition products and does not dissolve in or dissolve gasoline. After contact with alkali, the solution was thoroughly water-washed but not distilled.

In some of the treatments of the Midcontinent and California gasolines, 3 per cent of maleic anhydride was added direct to the gasoline, and the suspension was heated 4 hours under nitrogen in the bombs and washed with the alkaline solution. The induction period, with and without inhibitor, and gum content were then determined. The results of these treatments are presented in Table II.

The treatment did not increase the original induction periods, but this is probably because the effect of the maleic

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[1] The first paper in this series appeared on page 497 of the May number, 1934.

[2] Formula 30, consisting of ethanol denatured with 10 per cent methanol.

anhydride is offset by the alkali wash, which on a blank sample reduced the induction period from 75 to 35 minutes. The induction periods with inhibitor are in all cases greatly increased and are probably the best indication that diolefin removal reduces the tendency to be oxidized. The treatment did not stop the formation of copper-dish gum, though in the California gasoline it greatly reduced it.

TABLE II. TREATMENT WITH MALEIC ANHYDRIDE

	Pennsylvania Untreated Gasoline		Mid-continent Untreated Gasoline		California Untreated Gasoline	
Wood-tar distillate inhibitor, %	None	0.01	None	0.01	None	0.01
Original properties:						
Induction period, min.	80	150	195	270	445	480
Gum, mg./100 cc.:						
Copper-dish	100	9	223	136	495	231
Air-jet	0	0	2	2	26	14
Bromine No.	64	..	40	..	71	..
Octane No.[a]	75	..	64	..	76	..
Properties after treatment:						
Induction period, min.	75[b]	535	200	540	490	885
Gum, mg./100 cc.:						
Copper-dish	59	5	220	249	22	12
Air-jet	0	0	2	0	0	2
Bromine No.	53[b]	..	33	..	54	..
Octane No.[a]	75	..	64	..	75	..

[a] C. F. R. research method.
[b] Gasoline contains 7% benzene.

While this work was in progress, the paper of Martin, Gruse, and Lowy (*13*) appeared in which cracked gasoline was treated with maleic anhydride under reflux and the products removed with aqueous caustic soda. This procedure has been compared with that of the present authors; the latter gives slightly higher induction periods, both with and without inhibitor.

As a check on the efficacy of diolefin removal by maleic anhydride, 2 per cent of cyclopentadiene was added to a sample of the Pennsylvania cracked gasoline refined with fuller's earth, and it was then treated with maleic anhydride according to the last procedure outlined. The results are shown in Table III.

TABLE III. ADDITION OF DIOLEFIN TO PENNSYLVANIA TREATED GASOLINE

	Induction Period with 0.005% Wood-Tar Distillate Inhibitor
	Min.
Original gasoline	270
Gasoline treated with maleic anhydride	230
Gasoline + 2% cyclopentadiene	170
Gasoline + 2% cyclopentadiene treated with maleic anhydride	230

The treatment of the original gasoline with maleic anhydride reduced the inhibited induction period, probably because there were no diolefins to be removed, and because the alkali wash always has this tendency. Addition of cyclopentadiene reduced this induction period still further. Maleic anhydride treatment after this addition restored the induction period to its value when no diolefin was added, indicating that the anhydride had completely removed this hydrocarbon.

The removal of diolefins with maleic anhydride from these gasolines did not eliminate the tendency to absorb oxygen, which indicates that diolefins are not the only hydrocarbons contributing to gasoline instability.

To show the part played by olefins in gasoline oxidation, samples of the same oils were treated with sulfur monochloride by the procedure of Faragher, Morrell, and Levine (*8*) to remove all unsaturated hydrocarbons. The published method was slightly modified in that the final distillation was made with steam and fire rather than vacuum. Comparative tests showed that this made no difference in the results. After this treatment the gasoline showed great resistance to oxidation. Samples were exposed in the bombs for 44 hours at 100 pounds per square inch (7.03 kg. per sq. cm.) oxygen pressure and 100° C. without any break in the oxygen absorption curve and but slow drop in pressure. Other properties of the gasolines treated with sulfur monochloride are given in Table IV.

TABLE IV. REMOVAL OF OLEFINS WITH SULFUR MONOCHLORIDE

	Pennsylvania Gasoline	Mid-continent Gasoline	California Gasoline
Air-jet gum, mg./100 cc.	2	9	6
Bromine No.	18	7	8
Octane No. (C. F. R. research method)	53	44	52

PEROXIDES IN STRAIGHT-RUN GASOLINE

In their difficulty of oxidation, the cracked gasolines treated with sulfur monochloride are similar to straight-run gasolines. Yule and Wilson (*19*) mention the occurrence of peroxides in some straight-run products, but as a rule such products form peroxides with difficulty and do not give a break in the oxygen absorption curve when exposed to oxygen in the bombs.

Of sixteen gasolines derived from crude oil by atmospheric distillation which had been stored at this laboratory in more or less tight containers for 1 to 5 years, all but one, which had a peroxide number of 0.23, were peroxide-free. Peroxides are often found, however, in low concentration in straight-run gasoline samples exposed to air and light.

TABLE V. PEROXIDE FORMATION IN STRAIGHT-RUN GASOLINES

(Wood-tar distillate inhibitor used)

Time of Oxidation	Peroxide Number		Gum			
			Copper-dish		Air-jet	
	No inhibitor	0.01% inhibitor	No inhibitor	0.01% inhibitor	No inhibitor	0.01% inhibitor
Minutes			*Mg. per 100 cc.*			
			PENNSYLVANIA			
0[a]	0.00	0.00	7	14	0	1
120	0.22	0.08	4	5	3	1
720	0.53	0.22	10	8	8	5
1440	0.94	0.88	7	7	1	5
			MIDCONTINENT			
0[a]	0.00	0.00	2	1	0	0
120	0.07	0.07	7	4	0	0
720	0.47	0.67	2	1	1	1
1440	0.98	1.11	3	2	6	1
			CALIFORNIA			
0[a]	0.00	0.00	8	7	0	2
120	0.03	0.02	18	28	2	2
720	0.20	0.12	18	34	3	0
1440	0.32	0.26	11	8	2	2

[a] Original.

To measure quantitatively the tendency of straight-run gasolines to peroxidation, four samples, selected to be comparable with the cracked gasolines which had been peroxidized, were subjected to controlled oxidation. Samples were oxidized without inhibitor and after addition of 0.01 per cent of wood-tar distillate inhibitor, and peroxides were determined at regular intervals. The oxidation was carried out at 100 pounds per square inch (7.03 kg. per sq. cm.) oxygen pressure at 100° C.

These results show that, while very resistant to oxidation, straight-run gasoline may be made to develop peroxides to a limited extent. The inhibitor appears to have a very slight effect in checking the peroxide formation, particularly in the initial stages.

PURE HYDROCARBONS

The results on straight-run and cracked gasolines lead to the belief that both conjugated diolefins and simple olefins are concerned in the reactivity of gasoline toward oxygen. To confirm this statement, comparison was made of the behavior of hydrocarbons of different types on exposure to oxygen under the conditions to which the gasolines had been exposed.

The compounds were of the highest grade that could be purchased, and were purified by repeated fractionation in an

TABLE VI. OXIDATION OF PURE HYDROCARBONS

	Initial Properties					After 4-Hour Oxidation		
	Boiling Range	Pressure	Refractive index (20°)	Peroxide No.	Air-jet gum	Peroxide No.	Air-jet gum	Induction Period
	° C.	Mm. Hg			Mg./100 cc.		Mg./100 cc.	Min.
Paraffins:								
n-Heptane	97.4	747	1.3880	0.06	0	0.22	0	No break
n-Octane	124.6	742	1.3980	0.09	0	0.79	0	No break
2,2,4-Trimethylpentane	98.0	743	1.3893 (25°)	0.06	0	0.03	0	No break
Aromatics:								
Benzene	79.5	752	1.5010	0.02	0	0.03	2	No break
Toluene	110.1	749	1.4962	0.00	1	0.30	2	No break
Olefins:								
2-Octene	123.2–124.0	749	1.4134	0.00	0	Over 240	44	150
2-Pentene	35.2–36.0	748	1.3811	0.00	0	192	22	90
Trimethylethylene	37.0–37.3	749	1.3900 (15°)	0.00	1	138	10	75
Cyclohexane	79.8–80.0	744	1.4268	0.02	0	0.19	0	No break
Cyclohexene	82.2	747	1.4460	0.06	1	Over 240	290	75
Indene	181.7–181.8	754	1.5760	0.25	294	15.2	17	30
Limonene	176.4–177.0	750	1.4724	0.10	8	Over 240	1734	30

TABLE VII. OXIDATION OF HYDROCARBON BLENDS

	Initial Properties		After 4-Hour Oxidation		
Hydrocarbon in Blend	Peroxide No.	Air-jet gum	Peroxide No.	Air-jet gum	Induction Period
%		Mg./100 cc.		Mg./100 cc.	Min.
n-Heptane, 20	0.00	0	0.09	0	No break in curve
n-Octane, 20	0.06	0	0.12	0	No break in curve
2,2,4-Trimethylpentane, 20	0.02	0	0.09	1	No break in curve
Benzene, 20	0.02	1	0.12	1	No break in curve
Toluene, 20	0.00	1	0.15	3	No break in curve
2-Octene, 20	0.00	0	25.6	2	No break in curve
2-Pentene, 20	0.00	0	15.9	1	No break in curve
Cyclohexane, 20	0.01	0	0.12	0	No break in curve
Cyclohexene, 20	0.06	1	48	4	No break in curve
Styrene, 2	0.06	0	1.59	0	No break in curve
Cyclohexene, 20 Styrene, 1	1.9	0	140	50	180
Isoprene, 2	0.12	0	18	34	No break
Isoprene, 3.9	0.12	0	86	250	105
Cyclohexene, 20 Isoprene, 1	0.45	0	220	122	120
Indene	0.20	20	10	1318	60
Indene, 20 *n*-Heptane, 80	0.19	..	5.5	..	60
Limonene, 20	0.10	0	194	546	60
Straight-run gasoline alone	0.00	0	0.12	0	No break

efficient column until their properties were close to those given in the literature, and until peroxide numbers (which with the unsaturated hydrocarbons were initially very high) were reduced to near zero. Samples were then oxidized for 4 hours in bottles within the usual steel bombs at 100° C. and 100 pounds (7.03 kg.) oxygen pressure. The peroxide number and air-jet gum were determined at the end of this time, and the induction period was noted if a break in the oxygen curve occurred. The results appear in Table VI.

Oxidation of the paraffin hydrocarbons was very slight. It is interesting, however, to note that the final peroxide numbers of the compounds tested increase in the order 2,2,4-trimethylpentane (isoöctane), heptane, and octane, which is the order of increasing tendency to detonate in an engine, as reported by Lovell, Campbell, and Boyd (*12*). Cyclohexane and the aromatic hydrocarbons tested were also difficult to oxidize. Benzene was unchanged, while toluene shows slight peroxidation, which is in accord with the known tendency of an aromatic side chain to be oxidized more easily than the nucleus.

The straight-chain olefins, by contrast, oxidized rapidly and formed gum. Cyclohexene was also extremely reactive, and indene and limonene were the most easily oxidized of the compounds tested. Apparently under these vigorous oxidizing conditions indene goes to other oxidation products than gum, as very little is found in spite of rapid oxygen absorption. Limonene oxidizes readily, although it is not strictly a conjugated diolefin. Possibly the ready oxidizability of cracked distillates is in part due to compounds having structures related to that of limonene.

The hydrocarbons were also oxidized in blends with a Pennsylvania straight-run gasoline which had been heavily acid-treated. The results are shown in Table VII.

As would be expected, blending with this resistant gasoline reduces the rate of oxidation and increases the induction periods. Flood, Hladky, and Edgar also found that dilution greatly reduced the rates of oxidation of unsaturated hydrocarbons. Of particular interest are the results on blends containing an olefin and a diolefin. Styrene and cyclohexene together produced a far higher peroxide content and more gum than either oxidized alone. Isoprene and cyclohexene behaved similarly. This is perhaps due to condensation reactions, such as reported by Thomas and Carmody (*17*). Indene gave more gum in blend than when oxidized alone. Unless reaction takes place with the straight-run gasoline, which is unlikely, this is probably to be attributed to the fact that the dilution allows polymerization to occur while, when the hydrocarbon is alone, oxidation is rapid, outstripping the polymerization process and forming little gum.

CONCLUSIONS

1. The tendency of cracked gasolines to react with oxygen and form peroxides is attributable in part to conjugated diolefins and in part to other olefinic hydrocarbons. Removal of both produces a product extremely resistant to oxidation.
2. The tendency of olefins to form peroxides and also gum differs widely among different members of the series, and with any given olefin is greatly influenced by concentration. A gasoline may contain a high concentration of olefins and yet be very resistant to oxidation. In regard to gum formation, these results confirm those of Flood, Hladky, and Edgar (*9*).
3. Diolefins and olefins present together form more peroxidic compounds and more gum than when present singly in the same concentration.
4. Under the conditions employed, the oxidation of paraffins, cyclohexane, and aromatic hydrocarbons is zero or negligible.

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Thermal Conductivity of Silica Aërogel

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An apparatus is described for the measurement of heat conductivities of materials under variable mechanical and air pressures. Silica aërogel powders of different sieve analyses are measured and found to possess the lowest heat conductivity of any insulator so far reported at atmospheric pressure. The average value for the aërogel powder is 10 per cent less than that for still air. A 30 per cent decrease in conductivity is effected by measuring the gel in the presence of dichlorodifluoromethane, while the conductivity in vacuum is only 15 per cent of normal. Mechanical pressure up to 15 pounds per square inch does not greatly increase the conductivity in vacuum.

An explanation of the very low conductivity is given, and several suggestions for commercial utilization are offered.

All practical insulating materials of high thermal resistance are porous bodies in which the major part of the resistance depends upon the low conductivity of dead air held within them. It is desirable, but not imperative, that the substance of which the insulator is made should also have high thermal resistance. That this requirement may be of relatively little importance under certain circumstances is shown by Smoluchowski's measurements on zinc dust (*8*) and by those of Mason on crumpled aluminum foil (*5*).

Since no solid has been discovered with as low conductivity as air, the value for air is the limit toward which all insulators approach. To date, no insulating material has been measured with the conductivity of air, and most of the materials commercially used have conductivities from 50 to 100 per cent greater; those used for high temperatures often run several hundred per cent greater.

In general it is found that the thermal resistance of substances with fine structure such as pith, down wool, etc., is greater than that where the structure is coarse. This fact is due to several causes, prominent among which are reduced convection and the greater number of discontinuities over which the heat conveyed directly by the solid must pass. The resistance at a solid-to-solid contact is high compared with that of the solid itself. At high temperatures where radiation is of great importance, a fine structure is necessary to prevent large transfer of heat through the material by direct radiation from element to element.

Aërogels

Several years ago one of the authors (*4*) devised a method for removing water from a jelly without an accompanying large shrinkage. Many, if not most, jellies are composed of a felt of submicroscopic elements, probably in many cases fibrils, that hold the liquid phase just as a sponge holds water. When these jellies are dried, they shrink to a small fraction of their original volumes because of the very large capillary forces and the relatively small volume of the solid phase usually present. By replacing the liquid in the felt with a nonpeptizing liquid and heating the jelly to the critical temperature of the liquid under such pressure that it is not allowed to evaporate, the liquid is converted imperceptibly to a gas and can then be released without capillary compressive forces being brought to bear on the solid structure. The jelly skeleton thus left behind occupies substantially the same volume as it did formerly, but now it holds a gas within its meshes rather than a liquid; in other words, it is a true aërogel.

Many jellies have been converted to aërogels—for example, gelatin, agar, cellulose, thoria, alumina, silica. The physical properties of several of these appear ideal for heat insulators. They may easily be 95 per cent air by volume and yet possess adequate strength and high elasticity. The unit of structure is so extraordinarily fine that even in the ultramicroscope they appear optically empty (*7*).

Among the aërogels so far produced, that of silica is the cheapest and easiest to prepare, so that this investigation concerns it only. It is hoped that several of the more promising aërogels can be compared in a subsequent publication.

Silica aërogel is made by forming a jelly with water glass and acid, washing to remove excess acid and salts, replacing the water in it with alcohol, and liberating the alcohol in an autoclave. Prepared in this manner it has an apparent specific gravity of about 0.1, will bounce and exhibit a metallic ring when dropped, and in spite of an apparent fragility will withstand relatively large pressures without crushing if the pressure is applied uniformly. As a coarse powder it can be loaded with a pressure of 20 or 30 pounds per square inch (1.4 or 2.1 kg. per sq. cm.) without crushing. Even if finely ground under high pressure in a mortar, the powder produced has the same volume as the original gel, showing that the submicroscopic structure has not been broken down. In large pieces it is quite transparent and orange when viewed by transmitted light owing to the scattering of the blue light by the Rayleigh effect. It appears bluish white by scattered light.

Convection in such a structure is beyond imagination, and the opacity of silica to wave lengths beyond 6μ is such that no appreciable heat can pass by radiation at ordinary temperatures. Silica aërogel also appears to offer advantages at high temperatures, since it will stand 800° to 900° C. apparently indefinitely without breakdown of structure. At these temperatures where much heat can pass at wave lengths less than 6μ, it is a simple matter to include small amounts of opacifying agents, such as various metallic oxides, in the gel and thus effectually block radiation.

In spite of being a gel, silica aërogel has a sufficiently open structure so that capillary condensation of moisture is practically absent, and therefore moisture absorption is small even at large relative humidities.

One possibility appeared that made it particularly desirable to investigate the thermal conductivity of aërogels. The structure is so fine that it has been impossible to obtain more than a rough estimate of the size of openings. It is evident, however, that these are small with respect to the wave length of light and are probably well under 0.1μ in diameter. Now this is the order of magnitude of the mean free path of air molecules at atmospheric pressure. Should the structure of the aërogel be so fine that the mean free path of air molecules within it is smaller than normal, it is highly possible that the heat conductivity can be less than that of still air. This statement follows immediately from the fact that the thermal conductivity of a gas varies directly with the mean free path.

CALORIMETER AND ACCESSORIES

The aërogels are difficult to produce in sheets of any size, owing both to the small size of the autoclave convenient for laboratory use and to the many cracks that usually appear because of unequal contraction during the removal of the alcohol. It therefore became necessary to study the conductivity of the granular material.

Dewar (*2*), Smoluchowski (*8*), Aberdeen and Laby (*1*), and Kannuluik and Martin (*3*) have measured the thermal conductivity of powders both at atmospheric pressure and at reduced pressures, but no one has investigated the effect of mechanical pressure upon the contact resistance, which, as stated before, may be the major part of the over-all thermal resistance. It appeared advisable, therefore, to construct a calorimeter with which conductivities could be measured at various air pressures and also with different loads on the gel.

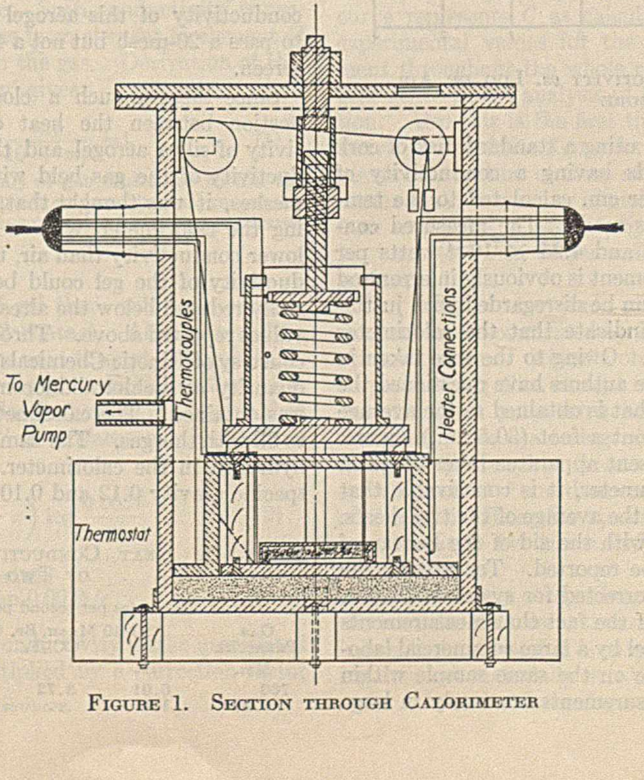

FIGURE 1. SECTION THROUGH CALORIMETER

Figure 1 is a drawing of the calorimeter which consists of a round brass case 15 cm. in inside diameter with a flat bottom. The material to be tested is spread evenly on the bottom, and the guarded-disk type of measuring element is carefully lowered onto it.

The disk is of copper, 10 cm. in diameter and 0.5 cm. thick. On the upper surface of this disk is soldered a polished copper box containing the 30-ohm heating element imbedded in alundum cement. The disk is supported on Bakelite pillars and carefully centered in the mouth of a flanged, cast-copper guard box in such a way that the lower surfaces of the disk and flange lie in the same plane. The guard box is wound with a heating coil.

The disk and box are electrically connected by a loop of No. 30 iron thermocouple wire; to the disk is soldered an iron-constantan thermocouple and a constantan lead is soldered to the flange of the guard box. All wires connected to the disk pass through a hole in the center of the guard box and then are cemented down to it with Glyptal lacquer for a distance of several centimeters in order to insure that they shall be maintained at the temperature of the box. All thermocouple wires are led to cold junctions with copper in a one-gallon (3.8-liter) vacuum flask filled with crushed ice. The thermocouples are calibrated at the boiling points of water and benzene and at the transition point of $Na_2SO_4 \cdot 10H_2O$.

Mechanical pressure is applied to the insulating material through the guard ring and disk by compressing a calibrated flat spiral spring supported by the top of the guard box. The spring is compressed by a screw passing through the center of a removable beam inside of the brass case. This screw can be turned by means of a tapered plug ground into the lid so that pressure can be applied without opening the case.

Two arms attached to the top of the spring make sliding contact with two parallel constantan wires, thus forming a simple potentiometer. By this means it is easy to read the compression of the spring by measuring the potential between the arms and one end of the slide wires. Two wires are used in order to compensate automatically for any tilting of the top plate on the spring.

The thickness of the insulation under test is initially obtained by means of a micrometer gage, graduated in thousandths of an inch, that rests on the flanged upper end of the brass case and measures the depth to the top of the guard box. To opposite sides of the plate supporting the spring, two No. 30 wires are attached. The one on the right passes counterclockwise over a small pulley attached to a graduated drum and supports a weight hanging from its free end. The wire on the left passes over a free pulley near the top of the case and then in a clockwise direction over a pulley attached to another graduated drum on the same shaft with the first. It also is held taut by a weight. By this means any change in thickness of the insulating material will be registered by a displacement of the scales on the drums with respect to each other. Any slight tilting of the guard box and disk will be compensated for automatically.

All wires are led out of the apparatus through two ground-glass thimbles fitted to two brass nipples soldered into the case. Vacuum-tight seals were obtained by imbedding the wires in Picein cement.

Connection is made to the McLeod gage, mercury vapor pump and oil forepump assembly by means of a copper-glass seal soldered into the case.

The whole calorimeter is closed by a brass lid carrying the ground plug for adjustment of the mechanical pressure and a window for observation of the scales on the drums. An equal mixture of beeswax and Venice turpentine is used as a vacuum seal.

The calorimeter is mounted in a water thermostat which contains a stirrer and mercury regulator. By this means the bottom is maintained at a constant temperature with maximum fluctuations less than 0.01° C.

During operation, the constantan leads from the guard ring and heated disk go directly to a Leeds and Northrup high-sensitivity low-resistance galvanometer. Since there is an iron bridge between them, the disk and ring form the two junctions of a thermocouple, and therefore any slight difference in temperature between them will cause a deflection of the galvanometer, the light index of which is focused on a slit in front of a photoelectric cell. By this means any slight difference in temperature will turn on or off a General Electric Thyratron tube, FG-57, which is in series with the heater wound on the guard box. The guard box is therefore maintained at all times within ±0.01° C. of the temperature of the disk.

Temperatures are measured by means of a Leeds and Northrup Type K potentiometer with sufficient external resistance added to make the potential read 0.1 of the low scale reading. Ad-

Table I. Heat Conductivity Measurements under Weight of Calorimeter Parts Only

(In calories per second per ° C. per cm.)

4–10 Mesh		10–20 Mesh		20–40 Mesh		100–200 Mesh		100–120 Mesh[a]	
Air pressure *Mm.*	Conductivity (× 10⁵)	Air pressure *Mm.*	Conductivity (× 10⁵)	Air pressure *Mm.*	Conductivity (× 10⁵)	Air pressure *Mm.*	Conductivity (× 10⁵)	Air pressure *Mm.*	Conductivity (× 10⁵)
760	5.10	760	5.47	760	5.04	760	5.37	760	6.17
410	4.84	56.5	4.44	760	5.08	51.5	3.83	5	3.32
170	4.26	10	4.01	760	5.06	8.8	2.87	0.7	2.20
53.8	3.92	1.6	3.65	10	3.67	2.5	2.02	0.0012	1.21
44	3.79	0.20	2.94	2	2.90	0.4	1.09		
10.5	3.73	0.081	2.56	0.11	1.83	0.12	0.98		
6.5	3.65	0.031	2.27	0.044	1.35	0.029	0.87		
1.0	3.44	0.0023	2.09	0.0007	1.27	0.00007	0.80		
0.053	2.73								
0.00011	2.23								

[a] This series was run on a batch that was lost before its density was determined; from the high values of the conductivity it is probable that the density was also high.

justment is effected with the aid of an auxiliary potentiometer of the student type. By this expedient very small differences in temperature can be read. Parasitic potentials are not evident. By using an air cell type of current supply for the potentiometer, frequent adjustment of the circuit is found unnecessary.

Current for the disk heater is supplied from a lead accumulator. The potential drop through it is measured with the small potentiometer.

Calculation shows that with a difference in temperature between the disk and guard box of 0.01° C., the heat flow from one to the other will at no time be greater than 0.1 per cent of the heat flowing from the disk through the insulation. It is felt that the accuracy of the apparatus is within 1 per cent. The reproducibility is in the neighborhood of 0.5 per cent.

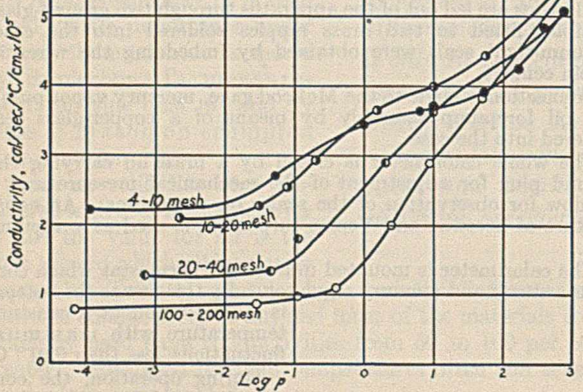

Figure 2. Heat Conductivity *vs.* Log of Air Pressure

The calorimeter was checked using a standard disk of cork from the Bureau of Standards having a conductivity of 4.35 × 10^{-4} watts per ° C. per cm. calculated to the temperature at which the test was made. The measured conductivity was 4.39, 4.23, 4.23, and 4.25 × 10^{-4} watts per ° C. per cm. The first measurement is obviously in error and by the theory of probabilities can be disregarded with justification. These measurements indicate that the calorimeter gives values 2 per cent too low. Owing to the care taken in the measurements, however, the authors have questioned the Bureau of Standards value. That is obtained as the average between two sheets of cork about a foot (30.5 cm.) square. Owing to the fact that the present apparatus takes one disk only 6 inches (15.2 cm.) in diameter, it is conceivable that this one disk does not represent the average of the two sheets. A further check is being made with the aid of the Bureau of Standards but cannot as yet be reported. Tentatively the values obtained have been uncorrected for systematic error. This seems justifiable in view of the fact that measurements made on a sample of silica aërogel by a large commercial laboratory checked those made here on the same sample within 0.4 per cent. That single measurements are rarely in large error is indicated by the fact that the points in Figure 2 fall on smooth curves.

Results of Heat Conductivity Measurements

The results of the measurements on silica aërogel broken up to pass various standard sieves are given in Table I. These measurements were not all made on the same batch of aërogel and therefore are not strictly comparable, which probably explains the range of results obtained at atmospheric pressure. Nevertheless, all batches included in this table were made in approximately the same manner so that only minor differences should exist. The apparent specific gravity of all of these powders was very near 0.1. Table I includes measurements made under the weight of the calorimeter parts only.

Figure 2 presents the data of Table I plotted against the logarithm of the air pressure.

In view of the probable close relationship between density and conductivity, a sample of silica jelly was prepared in the usual manner, but, before being placed in alcohol, it was dried to half its original weight. When put through the autoclave, however, it did not suffer as much shrinkage as normally so that the final specific gravity was 0.12. All densities reported are the apparent specific gravities of the powdered gel. Table II gives the heat conductivity of this aërogel ground to pass a 20-mesh but not a 40-mesh screen.

Since there is such a close connection between the heat conductivity of silica aërogel and the conductivity of the gas held within its meshes, it was thought that, by filling the calorimeter with a gas of lower conductivity than air, the conductivity of the gel could be materially reduced below the already low values reported above. Through the courtesy of Kinetic Chemicals, Inc., a quantity of dichlorodifluoromethane was obtained. The calorimeter was evacuated and allowed to fill with this gas. The same experiment was repeated with hydrogen in the calorimeter. The results using gel of both specific gravity 0.12 and 0.10 are given in Table II.

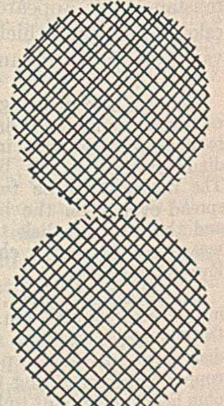

Figure 3. Aërogel Granules in Contact

Table II. Heat Conductivity Measurements on Gel of Two Densities

(Calories per second per ° C. per cm., × 10^{-5})

Gas Pressure	20–40 Mesh, Sp. Gr. 0.12			4–10 Mesh, Sp. Gr. 0.10	
Mm.	Air	CCl_2F_2	H_2	Air	CCl_2F_2
760	6.01	3.72	18.6	5.10	3.71
0.000	1.47	..	..	2.23	..

The average temperature of the aërogel during tests shown in Tables I and II was between 33° and 36° C. It was variable owing to the different temperatures at which the heat input and output from the disk became equal.

In order to investigate the effect of mechanical pressure on the contact resistance between the particles of gel under the simplest conditions, the measurements were made at such a low air pressure that only conductivities through the gel structure and through the solid-to-solid contacts is of significance. Table III shows the results obtained using the 20–40 mesh gel.

TABLE III. CONDUCTIVITY OF 20–40 MESH GEL AT 10^{-3} MM.

LOAD	DECREASE IN VOL.	CONDUCTIVITY ($\times 10^5$)
Lb./sq. in. (kg./sq. cm.)	%	
0.4 (0.028)	0.0	1.27
5.3 (0.373)	7	1.40
15.3 (1.076)	10	1.50

The elasticity of the silica aërogel is well shown by its behavior under repeated compression and release. At first there is some decrease in volume due to closer packing of the particles. After this initial reduction in volume, the gel springs back quite elastically when the pressure is released.

DISCUSSION OF RESULTS

An inspection of the conductivity values at atmospheric pressure shows the remarkable fact that this material possesses a decidedly lower thermal conductivity than still air. The International Critical Tables value for air at 34° C. is 5.8×10^{-5} calorie per second per ° C. per cm., about 10 per cent higher than the average of the values in Table I, exclusive of the 100–120 mesh figure. It is obvious that the mechanism of heat transfer in this case is different from that in the ordinary heat insulators, and the hypothesis mentioned earlier that the gel particles themselves have very low conductivity due to the reduction in mean free path of the air molecules within them is strongly supported.

Figure 3, which is a conventionalized drawing of two aërogel granules in contact, shows readily that there are two paths by which heat may pass through the aërogel particles and two paths through which it may flow between the particles.

Within the body of the aërogel, heat may pass by conduction through the solid structure. Such conductivity is represented by C_1. It also may pass from element to element of structure by conduction through the gas. Derivation of this conductivity from kinetic theory[1] gives:

$$C_{2(34°)} = 5.8 \times 10^{-5} \frac{mp}{10 + mp} \text{ cal.} \qquad (1)$$

where m = mean free path (in cm.) of gas molecules within the gel when the pressure is so low that all molecules travel in straight lines until they strike some structural element
p = pressure, mm. of Hg

Between the two granules of gel there will be a conductivity, C_3, due to the solid-solid contact. Also heat will be conveyed from one granule to the next through the gas phase. The derivation of this conductivity gives Equation 2 which is practically the same as that of Smoluchowski (*8*), except that the concept of a "displacement" of surfaces has been eliminated:

$$C_{4(34°)} = a\left(\frac{0.0075}{p} - r\right) \log \frac{0.0037}{p} \qquad (2)$$

where a = a constant
r = radius of spherical particle
C_4 = 0 at pressures less than $0.0075/r$

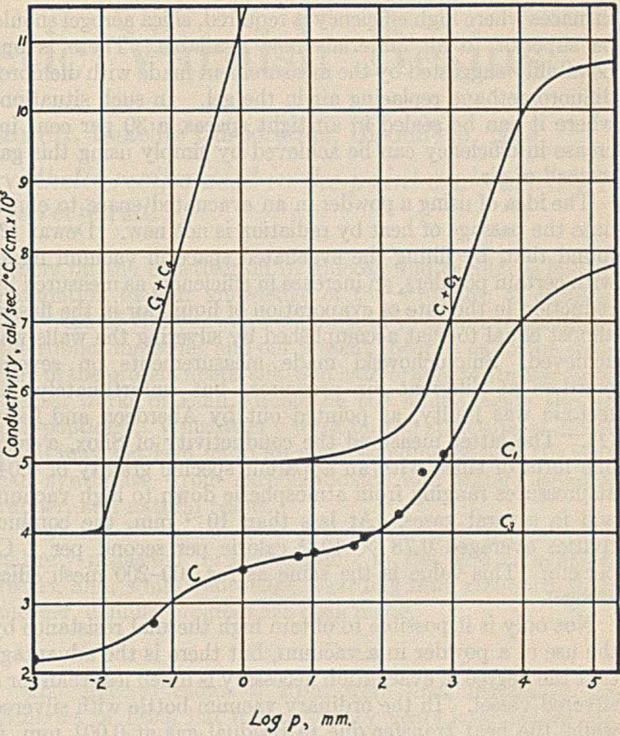

FIGURE 4. CURVES OF C_1 TO C_4

In representing the over-all conductivity of the granulated gel, Equation 1 should be multiplied by a correction factor to take care of the percentage by volume of gel in the powder, but, since this is large, the factor can be taken as 1 as a first approximation. The over-all conductivity, C, is then given by the equation:

$$\frac{1}{C} = \frac{1}{C_1 + C_2} + \frac{1}{C_3 + C_4} \qquad (3)$$

Multiplying the conductivities by 10^5 for convenience, and evaluating C_1, C_3, and a from the data for the 4–10 mesh gel, assuming $m = 4 \times 10^{-6}$ cm., one obtains $C_1 = 5$, $C_3 = 4$, and $a = 1.75$. Figure 4 gives the curves of C_1 to C_4. The heavy curve represents C as calculated, while the points are the experimental values for the aërogel. The excellent agreement throughout the whole range of pressures studied gives confidence in the analysis of the mechanism of heat conduction. Also this is the first time that it has been possible to arrive at a definite figure for the spacings between the elements of structure of silica aërogel. The mean free path, m, means that if a number of molecules start out in straight lines from any point in the gel, by the time they have gone 4×10^{-6} cm. (400 Å.), 63 per cent of them will have struck gel surfaces.

The order of magnitude of this distance between units of gel structure is confirmed by independent observations in two other directions. Riegel's observations with the ultramicroscope, showing silica aërogel to be optically empty, mean that the structural units must be much smaller than 10^{-5} cm. diameter. The scattering of light from clear specimens of aërogel indicates that these structural units are probably of the order of 10^{-6} cm. diameter. Since 5 per cent by volume of the gel is silica, the spacing between elements should be approximately five times their diameter, assuming that they are cylinders.

Even when the aërogel is ground to pass a 200-mesh screen, the particles are over a thousand times as large as these spacings calculated, and it is easy to understand why fine grinding does not materially break down the structure.

As a heat insulator for refrigerators, electric ovens, and

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[1] This derivation will be published elsewhere.

furnaces where high efficiency is required, silica aërogel should be superior to all materials now available. There is one possibility suggested by the measurement made with dichlorodifluoromethane replacing air in the gel. In such situations where it can be sealed in air-tight spaces, a 30 per cent increase in efficiency can be achieved by simply using this gas instead of air.

The idea of using a powder in an evacuated space to eliminate the passage of heat by radiation is not new. Dewar (*2*) found that, by filling the evacuated space in vacuum flasks with certain powders, an increase in efficiency, as measured by reduction in the rate of evaporation of liquid air in the flasks, almost equal to that accomplished by silvering the walls was achieved. Smoluchowski made measurements on several powders at different air pressures, but unfortunately his technic was faulty, as pointed out by Aberdeen and Laby (*1*). The latter measured the conductivity of Silox, a very fine form of silica with an apparent specific gravity of 0.04, at pressures ranging from atmospheric down to high vacuum and in several gases. At less than 10^{-3} mm. the conductivities averaged 0.78×10^{-5} calorie per second per ° C. per cm. This value is the same as for 100–200 mesh silica aërogel.

Not only is it possible to obtain high thermal resistance by the use of a powder in a vacuum, but there is the advantage that the degree of evacuation necessary is much less than for a silvered vessel. In the ordinary vacuum bottle with silvered walls, the heat transfer due to residual gas at 0.001 mm. is twelve times that of radiation, while the two are practically equal at 0.0001 mm. The maintenance of such high vacua in commercial vessels of glass is difficult and is practically impossible in vessels of metal because of the slow evolution of gas over an indefinite period from the metal walls. Figure 2 shows that already at 1 mm. pressure high insulation value is attained; with a pressure of 0.1 mm. almost as large advantage is gained as by 0.0001 mm. The reason for this fact is that conductivity by a gas between solid walls drops off in proportion to the pressure after it has reached the point where the mean free path of the gas is greater than the distance between the walls. In a 100–200 mesh powder, the particles are approximately 0.01 cm. in diameter, and the average distance through which a molecule must pass in going from one particle to the next is probably of the order of one-tenth of this. That means that at pressures less than 10 mm. the conductivity should drop off very rapidly.

The evolution of gas from metal walls is sufficiently slow so that a vacuum of 0.1 mm. can be maintained almost indefinitely. Manufacturers of metal vacuum bottles take advantage of this fact and fill the evacuated space with fine powders (*9*). It is of interest to compare the efficiency of the ordinary silvered vacuum bottle with the powder-filled vacuum bottle. When the bottle is used for the storage of liquid air with an ambient temperature of 20° C., the gain in heat through each square centimeter of wall lies between 15 and 80×10^{-5} calories per second for commercial silvered vacuum bottles (*6*). Assuming an average of 50×10^{-5}, it would require 3.4 cm. (1.3 inch) of 100–200 mesh silica aërogel in vacuum to provide the same protection.

The use of vacuum insulation for large containers is very attractive on account of reduction in storage losses and bulk, but for most large applications, such as commercial storage or transportation of liquid air or solid carbon dioxide, the mass of the vessel necessary to withstand atmospheric pressure would have to be so great as to defeat the purpose of the vacuum. The measurements presented here of the conductivity of silica aërogel under mechanical pressure, however, show that it is entirely feasible to construct a vacuum vessel of metal with walls just sufficiently thick to stand the handling necessary and to hold the vacuum. The powdered gel between the walls would support the atmospheric pressure with a loss of only about 15 per cent of its insulation efficiency. As far as the authors can find, such an arrangement has never been proposed. Any powder could serve as packing but the probabilities are that the aërogel, with its submicroscopic structure, would prove most efficient.

In this connection it was of interest to measure the heat conductivity of evacuated cork, since it seemed that a large fraction of its conductivity at atmospheric pressure might be due to air in the cells. A slab that measured 10×10^{-5} calorie per second per ° C. per cm. at atmospheric pressure showed only 3×10^{-5} in vacuum. If this cork had been finely powdered in order to break up the continuous paths through its cell walls, the probabilities are that it could have supported a pressure of 15 pounds per square inch and still maintained a conductivity well below the latter value.

A decided advantage of aërogels over most powders lies in the tremendous surface. By proper activation before introduction into the vacuum wall, the gel should serve to adsorb efficiently gases liberated from metal walls or entering through minute leaks, which, unfortunately, are difficult to prevent in metal apparatus.

The intermittent or continuous operation of a small oil pump sealed to the vacuum space would add little to the cost of storage with large installations.

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RECEIVED February 28, 1934. Presented before the Division of Industrial and Engineering Chemistry at the 87th Meeting of the American Chemcal Society, St. Petersburg, Fla., March 25 to 30, 1934.

U. S. Foreign Trade in Paint Products Increasing

Export demand for American pigments, paints, and varnishes increased considerably in 1933, according to the Chemical Division, Bureau of Foreign and Domestic Commerce. At the same time import demand for raw materials used in the paint and varnish industry increased notably.

Exports of pigments, paints, and varnishes from the United States were valued at $11,834,000 in 1933, an increase of $1,754,000 compared with 1932. Carbon black, the leading single item, was valued at $5,552,000 against $4,436,300 for 1932; foreign sales of ready-mixed paint were valued at $2,147,000, a slight increase over 1932 when shipments were valued at $2,015,000. A total of 100 markets shares in American ready-mixed paint export trade. Exports of turpentine in 1933 totaled 14,239,000 gallons, valued at $6,124,600, compared with 11,468,677 gallons, valued at $4,639,000, for 1932.

Imports of tung oil increased to 118,760,000 pounds in 1933 from 75,922,000 pounds in the preceding year, the value increasing from $3,434,000 to $4,833,000.

Chemistry of Synthetic Varnish Resins

Ivey Allen, Jr., V. E. Meharg, and John H. Schmidt, Bakelite Corporation, Bloomfield, N. J.

The chemistry of the nine outstanding types of synthetic resins used in the paint and varnish industry today is reviewed.

A CENTURY ago there were no synthetic resins, and throughout the following fifty years chemists were content to make no attempt to improve on Nature's handiwork. Some fifteen years after the Columbian Exposition, Baekeland announced the result of his researches on phenol-formaldehyde resins. This marked the beginning of the synthetic resin industry.

Varnish manufacturers remained quite conservative, however, and, while Albert and Berend, shortly after Baekeland's discoveries, introduced a modified, oil-soluble, phenol-formaldehyde resin, it was not until "the development of nitrocellulose lacquers gave new impetus to research in synthetic resins" (*12*) that rapid and definite progress was made.

Today the outstanding types of synthetic varnish resins are:

1. Ester gum
2. Cumar-indene resins
3. Phenolic resins
    a. 100 per cent
    b. Reduced
4. Polyhydric-polybasic resins
    a. Air-drying
    b. Baking

and of lesser importance:

5. Vinyl and styrene resins
6. Amide-formaldehyde resins
7. Chlorinated-diphenyl resins
8. Petroleum-hydrocarbon resins
9. Rubber-derivative resins

Chemically the synthetic resins are usually grouped under the all-inclusive and much abused term "polymers." In fact, as early as 1901 Krönstein (*15*) advanced the hypothesis that "resins owe their formation to polymerization."

Since that time chemists have been too easily satisfied to say that resins are polymers or that they contain resinophoric groups. The time-honored methods of organic chemistry for determining the constitution of compounds—namely, *Abbau* or degradation and *Aufbau* or synthesis—have been somewhat neglected for the more enticing methods of physical and colloid chemistry.

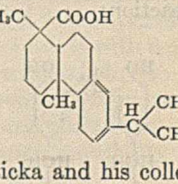
These older methods have achieved, however, quite notable success in elucidating the structure of other high polymers. Thus the work of Haworth, Irvine, Freudenburg, and others on the constitution of glucose and cellobiose laid the foundation for our knowledge of the structure of cellulose. The work of Harries was fundamental to an understanding of the rubber molecule, and our present theories as to the structure of the protein fibers, silk, and hair, originated in the monumental works of Emil Fischer on the amino acids and the polypeptides. Willstätter's work on the structure of chlorophyll may yet lead us to an understanding of how the plant can synthesize (from carbon dioxide and water) cellulose, rubber, and natural resins.

Fortunately fundamental organic research has not been entirely neglected by investigators in the field of synthetic resins, and, while knowledge regarding resin structure is still meager, definite progress has been made.

Ester Gums

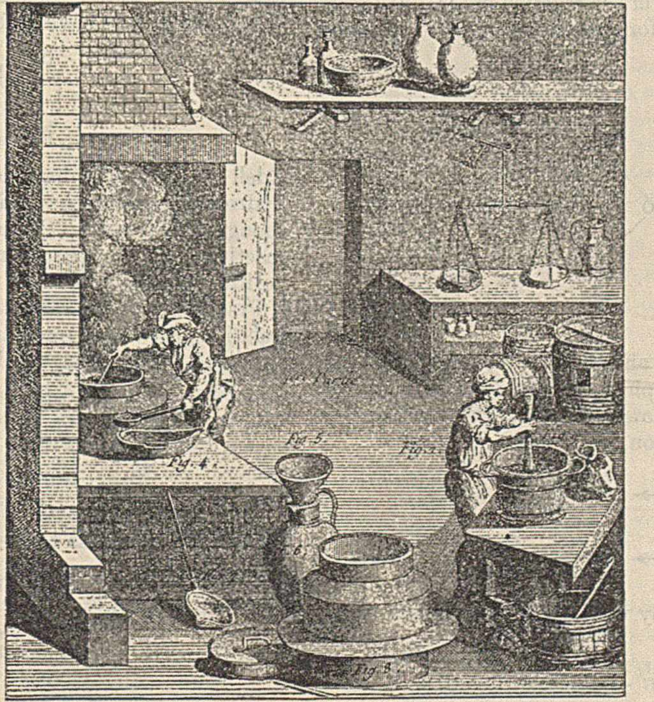
The glyceryl esters of rosin were first introduced into America in 1893, but it was twenty years later before they received wide application. Since they are simple esters of the natural resin acids, it is obvious that they possess a similar structure.

Following a suggestion of Wallach's that the structure of the terpenes could be related to that of naphthalene which in turn "might be considered as having been built up by the condensation of isoprene units," Ruzicka (*21*) has regarded the problem of the structure of abietic acid as one of terpene chemistry. Without going into the mass of experimental evidence which Ruzicka has advanced, suffice it to say that at present the structure of abietic acid is given as follows:



Ruzicka and his colleagues have extended their investigation to copal and kauri, and here again we find that, while their structure has not been definitely determined, the structure of copal bears a close relationship to trimethylnaphthalene and pimanthrene. The same investigators have shown that an ether-soluble amorphous acid in kauri is structurally related to methylethylnaphthalene and retene, while the crystalline acid is related to pimanthrene.

It is of passing interest to note that nature may possibly synthesize from the one hydrocarbon, isoprene, both



The Art of Varnishing and Lacquering

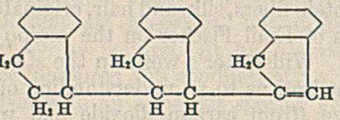
Reproduced from "Aikin's Dictionary of Chemistry" (published in London in 1807) for the "Century of Progress" Program of the Paint and Varnish Division, American Chemical Society, Chicago, 1933.

kauri and copal, and rubber. Between those two extremes certainly lies the perfect varnish resin which some chemist may yet discover.

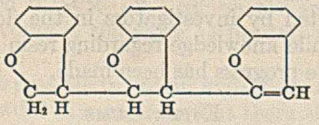
CUMAR-INDENE RESINS

These resins obtained by the polymerization of indene and of cumarone:

have been known for many years. The structure of *p*-indene as represented by Whitby and Katz (*26*) is:



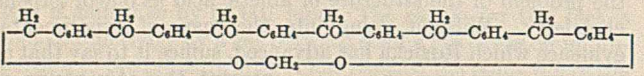
and the structure of *p*-cumarone is probably similar:



Such a structure is in accord with the chemical character of these resins—namely, their great stability towards alkalies and a certain susceptibility to oxidation.

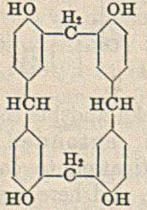
PHENOLIC RESINS

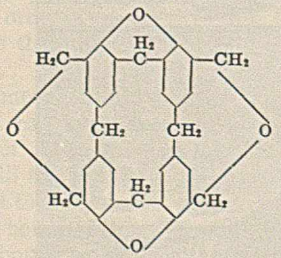
There has been much speculation and controversy concerning the structure of the phenol-formaldehyde resins since Baekeland (*2*) tentatively proposed "until we have something better" the following formula:



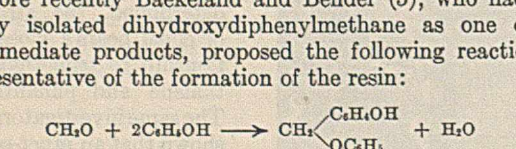
$$\overset{H_2}{-C}-C_6H_4-\overset{H_2}{CO}-C_6H_4-\overset{H_2}{CO}-C_6H_4-\overset{H_2}{CO}-C_6H_4-\overset{H_2}{CO}-C_6H_4-\overset{H_2}{CO}-C_6H_4- \quad (\text{ring closed through } -O-CH_2-O-)$$

Raschig (*20*) from a study of the reaction in alkaline media concluded that the following formulas more nearly represented the reaction:





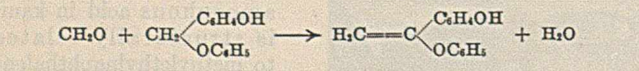
More recently Baekeland and Bender (*3*), who had definitely isolated dihydroxydiphenylmethane as one of the intermediate products, proposed the following reactions as representative of the formation of the resin:



$$CH_2O + 2C_6H_5OH \longrightarrow CH_2\genfrac{}{}{0pt}{}{C_6H_4OH}{OC_6H_5} + H_2O$$

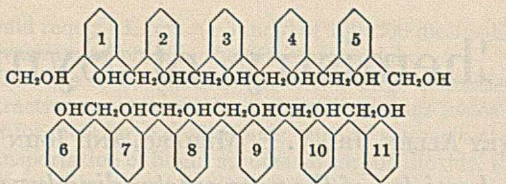
$$CH_2O + CH_2\genfrac{}{}{0pt}{}{C_6H_4OH}{OC_6H_5} \longrightarrow H_2C{=}C\genfrac{}{}{0pt}{}{C_6H_4OH}{OC_6H_5} + H_2O$$

This final product conceivably would polymerize thus:



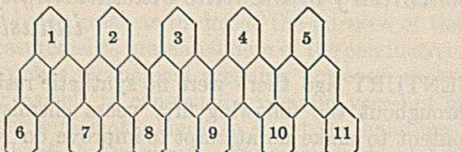
$$n\left(\overset{R\ R'}{C}=CH_2\right)\longrightarrow -\overset{R\ R'}{C}-\overset{H_2}{C}-\overset{R\ R'}{C}-\overset{H_2}{C}-\overset{R\ R'}{C}-\overset{H_2}{C}-\overset{R\ R'}{C}-\overset{H_2}{C}-$$

Blumfeldt (*4*) has taken exception to the formulas of Raschig and contends that the following more nearly express the facts:

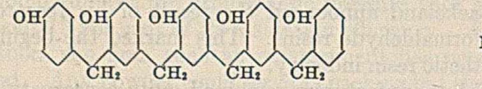


2 molecules

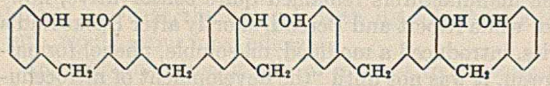
Bakelite A



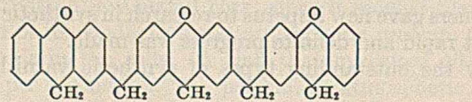
Bakelite C



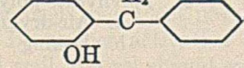
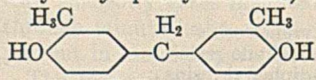
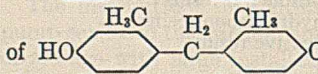
Novolak 1

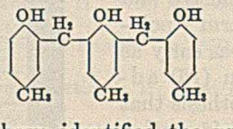


Novolak 2



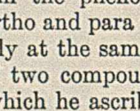
Novolak 3

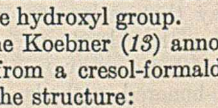
Abandoning mere speculation, Megson and Drummond (*17*) have attempted, like Baekeland and Bender, to isolate the intermediate products. They have succeeded in demonstrating the presence of  (2,4'-dihydroxydiphenylmethane) in the phenol condensation, of  in *o*-cresol condensation, and of  in the *m*-cresol condensation. From *p*-cresol condensation a product has been isolated presumably having the constitution:



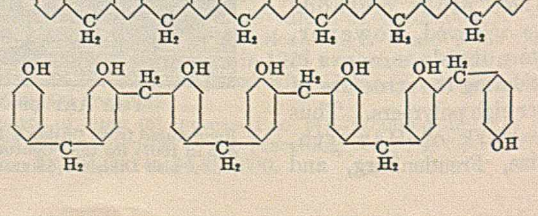
Edell (*7*) claims to have identified the presence of 2,3'-dihydroxydiphenylmethane in the phenol condensation although von Auwers (*1*) and Granger (*8*) maintain that the reactivity in the phenol molecule seems to be limited to positions ortho and para to the hydroxyl group.

Practically at the same time Koebner (*13*) announced the isolation of two compounds from a cresol-formaldehyde reaction to which he ascribed the structure:



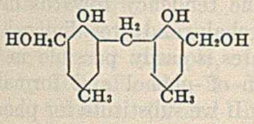


Very shortly thereafter Pollak and Riesenfeld (*19*) assigned the following formula to the Novolaks,

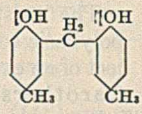


and stated that they on no account believe they have a polymerization product as supposed by Baekeland and Bender, since in that case the low values of the molecular weight would not be accounted for.

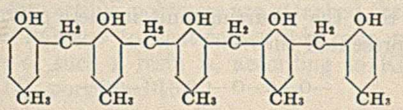
Granger (*8*) has reëxamined the results of earlier investigators of phenol alcohols and reports the isolation of a product having presumably the formula:



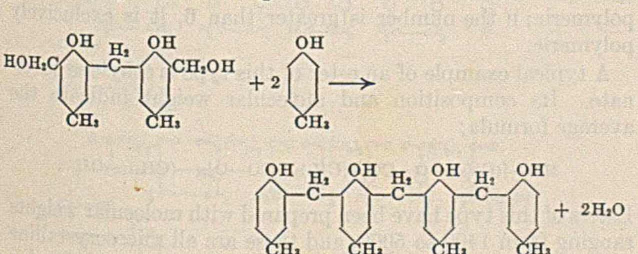
In a more recent and thorough study of the *p*-cresol-formaldehyde condensation, Koebner (*14*) has synthesized compounds varying from those possessing a binuclear structure thus,



to those of a pentanuclear structure,

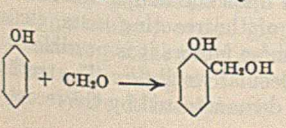


The general scheme for synthesis of these compounds is illustrated by the following reaction:

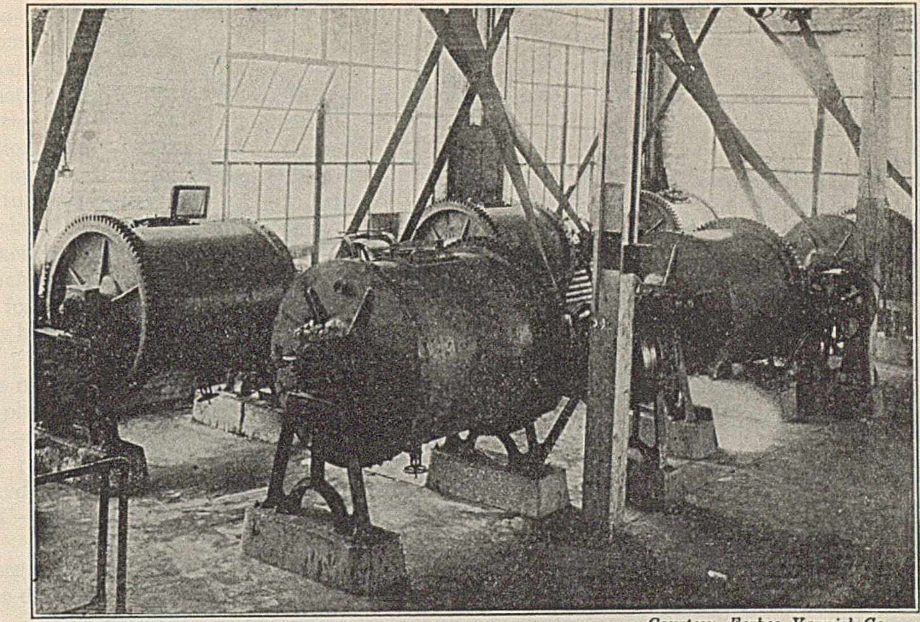


As a result of these investigations Koebner concludes that the acid-catalyzed, permanently fusible cresol-formaldehyde resins (Novolaks) are mixtures of di-, tri-, tetra-, and polynuclear compounds. The hydroxyl groups of the polynuclear compounds are unchanged and are difficultly soluble in dilute alkalies, owing to the formation of an insoluble sodium salt. Their resinous character is due to a mixture of innumerable isomers and the variety of large, and in some cases very large, molecules.

The great variety of reactions possible between phenol and formaldehyde either in neutral, acid, or alkaline solutions, and either with phenol or formaldehyde in excess are represented by Koebner by the following simple equations:

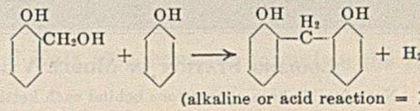


(alkaline reaction = phenol alcohol) (1)

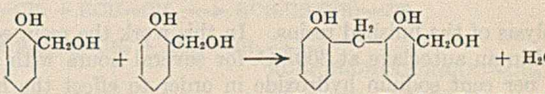


Courtesy, Forbes Varnish Co.

SECTION OF GRINDING ROOM SHOWING BALL AND PEBBLE MILL INSTALLATIONS



(alkaline or acid reaction = Novolak) (2)



(alkaline = Resol = Bakelite A) (3)

X Resol + Y Resol = Resit (Bakelite C) + water (4)

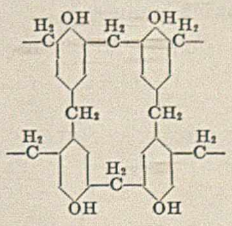
X Novolak + Y formaldehyde = Resit + water (5)

Novolak + Hexa = Resit + ammonia (6)

Equation 2 represents the formation of the simplest Novolak; Equation 3 the formation of the simplest Resol (Bakelite A).

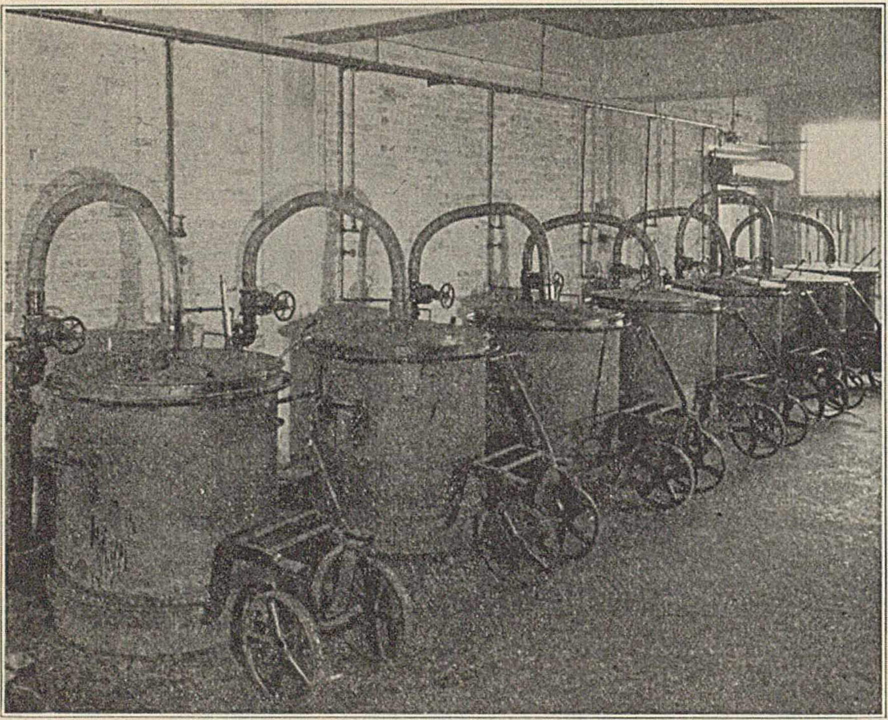
In Equation 2 one molecule of phenol reacts with 0.5 molecule of formaldehyde. As the ratio approaches 1 to 1, the chains which constitute the Novolak become longer, resulting in a resin of higher melting point, of lesser solubility in caustic or alcohol, and finally of infusibility and insolubility as the 1 to 1 limit is reached.

This limit 1 to 1 is reached only in the case of *o*- and *p*-cresol, whereas phenol and *m*-cresol may combine with more formaldehyde, up to a ratio 1 to 1.5, according to the following scheme:



It is to be understood, however, that there is no regular arrangement of the chains in the final infusible form of a phenol resin but rather a tangled mixture of various molecules whose structure is similar to that pictured above.

Some recent work in these laboratories by one of the authors (Ivey Allen, Jr.) is of interest in this connection. He has determined the nature of the products formed in the

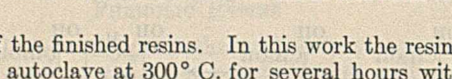


Courtesy, Devoe & Raynolds Co.

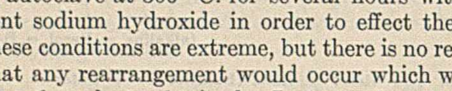
COOLING STATION IN MODEL VARNISH PLANT

Note flexible hose connections behind each kettle to carry away fumes.

hydrolysis of the finished resins. In this work the resin was heated in an autoclave at 300° C. for several hours with 10 or 15 per cent sodium hydroxide in order to effect the hydrolysis. These conditions are extreme, but there is no reason to believe that any rearrangement would occur which would yield the type of products obtained. In fact, when *o*-cresol was heated with alkali under even more extreme conditions, the effect was negligible. In the case of the resins the hydrolysis product always contained a greater proportion of higher boiling phenols than did the material from which the resin was made. That is, if the resin was made from a material containing 40 per cent phenol, 30 per cent cresol, and 30 per cent xylenols, these ratios in the hydrolysis products might be 10 of phenol, 40 of cresol, and 50 of xylenol. This shift toward the higher phenols was more noticeable the further advanced the resin was and the higher the ratio of formaldehyde to phenol. Quite often phenols were formed which did not occur in the original raw material. Also there was always a considerable amount of hydrogen formed. The mechanism of the reaction is not entirely clear and is probably somewhat involved. The net effects can be shown by an equation in the following manner:

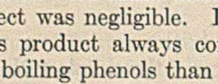


(7)

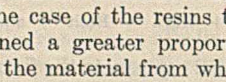


(8)

If in reaction 8 we take,



or



we might easily obtain xylenols and mesitol (*sym*-trimethylphenol) from a resin made with pure phenol and formaldehyde. In fact in the case of a resin in which the ratio of phenol to formaldehyde was 1 to 2.6, these compounds were actually obtained.

These theories of structure for the phenol-formaldehyde resins are in harmony with the present views as to the structure of high polymers. As pointed out by Meyer and Mark (*18*), the tendency towards interlocking chains and three-dimensional structures is easily possible in the reaction of phenol and formaldehyde. If we substitute for phenol, *o*- or *p*-cresol, in which one reactive position is blocked by a methyl group, we do not obtain such high-melting insoluble products but rather compounds which belong to the chain polymers.

POLYHYDRIC-POLYBASIC RESINS

The constitution of polyhydric-polybasic resins has been the subject of an extensive investigation by Carothers, Kienle, Hönel, and others.

The studies of Carothers (*5*) and his collaborators on the esterification of dibasic acids and the glycols have definitely established that the recurring unit in these polymerizations could be represented thus:

$$\text{—O—R—O—CO—R}'\text{—CO—}$$

It was further proved that, if the number of atoms contained in the unit chain is 5, the product is monomeric and cyclic; if the number is 6, it may be either monomeric or polymeric; if the number is greater than 6, it is exclusively polymeric.

A typical example of an ester of this type is ethylene succinate. Its composition and molecular weight indicate the average formula:

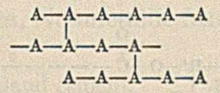
$$HO—[(CH_2)_2—O—CO—(CH_2)_2—CO—O]_{22}—(CH_2)_2—OH$$

Esters of this type have been prepared with molecular weights ranging from 1400 to 5000, and these are all microcrystalline solids. Thus ethylene succinate has an average molecular weight of 3000 and an average of 20 structural units per molecule.

The mechanism of the reaction in the alkyd resins is undoubtedly one of ester interchange. Thus the first result may be formation of the simple ester $HO(CH_2)_2O—CO(CH_2)_2COOH$. Two of these molecules may combine to form $HO(CH_2)_2O—CO(CH_2)_2COO(CH_2)_2O—CO(CH_2)_2COOH$ and so give ester molecules of ever-increasing length. The upper limit of molecular size is evidently determined by purely physical factors—namely, (1) increasing viscosity of the resin which hinders diffusion of the volatile by-product and (2) decrease in mobility and concentration of reactive groups. Carothers states "that the molecular weight at which a practical limit is reached will depend upon the temperature and pressure, the area and thickness of the reacting mass, etc., and by a suitable adjustment of these factors it is possible to obtain polyesters having high molecular weight." The truth of this statement has been amply demonstrated by the recent preparation by Carothers (*6*) of so-called superpolyesters with molecular weights ranging from 10 to 20 thousand. Such linear "superpolymers" can easily be drawn out into strong, pliable, transparent, permanently oriented fibers.

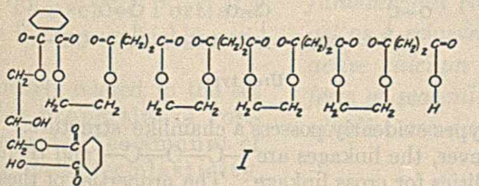
Kienle (*10*) has studied especially the kinetics of the polybasic acid—polyhydric alcohol reaction, and as a result developed three postulates "which are apparently requisite to formation of synthetic resin." Postulate 2 is particularly interesting, which states: "Interlocking of the molecules proceeds according to the chance contact of any two individual molecules . . . This leads to the conclusion that, when the reaction is 2,2, chain molecules will form. If, however, the reactivity is 2,3 or greater, presumably branching intertwining molecules will form."

As applied to the alkyd resins, this means essentially that the structure, for example, of glycol phthalate can be represented by HO—R—R′—R—R′—R - - - - - - - R′—COOH, whereas "chains formed in the reaction of glycerol with phthalic acid would bear hydroxyl groups, thus: $HO{-}\underset{OH}{R}{-}R'{-}\underset{OH}{R}{-}R'{-}\underset{OH}{R}\text{------}R'{-}COOH$." Conceivably such chains could be linked together through the hydroxyl group, resulting in complicated three-dimensional structure simply represented thus:



where A represents a monomeric group

Kienle and Schlingman (*11*) have made further application of this theory in the production of flexible, heat-convertible, alkyd resins. Here the structure is assumed to be such that flexible, heat-convertible polymers are attached through primary valence linkages to heat-convertible resin molecules. The structure of such a resin is, according to Kienle and Schlingman (*11*), portrayed thus:



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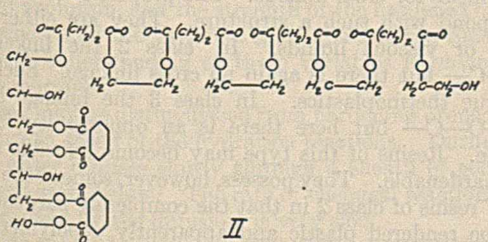


II

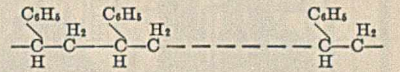
Hönel (*9*) in an extensive investigation of the various stages of the formation of alkyd resins has pictured the final products either as possessing an open chain structure, closed ring structure, or combination of both. He states also that "it seems almost as if the glycerol when partly esterified with the monobasic acid functions similarly to glycol." We would expect, therefore, that the modified alkyd resins have a linear two-dimensional structure similar to that proposed by Carothers for a dibasic acid and a dihydric alcohol.

Before leaving the problem as to the structure of the alkyd resins, particularly of the glyptal type, it should be pointed out that no actual chemical evidence is available on which to base a formulation of the structure of the final, infusible stage. While it is evidently apparent that there are cross linkages between the chains, the nature of these linkages still remains to be determined. Presumably this might be accomplished by some means of *Abbau* less drastic than for example, hydrolysis, which always leads to the polyhydric alcohol and polybasic acid.

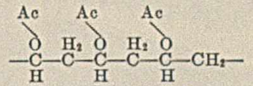
VINYL AND STYRENE RESINS

Vinyl and styrene resins have not as yet achieved in the varnish and lacquer industry the recognition accorded the phenolic and alkyd types, but the facts resulting from the study of these compounds by Staudinger (*22*) and his co-workers have been the basis for most of the modern theories as to the structure of synthetic resins.

Styrene itself has the formula $C_6H_5CH{=}CH_2$, whereas polystyrene is a completely saturated compound the structure of which according to Staudinger is:



The structure of polymerized vinyl acetate is probably similar to that of styrene polymer:



Whitby and Katz (*26*), however, formulate the polymerization thus:

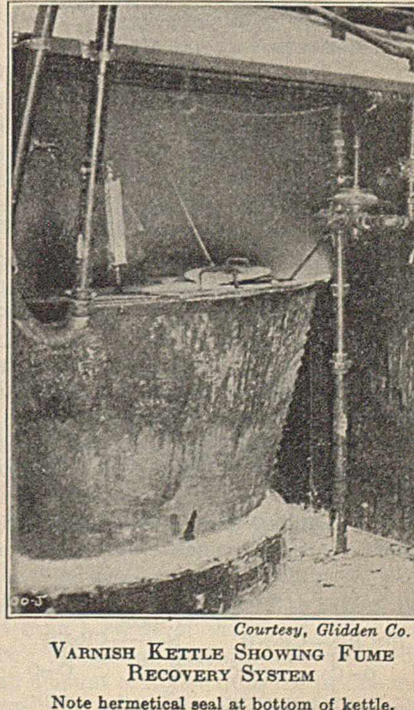
$$RCH{=}CH_2 + RCH{=}CH_2 \longrightarrow RCH_2CH_2C(R){=}CH_2$$

$$RCH_2CH_2C(R){=}CH_2 + RCH{=}CH_2 \longrightarrow RCH_2CH_2CH(R)CH_2C(R){=}CH_2, \text{ etc.}$$

It has been difficult to arrive at the exact structure of these compounds either from a study of their chemical behavior or of the formation of the polymer.

AMIDE-FORMALDEHYDE RESINS

Toluene sulfonamide resins result from the reaction of formaldehyde with toluene sulfonamide. While their exact constitution is still unknown, McMaster (*16*) has succeeded in isolating —C—N— ring compounds similar in structure to those found when benzene sulfonamide is condensed with formaldehyde. Walter and Glück (*25*) have studied these resins in connection with the general question of hardenability and have iso-



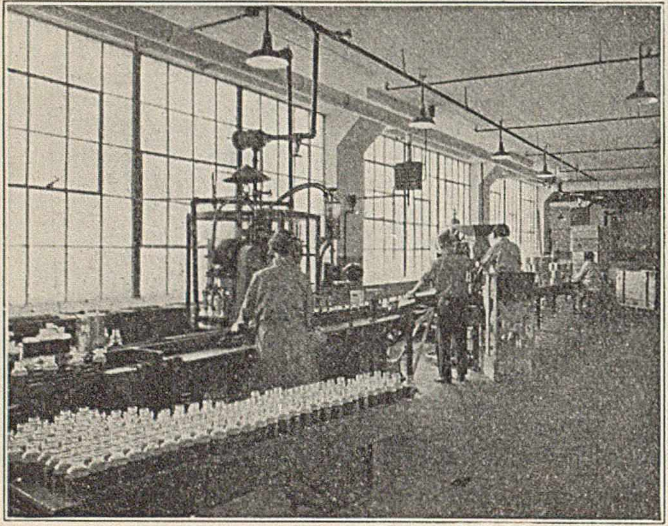
Courtesy, Glidden Co.

VARNISH KETTLE SHOWING FUME RECOVERY SYSTEM

Note hermetical seal at bottom of kettle.

lated a crystalline dimethylene methylol-tri-*o*-toluene sulfonamide. It is quite possible that the chemical reactions involved are similar to those which occur in the urea-formaldehyde condensation.

The urea or amide resins, while important as plastics, have not been extensively used as resins by the varnish manufacturer. His constant search for new resins may, however, conceivably result in their future adaptability.



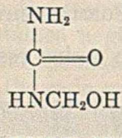
Courtesy, S. C. Johnson & Sons

Automatic Filling Machine

Machine in the background caps the containers.

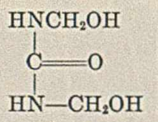
Little is known regarding the actual structure of these resins formed by the interaction of formaldehyde on urea although a number of intermediate products have been isolated:

Monomethylol urea:



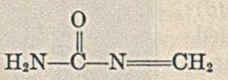
$$NH_2-C(=O)-HNCH_2OH$$

Dimethylol urea:



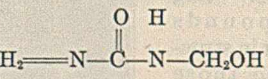
$$HNCH_2OH-C(=O)-HN-CH_2OH$$

Methylene urea:



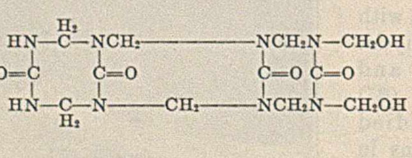
$$H_2N-\overset{O}{\overset{\|}{C}}-N=CH_2$$

Methylol methylene urea:

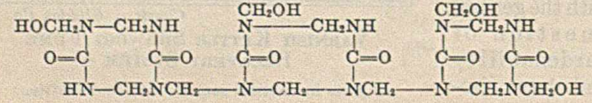


$$CH_2=N-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2OH$$

Walter and Gewing (*24*) believe that the structure of the resin is best represented by the following formula:



or



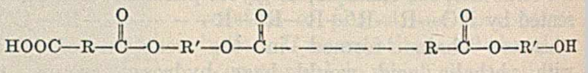
Chlorinated-Diphenyl, Petroleum-Hydrocarbon, and Rubber-Derivative Resins

Information is meager regarding the chemistry of these resins. The first are mixtures of chlorinated diphenyl and polyphenyl derivatives and the second reaction products of diolefins and olefins or of diolefins with substituted aromatics (*23*). The rubber-derivative resins are chiefly resin-like substances which result from the chlorination of unvulcanized rubber.

Summary

If the type formulas for the various synthetic resins which have been discussed are now compared, there is evident a certain similarity:

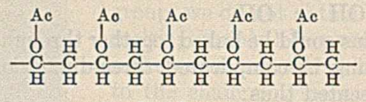
(1)



$$HOOC-R-\overset{O}{\overset{\|}{C}}-O-R'-O-\overset{O}{\overset{\|}{C}}-------R-\overset{O}{\overset{\|}{C}}-O-R'-OH$$

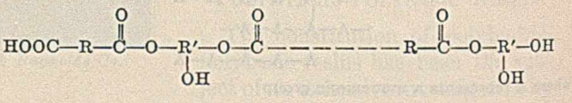
Fusible alkyd type (heat non-hardenable)

(2)



Vinyl type

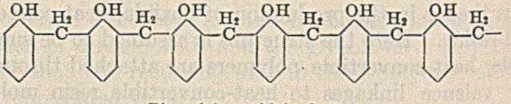
(3)



$$HOOC-R-\overset{O}{\overset{\|}{C}}-O-\underset{OH}{R'}-O-\overset{O}{\overset{\|}{C}}-------R-\overset{O}{\overset{\|}{C}}-O-\underset{OH}{R'}-OH$$

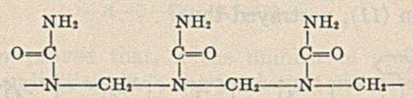
Infusible alkyd type (heat-hardenable)

(4)



Phenol-formaldehyde type

(5)



Urea type

All types evidently possess a chainlike structure. In class 1, however, the linkages are —C—O—C— and there are no possibilities for cross linkage. The properties of these resins correspond with such a structure. They are either fusible solids or viscous liquids. In class 2 the linkages are —C—C— but there is again no cross linkage. Such resins are true thermoplastics. In class 3 the linkage is again —C—O—C— but here there is an opportunity for cross linkage. Resins of this type may become infusible and are heat-hardenable. They possess, however, some of the properties of resins of class 2 in that the completely hardened resin may be rendered plastic and apparently depolymerized by mechanical working. In class 4 the linkage is again —C—C—; there is cross linkage between the chains and such linkage is also probably —C—C—. Such resins may become infusible and are heat-hardenable. In their final infusible state they are rigid and not subject to depolymerization. In class 5 the linkage is —C—N—C—, this same grouping of atoms being evident in the cross linkages. Resins of this type become infusible and are heat-hardenable. The —C—C— linkage is probably a stronger bond in some respects than either —C—N—C— or —C—O—C— linkage, since resins of both types 3 and 5 are less resistant to water than type 4.

The structure of the chain seems fairly well established, but the nature of the cross linkages between such chains is uncertain. This is a problem yet to be solved.

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The Setting of Portland Cement

Chemical Reactions and the Role of Calcium Sulfate[1]

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Analyses of the liquid phase and time-of-set tests have been made for three cements, and for several clinkers under different conditions of added reagent and of seasoning. The direct hydration of tricalcium aluminate is hindered by its reaction with calcium hydroxide above a threshold concentration to give stable tetracalcium aluminate. The set is thus delayed. Tricalcium silicate is a fundamental retarder, and calcium sulfate may act as a retarder in virtue of the formation of reactive calcium hydroxide in solution. The effects of seasoning, of slaked lime, and of soluble alkalies are discussed.

WHEN Portland cement is tempered with water, the mixture becomes decreasingly plastic with time and in the course of a few minutes or a few hours sets to a more or less rigid mass. The proper utilization of the cement requires that it remain plastic for at least a certain length of time. The set of Portland cement is, however, highly variable.

Intimately related to the set are other properties of Portland cement. The amount of water required for plasticity, the heat evolution, and the strength of the hardened mass are all dependent on the variables that influence the time of set. A correct understanding of these variables is obviously of great importance.

Setting may be distinguished from hardening proper by the difference in speed of the hydration reactions. During hardening, water diffuses slowly through a sheath of gel to the unaltered grain below. The rate of chemical reaction, which is determined by the diffusion, is very slow.

During the early period of setting, on the other hand, the mixing water is in immediate contact with the reactive surfaces of the cement grains. Solution, hydration, and hydrolysis may then take place with relative rapidity.

As the mixing water leaves the free condition to become fixed as hydrate, the plastic mass stiffens and sets. If the rate of hydration is rapid, the plastic mass will set rapidly; conversely, if the rate of hydration is slow, the set is slow.

Of the compounds normally[2] present in Portland cement, tricalcium aluminate ($3CaO\cdot Al_2O_3$, or C_3A for short) is the only compound that may hydrate with sufficient rapidity to give rise to an undesirably quick set. The variations in rate of set may therefore be ascribed to variations in the rate of hydration of the aluminate.

It is not known whether hydration of the C_3A takes place directly or by way of solution and subsequent crystallization as the hydrate. Possibly both reactions are involved. In any case, those conditions that alter the over-all rate of hydration of C_3A will alter the rate of set.

It has been known for a long time that gypsum added in small amounts to Portland cement may greatly retard the set. The earliest hypothesis as to the action of gypsum was a simple physical one. It was thought that the gypsum crystallized and coated the surface of the cement grains (*40*). Later, when the compound of calcium sulfate and C_3A had been discovered and had been well established, it was assumed a priori that the formation of this compound was the cause of the slow set. At various times other *ad hoc* hypotheses as to the cause of changes in the time of set and of the behavior of gypsum have been proposed.

In order to understand with assurance the variables that control the set of Portland cement, it is unsuitable merely to know the reactions that may take place on the basis of studies with pure compounds in contact with excess water. This knowledge is indispensable as a guide, but in the end it is necessary to recognize and to evaluate the reactions that actually take place when Portland cement is mixed to normal consistency with the usual small amount of water.

It was felt that a glimpse of the reactions taking place might be obtained from a study of the liquid phase under different conditions. To this end a technic was developed for extracting the small amount of liquor from the plastic mass. The liquid phase was then analyzed microchemically and by

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[1] This paper is one of a series from the Nonmetallic Minerals Experiment Station connected with the problem of the utilization of natural anhydrite as a retarder of the set of Portland cement.

[2] $5CaO\cdot 3Al_2O_3$ may be present also in small amounts. However, its activity toward water is distinctly less than that of the tricalcium aluminate (*4*). It yields the same hydrated aluminate, along with alumina (*4, 19*). Reference to C_3A, therefore, is taken to include any of the 5:3 compound that may be present.

other means. Simultaneously, the time of set was measured and an attempt was made to correlate the chemical reactions, deduced from the changes in liquid-phase composition, with the rate of set.

EXPERIMENTAL METHOD

Six Portland cement clinkers obtained from plants in Texas, Iowa, Pennsylvania, and New York form the basis of this study. The analyses of these clinkers are given in Table I, together with the compound composition calculated according to the method of Bogue (*8*). The clinkers were ground in the laboratory till their particle size distribution corresponded to that of commercial cements (*39*).

TABLE I. CHEMICAL ANALYSES OF CLINKERS

(Per cent by weight)

	A	B	C	D	E	F
Loss in ignition	0.95	0.81	0.21	1.66	1.04	0.37
Insol. residue	0.06	0.06	0.09	0.15	0.06	0.09
SO_3	0.23	0.17	0.37	0.23	0.52	1.02
SiO_2	21.64	22.22	21.27	22.50	20.78	21.25
Fe_2O_3	3.35	3.70	3.33	3.54	4.18	2.81
Al_2O_3	7.18	5.33	7.73	4.59	7.14	6.69
CaO	63.94	65.40	62.71	66.04	64.38	63.19
MgO	2.47	1.68	3.16	1.10	0.49	3.99
K_2O	0.58	0.47	0.74	0.44	0.98	0.90
Na_2O	0.35	0.27	0.51	0.52	0.29	0.51
Free CaO	0.7	0.8	1.0	1.7	2.1	0.8
$3CaO \cdot SiO_2$	40	53	32	54	41	42
$2CaO \cdot SiO_2$	32	24	37	24	29	30
$4CaO \cdot Fe_2O_3 \cdot Al_2O_3$	10	8	10	11	13	9
$3CaO \cdot Al_2O_3$	13	11	15	6	12	13
Ratio: $3CaO \cdot SiO_2/3CaO \cdot Al_2O_3$	3.1	6.6	2.1	8.4	3.5	3.2

The gypsum and plaster that were, in certain tests, added to the clinker were very fine, averaging 2.5 microns unless otherwise noted. The solubility of the freshly ground gypsum was high. This was imputed to partial dehydration on grinding. When the gypsum had been treated by stirring in contact with water for a few hours, filtering, washing with alcohol and ether, and drying at 80° C., it showed the correct solubility. The plaster was prepared from the gypsum by heating for 36 hours at 130° C.

In adding the calcium sulfates and other solid reagents to the ground clinker, the latter was spread out in a thin layer, the reagent sprinkled over it and incorporated with a trowel, and the mixture rotated in a mason jar for 30 minutes.

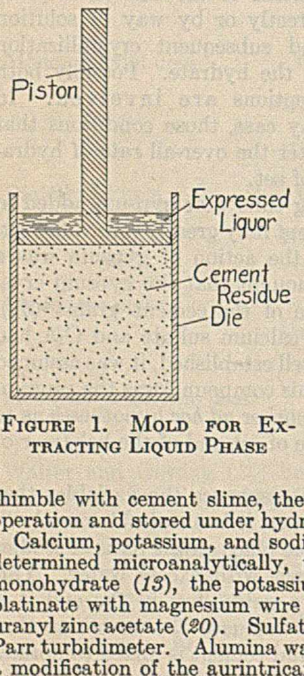

FIGURE 1. MOLD FOR EXTRACTING LIQUID PHASE

The liquid phase was extracted from the plastic mass in a mold shown in Figure 1. The liquid was squeezed out of the pat under a pressure of 280 kg. per sq. cm. through the clearance of a few thousandths of a centimeter between the piston and the walls of the die. The murky liquor which collected on the upper surface of the piston head was rapidly sucked up in a pipet and suction-filtered through a G-3 Jena glass thimble into a Pyrex glass test tube. The volume of the clear liquid was determined by weighing the test tube before and after filling. In order to prevent clogging of the filter thimble with cement slime, the thimble was cleaned after each operation and stored under hydrochloric acid.

Calcium, potassium, and sodium in the extracted liquor were determined microanalytically, the calcium as calcium oxalate monohydrate (*13*), the potassium by reduction of the chloroplatinate with magnesium wire (*18*), and the sodium as sodium uranyl zinc acetate (*20*). Sulfate was determined with a Burgess-Parr turbidimeter. Alumina was determined colorimetrically by a modification of the aurintricarboxylic acid test (*38*). For the alumina determination, to eliminate by dilution the yellowish color of many of the liquors, it was necessary that not more than 1 cc. be taken for analysis. Silica was not determined owing to contamination by the glass. All methods of analysis were proved against known standards; the analyses themselves were made in duplicate and could be checked generally to about 3 per cent.

For the time of set and liquor extraction tests, 300 grams (*2*) of clinker with or without added reagent were taken. The clinker was mixed with an amount of distilled water required to give a plasticity equal to or nearly equal to that described as normal consistency (*1*). The percentage of water refers to the weight of clinker, neglecting any addition of reagent. The mixture was thoroughly kneaded for 3 to 3.5 minutes (*2*) and then stored in a forced-draft air thermostat at 23° C. and at a relative humidity of 75 per cent. The initial and final time of set were measured with the Vicat needle (*1*). The set is considered quick when initially less than 45 minutes (*1*).

SEASONING OF A CLINKER

All clinkers experienced profound changes of set when exposed to the atmosphere. These changes will be considered in detail in a later paper. The results of the present work on the set proper cannot, however, be correctly comprehended without some understanding of the state of the clinker due to its exposure to the atmosphere. The effect of exposure will therefore be considered briefly and merely to the extent required for a correct comprehension of the present results.

All clinkers that were exposed after grinding in 40-pound (18.1-kg.) batches to the air of the laboratory (20 to 70 per cent relative humidity, average 45 per cent) through closed but not air-tight containers absorbed water vapor in excess of the absorption of carbon dioxide. The absorption of water vapor is referred to as seasoning. On seasoning, all clinkers experienced in time a transition from quick set at the start to extreme slow set.

The state of seasoning, which is based upon concordant results with the different clinkers, is described partially in Table II. It is understood that the seasoning is continuous, but for convenience of reference certain characteristic states may be differentiated and defined.

TABLE II. SEASONING OF A GROUND CLINKER

					Absorption by Clinker A	
State of Seasoning	Designation	Time of Set	Degree of Gypsum Satn. of Clinker Liquid Phase	Effect of Added Gypsum on Set	Loss on ignition %	Mean ratio, *R*
Fresh	f	Quick	Slight	Negligible	0.70	0.35
Slightly seasoned	s	Quick	Slight	Causes slow set	0.95	0.50
Moderately seasoned	m	Slow	Partial (0.3)?	Causes increased slow set	1.05	0.65
Thoroughly seasoned	t	Slow	Complete	Negligible	1.25	0.90

In column 2, Table II, a letter has been used to designate the state of seasoning described in column 1. Since the state of seasoning of the clinker is of greatest importance in determining its properties, it is necessary to characterize this state at all times. This may be conveniently done by prefixing the letter of column 2 before the word "clinker." Thus f-clinker stands for the fresh clinker which is quick-set; m-clinker for the moderately seasoned clinker which is slow-set, etc.

In column 3, Table II, the time of set of a given clinker in the different states of seasoning is given. From quick set when freshly ground, the clinkers passed in time to extreme slow set. Under the stated conditions of low humidity and restricted exposure, this change occurred in 1 to 2 years, but a similar change could be secured in much shorter time artificially.

The concentration of calcium sulfate in the clinker liquid phase referred to the degree of gypsum saturation is given in column 4, Table II. The concentration varies greatly for a given clinker, depending on its state of seasoning. The concentration of calcium sulfate in the liquid phase is, for the same clinker, indicated by the relative amount of sulfate ion in solution. An exact definition of the concentration of calcium sulfate in the mixed-electrolyte liquid phase, based on ion product and ionic strength considerations and analogous to that employed later for calcium hydroxide, will be given in a subsequent paper.

In column 5, Table II, the effect of the usual small addition of gypsum on the set of the differently seasoned clinker is given.

In addition to these characteristics of the state of seasoning, an empirical relationship appears to exist between the state of seasoning and the absorption as measured by the loss on heating. The loss on ignition at 1000° C. after 15 minutes, and the loss on heating at 500° C. for 1 hour were determined. These losses correspond roughly to that of absorbed carbon dioxide plus water, and of water, respectively, and in the course of this work the losses are at times referred to in terms of carbon dioxide and water in a qualitative sense. As a datum of the state of seasoning, the absorption ratio (loss at 500° to loss at 1000° minus the loss at 500° C.), hereafter referred to by *R*, has been constructed. As the seasoning proceeds, moisture in excess of carbon dioxide is absorbed, and so *R* increases.

Clinker A, on the basis of a variety of tests and in comparison with the other clinkers, was found to be typical of a well-burnt and normally behaving material. The reactions of this clinker have been followed in some detail, and it is desirable that its approximately mean value of *R* be given in the different states of seasoning mentioned. This has been done in the last column of Table II.

COMPOSITION OF LIQUID PHASE

Although Portland cement consists essentially of calcium compounds, the liquid phase is mainly a solution of the alkalies. The alkalies total only 0.75 to 1.50 per cent in cement, but their high concentration in the liquid phase is in accord with the great solubility of the alkali compounds relative to the alkaline earth compounds.

In Table III are given the analyses of the liquid phases of three commercial slow-setting Portland cements. The specific conductivities are high while the pH is above that for saturated lime water, 12.3. The solution consists mainly of alkali sulfate and hydroxide, the alkali being predominantly potassium.

TABLE III. LIQUID PHASE OF COMMERCIAL CEMENTS

CEMENT	I	II	III
Mixing water, %	26.0	24.2	24.5
Water retained, cc./100 g.	15.3	15.7	16.5
Sp. conductivity at 25° C., mho × 10^2	2.32	3.70	4.88
pH	12.5	12.8	12.9
K^+, m. eq./cc.	0.1100	0.2308	0.2907
Na^+, m. eq./cc.	0.0242	0.0300	0.0827
$^1/_2\ Ca^{++}$, m. eq./cc.	0.0411	0.0368	0.0378
$^1/_2\ SO_4^{--}$, m. eq./cc.	0.0980	0.1822	0.2714
OH^-, m. eq./cc.	0.0730	0.1030	0.1150
Reducing anions, m. eq./cc.	0.0020	0.0139	0.0382
$^1/_2\ S_2O_3^{--}$, m. eq./cc.	0.0002	0.0027	0.0056
Σ^+	0.1753	0.2976	0.4112
Σ^-	0.1732	0.3018	0.4302
Al_2O_3, mg./cc.	0.0015	0.0010	0.0010

TABLE IV. LIQUID PHASE OF QUICK-SETTING CLINKERS

	s-Clinker A	f-Clinker B	f-Clinker C
Mixing water, %	30.0	22.0	34.0
Water retained, cc./100 g.	18.3	17.4	23.7
Sp. conductivity at 25° C., mho × 10^2	4.91	......	......
pH	13.1	......	......
K^+, m. eq./cc.	0.1766	0.2742[a]	0.4260[a]
Na^+, m. eq./cc.	0.0666	......	......
$^1/_2\ Ca^{++}$, m. eq./cc.	0.0037	0.0063	0.0019
$^1/_2\ SO_4^{--}$, m. eq./cc.	0.0060	0.0162	0.0150
OH^-, m. eq./cc.	0.2320	0.2638	0.3860
Reducing anions, m. eq./cc.	0.0097	0.0005	0.0220
$^1/_2\ S_2O_3^{--}$, m. eq./cc.	0.0017	0.0000	0.0050
Al_2O_3, mg./cc.	0.0060	0.0058	0.0250

[a] $K^+ + Na^+$ by difference.

The liquid phase of f- and s-clinkers consists mainly of alkali hydroxide. Sulfate is nearly absent. This is shown in Table IV for s-clinker A and f-clinkers B and C. It may be mentioned that, as the clinkers season and advance into the m- and t-stages, sulfate appears in solution in increasing amounts as indicated in Table II.

The liquors are all reducing. Reducing anions were determined by titration with acid permanganate. Sulfite and thiosulfate present in traces were determined by the iodine-formaldehyde titration of Kurtenacker (*27*). Neither heavy metal cations nor sulfide could be detected in solution.

The liquors are, in general, yellowish but are colorless in the absence of dissolved sulfate. They ordinarily remain clear on standing.

COMPOSITION AND TIME OF EXTRACTION

The liquid phase reaches the high observed concentrations with rapidity. Hänsel, Steinherz, and Wagner (*16*) find that the composition is similar after 5 minutes, as after 60 minutes, the amount of dissolved alkalies being somewhat greater at the later time.

To discern the effect of time in the present experiments, the composition of the liquid phase of t-clinker F was measured at the end of different periods. The t-clinker had an initial set of 1 hour 50 minutes and a final set of 4 hours 30 minutes. The composition 7.5, 15, and 30 minutes after the addition of the mixing water is shown in Table V. The sulfate ion is high and practically constant; the increase in hydroxyl ion is due to the steady dissolution of alkali compounds in contact with generated calcium hydroxide to give alkali hydroxide in accordance with Equation 6 below. Both the change in amount of mixing water retained by the setting clinker and the change in composition of the liquid phase are relatively small after the first measurement at the end of 7.5 minutes.

TABLE V. LIQUOR COMPOSITION OF t-CLINKER F AS A FUNCTION OF TIME FROM THE MOMENT OF ADDITION OF MIXING WATER

(20.0 per cent for normal consistency)

TIME	WATER RETAINED	OH^-	$^1/_2\ SO_4^{--}$	Al_2O_3
Min.	*Cc./100 g.*	*M. eq./cc.*		*Mg./cc.*
7.5	13.0	0.191	0.640	0.0013
15	13.3	0.211	0.638	0.0015
30	13.6	0.250	0.634	0.0019

In this study, interest was centered in the changes effected in the clinker by varying external conditions; therefore, unless otherwise noted, all the liquid-phase extractions were made at the end of the same fixed time after the addition of the mixing water. This time was chosen conveniently at 15 minutes, which is sufficiently close to the mixing period to conform to the primary reactions of set, and yet is also sufficiently removed therefrom so that these reactions have slackened and are continuing but slowly.

REACTIONS OF ADDED GYPSUM

When gypsum is incorporated with an s-clinker, the set becomes slow. The change in liquid phase on the gypsum addition is seen by comparing Table VI for s-clinker A with 2 per cent gypsum addition, with Table IV for the same clinker straight.

TABLE VI. LIQUID PHASE OF S-CLINKER A CONTAINING 2 PER CENT ADDED GYPSUM

Mixing water, %	22.0
Water retained, cc./100 g.	14.0
Sp. conductivity at 25° C., mho × 10^2	3.44
pH	12.7
K^+, m. eq./cc.	0.1899
Na^+, m. eq./cc.	0.0433
$^1/_2\ Ca^{++}$, m. eq./cc.	0.0328
$^1/_2\ SO_4^{--}$, m. eq./cc.	0.1542
OH^-, m. eq./cc.	0.1030
Reducing anions, m. eq./cc	0.0114
$^1/_2\ S_2O_3^{--}$, m. eq./cc.	0.0023
Al_2O_3, mg./cc.	0.0015

In the first place, the amount of mixing water retained by the setting clinker is decreased considerably, in this case from 18.3 to 14.0 cc. per 100 grams of clinker, or by 23 per cent.

Water is retained by the residue of the high-pressure extraction in three ways—as capillary water, as adsorbed water, and as water of chemical hydration. The amount of adsorbed water in the absence of any appreciable gel formation, as under the present conditions of a few minutes' reaction, corresponds probably to one or two molecular layers of the cement surface and so is negligible in amount. The water retained should consist therefore essentially of capillary water and water of chemical hydration. An idea of the relative amounts of these is obtained from the observation that the extraction residue of cement I lost 80 per cent of its water and that of m-clinker A with 1 per cent added gypsum lost 65 per cent of its water, on heating to nearly constant weight at 110° C.

It is reasonable to assume that the amount of capillary water is substantially constant for the same clinker extracted under the same pressure. It follows, as is assumed throughout, that the observed changes in the total amount of retained water are due solely to changes in the water of chemical hydration.

The water of hydration will depend upon the time of reaction and on the changes in rate of chemical reaction due to change in conditions. From Table V for t-clinker F, the percentage hydration has increased by 0.3 per cent between 7.5 and 15 minutes, and 0.3 per cent between 15 and 30 minutes. For the same reaction time and temperature, the change in hydration due to change in conditions is in general much greater. For example, the addition of 2 per cent gypsum to s-clinker A has decreased the amount of water retained by 23 per cent as mentioned above, or decreased the per cent hydration by 4.3 per cent.

The compound which may hydrate rapidly in cement is tricalcium aluminate, C_3A. Since C_3A is in the solid state, the chemical effect due to gypsum need be restricted only to the surface of the aluminate, to the extent of one or more molecular layers, in order to produce a great change in the rate of hydration of the remaining unaltered compound. From this point of view the ability of a small amount of gypsum to produce a great change in the hydration of C_3A is readily understood.

A comparison of the liquid-phase composition of Table VI with Table IV shows that the added gypsum on dissolving has entered into the following reaction:

$$\mathrm{CaSO_4} + 2\left\{\begin{matrix}\mathrm{KOH}\\ \mathrm{Na}\end{matrix}\right\} \rightleftharpoons \mathrm{Ca(OH)_2} + \left\{\begin{matrix}\mathrm{K_2SO_4}\\ \mathrm{Na_2}\end{matrix}\right\} \qquad (1)$$

A second reaction into which the calcium sulfate in solution may enter but which is not apparent from the results of Tables IV and VI is that to form sulfoaluminate. This reaction may proceed according to Equation 2 as follows:

$$\mathrm{3CaSO_4 + 3CaO\cdot Al_2O_3(s) \rightleftharpoons 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot}X\mathrm{H_2O(s)} \qquad (2)$$

Two sulfoaluminates have been described by Lerch, Ashton, and Bogue (*31*), a low sulfate form containing one mole of calcium sulfate, and a high sulfate form containing 3 moles of calcium sulfate per mole of C_3A. In Portland cement, Koyanagi (*22*) reports that only the high sulfate form exists; this is the compound that is given in Equation 2.

According to this equation, the calcium sulfate in solution is supposed to react with or at the surface of solid C_3A, which reaction alone is significant as regards the hydration rate of C_3A. Reaction in solution to form sulfoaluminate is restricted by the vanishingly small concentration of alumina in the liquid phase.

No other chemical reactions besides 1 and 2 into which the added calcium sulfate may enter can be deduced from the liquid-phase compositions, nor are any known.[3] The chemical effects of reactions 1 and 2 are as follows: (*a*) formation of calcium hydroxide in solution, (*b*) reduction of the pH of the solution (from 13.1 to 12.7 for s-clinker A), and (*c*) sulfoaluminate formation.

It is postulated that one or more of these chemical effects is responsible for the decrease in the rate of hydration of C_3A, and consequently of the retardation of the set, by the small amount of added gypsum.

EFFECT OF CALCIUM HYDROXIDE ON SET

All available evidence shows in short that the action of gypsum in retarding the set concerns solely its formation of calcium hydroxide in the liquid phase according to Equation 1. The primary retarding action of calcium hydroxide will therefore be considered in detail.

That calcium hydroxide or lime tends to retard the set of Portland cement is well established on the basis of widespread observation and has been known for a long time. Candlot in 1890 (*10*) extensively described the retarding action of lime, and both Candlot and Ljamin (*34*) in considering the converse effect showed that substances such as sodium carbonate that react with calcium hydroxide, thus making it unavailable in the setting cement, cause quickening of the set.

The action of lime on pure tricalcium aluminate has also been studied, and its effect in restraining the hydration and the set of this reactive compound observed. Bates (*5*) writes: "... it (lime) very materially modifies the activity of the tricalcium aluminate. If this aluminate in pure condition is mixed with hydrated lime, in amounts not exceeding 10 per cent, and is then gaged with water, a very smooth, plastic paste, which hardens in air quite similarly to Portland cement, is obtained. This action is strikingly different from that of water on the tricalcium aluminate when hydrated lime is not present ... in the latter case a smooth paste was not obtainable, nor one which would harden, on account of the almost instantaneous action of the water." The retardation by slaked lime of the set of tricalcium aluminate has also been described by Phillips (*36*). The link between rate of set and rate of hydration of C_3A is established by conjunction of these results with those of Koyanagi (*21*), according to which the rate of hydration of C_3A in Portland cement is materially decreased by the presence of lime.

TRICALCIUM SILICATE AS RETARDER IN CEMENT

The action of lime on C_3A draws attention to tricalcium silicate (C_3S) as a possible retarder in Portland cement. The C_3S, which exists in two- to tenfold excess over C_3A and is in intimate admixture with it, hydrolyzes according to the equation:

$$\mathrm{3CaO\cdot SiO_2(s)} + X\mathrm{H_2O} = Y\mathrm{CaO\cdot SiO_2\cdot}X\mathrm{H_2O(s)} + (3-Y)\mathrm{Ca(OH)_2} \qquad (3)$$

The composition of the hydrated silicate residue has been variously given as $2CaO\cdot SiO_2\cdot XH_2O$, $3CaO\cdot 2SiO_2\cdot XH_2O$, and $CaO\cdot SiO_2\cdot XH_2O$. Recently Koyanagi (*24*) has concluded in practical agreement with the original conclusion of Le Chatelier (*29*) that the end product is the lowest silicate, $CaO\cdot SiO_2\cdot 2H_2O$. In the early stages of hydrolysis, coefficient Y in Equation 3 appears to be greater than 1 and is probably 2.

The C_3S, though far from being as reactive as C_3A, hydrolyzes at a moderately rapid rate (*7, 32*). Furthermore, it yields a supersaturated solution of lime (*7, 24, 25, 32*). Beckmann (*7*), for example, finds on agitating only 1 gram of C_3S with 50 cc. of water that lime saturation is reached in 10

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[3] A sulfoferrite, analogous to the sulfoaluminate, has not been definitely obtained up to the present. If such a compound does exist, its formation is apparently quite difficult and may be neglected in comparison to sulfoaluminate. In this connection the compound in Portland cement containing most of the iron, $4CaO\cdot Al_2O_3\cdot Fe_2O_3$, reacts with water slowly (*28*) in distinction to the rapid reaction of C_3A.

minutes, and thereafter the concentration continues to increase to a maximum supersaturation of 50 per cent after several hours.

As might be expected from the above facts, C_3S in contact with C_3A has been found to retard the set of the aluminate. Bates and Klein (*6*) state: "The mixture of dicalcium silicate and tricalcium aluminate has the properties of the aluminate . . . (but) . . . The mixture of tricalcium silicate and tricalcium aluminate shows the ability of the former materially to modify the properties of the latter."

Free lime in Portland cement is usually present only in slight amount. As a source of calcium hydroxide, both as regards abundance and maximum concentration in solution, free lime may be neglected against tricalcium silicate.

LIME SATURATION OF THE LIQUID PHASE

In order to examine more closely the primary retarding action of calcium hydroxide, it is desirable to ascertain its actual concentration in the liquid phase. This is at first sight difficult, owing to the interference caused by the presence of alkali and sulfate ions in solution.

However, the difficulties may be surmounted by simple considerations based on theory of solutions. In any solution the geometric mean product of the ion activities (*33*), $(a_{Ca^{++}} \times a^2_{OH^-})^{1/3}$, represents the effective concentration of calcium hydroxide in solution. When the ionic strength (*33*) of the solution is constant and the ion type not too different, the mean product of the ion concentrations $[Ca^{++} \times (OH^-)^2]^{1/3}$ may be taken as a measure of the effective concentration of calcium hydroxide in solution.

In order to compare the calcium hydroxide concentration in the liquid phase with that of a solution of saturated lime, a plot has been made in Figure 2 of the mean ion product against the ionic strength for saturated lime solutions containing different electrolytes. The available data (*41*) pertain to lime-saturated solutions of calcium sulfate, calcium nitrate, and sodium hydroxide. The points for the calcium sulfate and calcium nitrate solutions when plotted logarithmically fall on a straight line. This may be called the "line of lime saturation." The points for the sodium hydroxide solutions fall somewhat irregularly below the line. The difference may be due to the difference in ion valence type, but is probably due at least in part to the apparent lesser accuracy of the sodium hydroxide data.

In Figure 2 there is also plotted the mean ion product against ionic strength for the liquid phase of Portland cements I, II, and III (Table III); s-clinker A and f-clinkers B and C (Table IV); s-clinker A with 2 per cent gypsum addition (Table VI); and t-clinkers A, D, E, and F. The points fall close to and irregularly on either side of the line of lime saturation. It is concluded that the liquid phase of Portland cement and of Portland cement clinker contains calcium hydroxide at an effective concentration approximately equal to that of saturated lime.

While this conclusion refers strictly to the liquid phase 15 minutes after the addition of the mixing water, it may be extended to apply to the liquid phase sometime during mixing or immediately on the completion of mixing because of the observed rapidity of the solution processes.

MECHANISM OF RETARDING ACTION OF CALCIUM HYDROXIDE IN SOLUTION

Explanation of the retarding action of calcium hydroxide in solution is to be sought in its chemical effect on C_3A in relation to the hydration compounds of the aluminate.

In contact with pure water, the hydration of C_3A, presumably after an initial limited hydrolysis, proceeds directly. Two tricalcium hydrates have been described, one $3CaO \cdot Al_2O_3 \cdot 7\text{–}12.5H_2O$ (*3*, *19*, *37*, *42*, *43*) consisting of hexagonal plates, the second a seemingly less common isometric hydrate, $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (*3*, *42*).

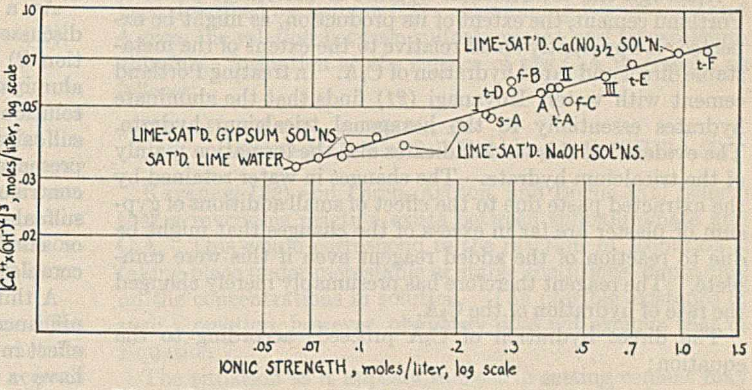

FIGURE 2. MEAN ION PRODUCT *vs.* IONIC STRENGTH FOR SATURATED LIME SOLUTIONS CONTAINING VARIOUS ELECTROLYTES AND FOR LIQUID PHASE

In the presence of calcium hydroxide a hydrated tetracalcium aluminate can be formed. This hydrate was originally obtained by Le Chatelier (*29*) and later by Desch (*12*), Kühl and Thüring (*26*), Lafuma (*28*), Wells (*43*), and Forsén (*15*). The tetracalcium aluminate has been described and its stability regions have been defined in the recent extended phase-rule studies of Assarsson (*3*). The tetracalcium hydrate, $4CaO \cdot Al_2O_3 \cdot 12\text{–}13.5H_2O$, like the hexagonal tricalcium hydrate, forms hexagonal plates and possesses nearly the same optical constants (*3*, *15*, *43*).

The composition of the stable hydrated aluminate depends on the composition of the solution with which the hydrate is in contact. The liquid phase of Portland cement, as has been seen, is approximately saturated with lime. The concentration of alumina in the liquid phase is extremely low, usually much less than 0.025 mg. per cc. These concentrations of lime and alumina are those in contact with which the tetracalcium aluminate alone is stable. It is concluded therefore that in Portland cement or cement clinker paste, hydrated tetracalcium aluminate is the stable phase. In other words, C_3A may react with calcium hydroxide in solution to form the tetracalcium compound.

It is not to be supposed however that reaction to form the C_4A hydrate in the cement paste takes place readily. Formation of the tetracalcium compound is known to proceed ordinarily only in the presence of high concentrations of calcium hydroxide. The approximate lime saturation of the liquid phase of quick setting f- and s-clinkers (Figure 2), in which tricalcium aluminate is reacting rapidly, confirms the necessity of a high concentration of calcium hydroxide for interaction with the aluminate in cement.

The exact concentration of calcium hydroxide at which, practically speaking, reaction with C_3A will take place, will depend on the particular activity of the C_3A. If the activity is relatively low, the concentration of calcium hydroxide for interaction will have to be somewhat above lime saturation; if the activity of the C_3A is relatively high, the concentration of calcium hydroxide at which reaction may take place with practicable speed can be somewhat less than lime saturation. It will be convenient to designate that fraction of the calcium hydroxide in solution which may combine with C_3A as reactive calcium hydroxide or $Ca(OH)'_2$. In other words, $Ca(OH)'_2$ is that fraction of all the calcium hydroxide in solution which is in excess of a certain threshold concentration in the neighborhood of lime saturation.

The reaction to form the tetracalcium hydrate, involving reactive calcium hydroxide and tricalcium aluminate, may be written:

$$Ca(OH)_2' + 3CaO{\cdot}Al_2O_3(s) = 4CaO{\cdot}Al_2O_3{\cdot}XH_2O(s) \quad (4)$$

Although the tetracalcium hydrate is the stable phase in Portland cement, the extent of its production, as might be expected, is apparently small relative to the extent of the metastable direct and rapid hydration of C_3A. In treating Portland cement with water, Koyanagi (*21*) finds that the aluminate hydrates essentially to the hexagonal tricalcium hydrate. The evidence of this work indicates also the formation mainly of the tricalcium hydrate. The changes in water retained by the extracted paste due to the effect of small additions of gypsum or plaster are far in excess of the changes that might be due to reaction of the added reagent even if this were complete. The reagent therefore has presumably merely changed the rate of hydration of the C_3A.

The direct hydration of C_3A proceeds according to the equation:

$$3CaO{\cdot}Al_2O_3(s) + XH_2O = 3CaO{\cdot}Al_2O_3{\cdot}XH_2O(s) \quad (5)$$

The action of calcium hydroxide in restraining the direct hydration of C_3A described by Equation 5, and consequently its action in retarding the set, may be explained chemically by its formation of the stable tetracalcium hydrate according to Equation 4. The formation of the tetra compound by reaction in the liquid phase can barely take place owing to the vanishingly small amount of alumina in solution. It is believed therefore, as indicated by Equation 4, that its formation in Portland cement takes place mainly at the surface of the crystals of C_3A. The hydration of the residual C_3A to the metastable tricalcium hydrate, whether by way of solution or directly, presumably is slowed down by the surface formation of the stable and insoluble tetracalcium aluminate.

The amount of tetracalcium aluminate that may be effective in causing slow set can be deduced from the results of Tables IV and VI. From the amount of new sulfate and calcium ions that have appeared in solution on the addition of 2 per cent gypsum to s-clinker A, it is calculated that 0.83 mg. of calcium hydroxide per gram of clinker has been formed in the approximately lime-saturated solution. Even if all this $Ca(OH)_2'$ united with the C_3A, only one or two score molecular layers of C_4A will have formed. The amount of water that might be fixed by this amount of the tetra compound is only about one-twentieth of the actual decrease, which decrease may be assigned to a decreased rate of hydration of the C_3A.

SLAKED LIME AND TRICALCIUM SILICATES AS RETARDERS

The ability, essentially, of reactive calcium hydroxide alone to form hydrated tetracalcium aluminate places a restriction on the use of ordinary slaked lime as a retarder of the set of cement. For example, if the particular activity of C_3A is such that it can react with calcium hydroxide only when the latter is in slightly supersaturated solution, then obviously slaked lime in itself will have no direct retarding effect. On the other hand, a direct effect will exist if the threshold concentration for reaction is just below lime saturation. Slaked lime will hasten the condition of lime saturation of the liquid phase, but this effect, though it may be important, is secondary compared to that of direct reaction.

Application of these considerations may be made to explain the apparently perplexing fact that slaked lime has a retarding effect when added to a clinker containing gypsum, but for the same clinker may have little or no effect in the absence of gypsum (*11*, *35*). When using gypsum alone, a portion of the calcium hydroxide formed in solution by the gypsum may not be available for direct reaction since it might function merely to increase the calcium hydroxide concentration up to the threshold value required for reaction with C_3A. In the presence of slaked lime the threshold concentration is more rapidly reached, even though it may not be exceeded; virtually all of the calcium hydroxide formed by the gypsum may now be reactive, and so complete retardation is effected.

As a second consideration, there is evidence, which is discussed later, that reaction to form sulfoaluminate (Equation 2) is competitive with reaction to form tetracalcium aluminate (Equation 4). Gypsum which has entered into a solution in which no $Ca(OH)_2'$ is present will tend to form sulfoaluminate and thus per se may speed the set. In the presence of $Ca(OH)_2'$, the earlier appearance of which is contributed to, if not added to, by the addition of slaked lime, sulfoaluminate formation by the added gypsum is decreased or eliminated. The gypsum may now fulfil to practical completion its function of supplying $Ca(OH)_2'$.

A third consideration appears to be of generally lesser significance. The slaked lime in addition to its major positive effect in contributing calcium hydroxide may conceivably also have a slight negative effect by presenting precipitation nuclei for $Ca(OH)_2'$. It appears from the observations of Koyanagi (*23*) that crystallization of calcium hydroxide is delayed by calcium sulfate in solution. Therefore, added gypsum should have the tendency to overcome any negative precipitation effect of the slaked lime.

In the present work the retarding behavior of saturated lime water, analogous to the behavior of slaked lime in the presence and absence of gypsum, was found to depend on the state of seasoning of the clinker. The results are shown in Table VII. For the quick-setting f-clinker, the effect of the lime water, as of added gypsum, is practically negligible. With the partly seasoned m-clinker, definite retardation is obtained. For a t-clinker, the effect of lime water is again negligible or slightly negative. For the t-clinkers, as will be discussed more fully in a subsequent paper, $Ca(OH)_2'$ appears to be abundant. The contribution of calcium hydroxide by added reagent is presumably negligible in view of the abundant $Ca(OH)_2'$ already present. Therefore the effect in retarding the set is negligible, as for added gypsum and as for lime water. In the latter case, furthermore, with calcium sulfate initially absent in the lime-saturated solution, precipitation nuclei might be formed with crystallization of some of the abundant $Ca(OH)_2'$. This would account for the slight negative effect of saturated lime water on the set of the t-clinkers.

TABLE VII. EFFECT OF SATURATED LIME WATER ON TIME OF SET

CLINKER	TIME OF SET: MIXING WATER	INITIAL Hr.	INITIAL Min.	FINAL Hr.	FINAL Min.	CLINKER CONTROL: MIXING WATER	TIME OF SET: Initial Hr.	Initial Min.	Final Hr.	Final Min.
	%					%				
f-Clinker B	22.0	0	15	2	30	22.0	0	10	2	00
f-Clinker C	32.0	0	35	...		34.0	0	50	...	
m-Clinker A	20.9	2	15	5	30	20.9	1	15	4	00
m-Clinker A	20.9	2	53	6	00	20.9	2	26	5	00
t-Clinker A	19.9	2	45	6	30	19.9	2	55	6	30
t-Clinker D	20.8	2	27	8	00	20.8	2	47	8	30
t-Clinker E[a]	23.5	1	13	4	30	23.5	1	02	4	30
t-Clinker F	19.9	2	16	5	00	19.9	2	31	5	00

[a] Partially reverted in set on storage.

In contrast to slaked lime, tricalcium silicate (the properties of which have been described above) continues to form calcium hydroxide even in supersaturated solution. C_3S is therefore a potent source of $Ca(OH)_2'$ and, based on this and other evidence already cited, is regarded as a fundamental retarding agent in Portland cement.

ALKALIES AND SET

The alkali compounds in Portland cement are probably simple or multiple aluminates, silicates, carbonates, or sulfates. That they do not exist as oxide or hydroxide in general is shown by the fact that no phenolphthalein alkalinity is obtained on shaking a cement or clinker with 95 per cent alcohol (cf. also citation *30*).

Alkali aluminate, silicate, and carbonate solutions react with calcium hydroxide to give alkali hydroxide saturated with lime (*17*). The equation is:

$$2\left\{\begin{matrix}\mathrm{KA}\\ \mathrm{Na}\end{matrix}\right\} + \mathrm{Ca(OH)_2} = \mathrm{CaA}\downarrow + 2\left\{\begin{matrix}\mathrm{KOH}\\ \mathrm{Na}\end{matrix}\right\} \qquad (6)$$

The alkali compounds in cement, dissolving rapidly, are, in accordance with Equation 6, converted into hydroxide at the expense of calcium hydroxide which reacts to form the insoluble calcium compound. With alkali sulfate the reaction is much less complete than with the other alkali compounds. Since calcium hydroxide in solution functions as the ultimate retarder in Portland cement, the alkalies, by removing the calcium hydroxide, appear to be detrimental as regards the set.

In restoring the calcium hydroxide by double decomposition with the secondary alkali hydroxide, added gypsum functions so as partially to overcome the detrimental effect as regards set of the alkali compounds in the clinker.

It should be expected that all soluble calcium salts would act as retarder, since they may form $Ca(OH)'_2$ like gypsum. This expectation is found to be fulfilled. Candlot (*9*) has observed that, besides calcium sulfate, calcium chloride and nitrate are retarders, and Forsén (*14*) has extended the list of calcium salt retarders to include the nitrite, chlorate, iodide, and bromide. Just as for calcium sulfate, restrictions may exist with respect to the upper limit of concentration of some of these salts owing to the possible formation with tricalcium aluminate of compounds (*14*) analogous to sulfoaluminate.

EFFECT OF SULFOALUMINATE FORMATION ON SET

Besides the formation of $Ca(OH)'_2$, two other chemical effects of added gypsum must be considered—namely, sulfoaluminate formation and reduction of the pH of the liquid phase.

It probably is impossible to correlate the changes in set with an estimate of sulfoaluminate formation based upon observation and estimation of the amount of sulfoaluminate crystals in the normal cement paste. In the first place, the amount of gypsum added is slight, and only a fraction of this (which may be zero) normally reacts with the clinker to form sulfoaluminate. Furthermore, this compound frequently occurs as minute needles or "bacilli." The determination of these in slight amounts in the presence of relatively large amounts of diluent material will be practically impossible.

However, the degree of sulfoaluminate formation may be inferred from the amount of sulfate ion in solution in the liquid phase. A relative decrease in sulfate ion, or the absence of sulfate ion in the presence of added gypsum, will point to the formation of sulfoaluminate.

Candlot (*10*), who discovered the sulfoaluminate compound, examined the liquid phase in relation to the time of set. He came to the following conclusions: (*a*) The disappearance of sulfate ion is more rapid the greater the amount of aluminate; (*b*) sulfoaluminate formation, inferred from the change in sulfate-ion concentration, is associated with quickened set; and (*c*) the presence of lime prevents the formation of sulfoaluminate. It is remarkable that these conclusions of Candlot have been almost completely forgotten in the later cement literature. In fact, the hypothesis of sulfoaluminate formation as a cause of slow set has at times been made without reference to experimental evidence (cf. citation *14*). No retardation of the set of C_3A by gypsum or plaster in amounts up to 20 per cent was observed by Phillips (*36*).

Conclusion *c* of Candlot suggests that sulfoaluminate formation in Portland cement depends on the concentration of calcium hydroxide and calcium sulfate in the liquid phase. This is substantially the conclusion that has been reached in the present work. If the reactions to form sulfoaluminate (Equation 2) and tetracalcium aluminate (Equation 4) at the surface of C_3A are reversible, a reversible reaction involving C_4A and sulfoaluminate should obtain. Such a reaction has been described by Lafuma (*28*). Combining Equations 2 and 4 gives the relation between sulfoaluminate and tetracalcium aluminate formation at the surface of the C_3A in cement as follows:

$$4CaO \cdot Al_2O_3 \cdot XH_2O(s) + 3CaSO_4 \rightleftharpoons 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot XH_2O(s) + Ca(OH)'_2 \qquad (7)$$

Koyanagi (*22*) and Lerch, Ashton, and Bogue (*31*) believe that a reversible reaction exists between sulfoaluminate and C_3A. This would correspond to the reaction of Equation 2 taking place under metastable or stable conditions, depending on the concentrations in solution. The possible existence of such a reaction, however, obviously does not exclude that of Equation 7.

The situation as it appears to exist in setting cement may be simply summarized in terms of Equations 2, 4, and 7 as follows: If in the liquid phase reactive calcium hydroxide is rapidly generated and is maintained in sufficient abundance, tetracalcium aluminate will form in preference to sulfoaluminate. Conversely, if insufficient $Ca(OH)'_2$ is present, sulfoaluminate will tend to form. A deficiency of $Ca(OH)'_2$ results, however, in quick set. Therefore, pronounced sulfoaluminate formation, indicated by the absence of sulfate ion, accompanies quick set as observed throughout in this work.

Formation of sulfoaluminate may take place by reaction of calcium sulfate with C_3A (Equation 2), but also with $C_4A \cdot XH_2O$ (Equation 7). Therefore, besides being indicative of the absence of sufficient $Ca(OH)'_2$, sulfoaluminate formation apparently may in itself cause quickened set since it may take place, at least in part, by decomposition of a previously formed protective tetracalcium aluminate.

In order to ascertain the existence of such an accelerating effect on the set, sulfoaluminate may be selectively caused to form by increasing the initial concentration of calcium sulfate in the liquid phase. A high concentration of calcium sulfate may be obtained either by adding a small amount of the more soluble plaster, or by means of saturated solutions of gypsum or plaster.

With saturated gypsum or plaster water, though the amount of calcium sulfate thus added was only 0.04 and 0.20 per cent, respectively, a marked quick set of m-clinker A was induced. This is seen in Table VIII, in which is given also the liquid-phase composition for the m-clinker and for the same clinker gaged with saturated gypsum water. By comparison, it is found that 0.027 mg. of calcium sulfate per gram of clinker has been fixed when using the gypsum water over that for the straight clinker.

TABLE VIII. EFFECT OF CALCIUM SULFATE IN HIGH INITIAL CONCENTRATION ON TIME OF SET OF m-CLINKER A

(20.9% mixing water)

REAGENT	TIME OF SET Initial		TIME OF SET Final		WATER RETAINED	OH^-	$\frac{1}{2}SO_4^{--}$
	Hr.	*Min.*	*Hr.*	*Min.*	*Cc./100 g.*	*M. eq./cc.*	
None (control)	2	26	5	00	13.9	0.176	0.0748
Satd. gypsum water	0	43	3	00	14.1	0.172	0.0884
Satd. plaster water	0	04	2	30	..	...	....

If this fixation, assumed to be due to sulfoaluminate formation, had merely had a neutral effect, then no change in set would have been observed; in fact, a retarded set should have resulted since some of the calcium sulfate would react with alkali to give $Ca(OH)'_2$. The quickening of the set, however, makes it appear that in Portland cement sulfoaluminate formation in itself may occasion an acceleration of the set.

Observations of the effect of small amounts of solid gypsum and plaster throw further light on this question. With s-clinker A (Table IX), 1 per cent of gypsum changed the set from quick to slow; 1 per cent of plaster gave at first plasticity and then, on continued working, flash set with an evolution of heat. The water retained by the flash-setting cement was more than 20 per cent greater than for the same clinker with added gypsum and about equal to that for the straight clinker. As regards the liquid-phase composition, the sulfate ion with the gypsum addition is high; with the plaster addition the sulfate ion is practically nil.

TABLE IX. EFFECT OF PLASTER ON TIME OF SET OF s-CLINKER A

REAGENT	SET	MIXING WATER	WATER RETAINED	OH^-	$^1/_2\ SO_4^{--}$	$^1/_2\ Ca^{++}$	Al_2O_3
		%	*Cc./100 g.*	*M. eq./cc.*			*Mg./cc.*
None	Quick	30	18.3	0.232	0.006	0.0036	0.0060
1% gypsum	Slow	22	14.3	0.115	0.155	0.0320	0.0015
1% plaster	Flash	25	18.0	0.260	0.007	0.0018	0.0090

The difference in the action of gypsum and plaster on the s-clinker is interpreted as follows: The initial plasticity with 1 per cent plaster addition corresponds to the formation by the plaster of $Ca(OH)'_2$ which reacted with the C_3A to give the protective C_4A hydrate. As the mixing proceeded, solution of the plaster slowed down considerably. The C_3S alone was unable to form sufficient $Ca(OH)'_2$ against the loss of $Ca(OH)'_2$ by reaction with dissolving alkali compounds and with C_3A to prevent the calcium sulfate, left in solution at a high concentration, from reacting. Sulfoaluminate formation took place, and a rapid hydration of the C_3A was induced with evolution of heat. The sudden and pronounced nature of this effect is in agreement with the hypothesis that the sulfoaluminate formation has taken place at the expense of the molecular layers of C_4A hydrate, decomposing them in accordance with Equation 7 and destroying their protective effect.

With the $Ca(OH)'_2$ that had been formed by the plaster and that had reacted to give C_4A now seemingly unavailable for retardation, sulfoaluminate formation was able to proceed to completion leaving a solution practically free of sulfate ion as for the straight clinker.

With 1 per cent gypsum added to the s-clinker, the result was different because of the lower calcium sulfate concentration on saturation than with 1 per cent plaster. Sulfoaluminate formation therefore did not take place when gypsum saturation had been reached, and the production of $Ca(OH)'_2$ by C_3S was sufficient to prevent sulfoaluminate formation and to sustain with additional $Ca(OH)'_2$ the formation of $Ca(OH)'_2$ by the gypsum, leading to a complete retardation of the set.

As seasoning of the clinker proceeds, the accelerating effect of a high initial concentration of calcium sulfate tends to vanish. For example, the flash set noticed with only 1 per cent plaster when added to s-clinker A, has completely disappeared for m-clinker A. In fact, the added solid plaster has now produced a marked retardation of the set.

Similarly the accelerating effect of plaster water on m-clinker A has practically vanished for t-clinker A. This is shown in Table X together with similar results for some other t-clinkers. An attempt to interpret in detail these effects of seasoning will be made in a later paper. It may be stated, however, that they are explained by an increased formation of $Ca(OH)'_2$ in the liquid phase of the seasoned clinker. The formation of sulfoaluminate is thereby curtailed or eliminated in accordance with Equation 7, and the calcium sulfate may react freely to form $Ca(OH)'_2$ and thus help retard the set.

EFFECT OF REDUCTION OF pH ON THE SET

In considering the final effect of added gypsum, slight amounts of acid, less than that required to reduce the pH to the extent effected by gypsum, were added to the m-clinker A. Table XI shows that the addition of a slight amount of acid to the slow-setting m-clinker has greatly accelerated the set.

TABLE X. EFFECT OF SATURATED PLASTER WATER ON TIME OF SET OF t-CLINKERS

CLINKER	MIXING WATER	TIME OF SET: INITIAL		FINAL		CLINKER CONTROL WITHOUT ADDED REAGENT: Initial		Final	
	%	*Hr.*	*Min.*	*Hr.*	*Min.*	*Hr.*	*Min.*	*Hr.*	*Min.*
A	19.9	2	37	6	30	2	55	6	30
D	20.8	2	48	6	30	2	47	8	30
E	23.5	2	20	6	30	2	08	6	15
F	19.9	1	58	4	00	1	50	4	30

TABLE XI. EFFECT OF DILUTE ACID AND BASE, AND OF GYPSUM, ON TIME OF SET OF m-CLINKER A

(20.9 per cent mixing water)

REAGENT	TIME OF SET: INITIAL		FINAL		CLINKER CONTROL WITHOUT ADDED REAGENT: Initial		Final	
	Hr.	*Min.*	*Hr.*	*Min.*	*Hr.*	*Min.*	*Hr.*	*Min.*
HCl solution (0.037 *N*)	0	24	3	00	1	15	4	00
Boric acid powder (0.20% by wt.)	0	23	3	00	1	15	4	00
Acetic acid soln. (0.037 *N*)	0	14	3	00	1	53	6	00
NaOH soln. (0.075 *N*)	2	12	5	00	1	35	4	30
Gypsum powder (1% by wt.)	1	53	5	00	0	50	3	30

Dilute sodium hydroxide solution (carbonate-free), just as 1 per cent gypsum, was found to retard the set (Table XI) contrary to the effect of the acids.

The addition of slight amounts of acid or of alkali was found to have a negligible effect on the set of the slow-setting t-clinker (Table XII), just as previously noted for lime water and plaster water.

Reduction of the pH, in so far as it implies the loss of hydroxyl ions in solution and consequent reduction in the effective concentration of $Ca(OH)'_2$, as measured by the mean ion product $[Ca^{++} \times (OH^-)^2]^{1/3}$, might be expected to accelerate the set. For t-clinkers the effect is apparently negligible in comparison to the large amount of $Ca(OH)'_2$ that appears to be available.

TABLE XII. EFFECT OF DILUTE ACID AND BASE ON TIME OF SET OF t-CLINKERS

CLINKER	REAGENT	MIXING WATER	TIME OF SET: INITIAL		FINAL		CLINKER CONTROL WITHOUT ADDED REAGENT: Initial		Final	
		%	*Hr.*	*Min.*	*Hr.*	*Min.*	*Hr.*	*Min.*	*Hr.*	*Min.*
A	Acetic acid soln. (0.037 *N*)	19.9	2	50	6	30	2	55	6	30
A	HCl soln. (0.037 *N*)	19.9	2	46	6	30	2	55	6	30
A	NaOH soln. (0.075 *N*)	19.9	3	00	6	30	2	55	6	30
D	Acetic acid soln. (0.037 *N*)	20.8	2	37	6	00	2	47	8	30

CONCLUSIONS

Gypsum added to a clinker may, on dissolving, react with alkali in the liquid phase (*a*) to form calcium hydroxide in solution and (*b*) to lower the pH. It may also react (*c*) to form calcium sulfoaluminate.

Calcium hydroxide delays the hydration and set of tricalcium aluminate and retards the set of Portland cement. The retardation of the set by gypsum is interpreted as being due to its formation of calcium hydroxide in solution. The other two reaction effects of gypsum produce no retardation of the set.

The mechanism of the retarding action of calcium hydroxide is examined in detail. It is shown experimentally that the liquid phase is approximately saturated with lime a few minutes after the addition of the mixing water. The concentration of alumina is vanishingly small, usually much less than 0.025 mg. of alumina per cc. In a solution of this composition, hydrated tetracalcium aluminate is the stable phase.

Formation of the stable tetracalcium aluminate may take place by compound formation between calcium hydroxide in solution and tricalcium aluminate. However, this reaction appears to proceed usually only at high concentrations of calcium hydroxide. The approximate lime saturation of the liquid phase, even of quick-setting clinkers in which the aluminate is reacting rapidly, shows that only calcium hydroxide above a threshold value of concentration which is in the neighborhood of lime saturation may react with practicable speed to form the tetracalcium aluminate in setting cement. That fraction above the threshold value of concentration for interaction has been designated "reactive calcium hydroxide."

The retarding action of calcium hydroxide in solution is explained by its formation of the stable and insoluble hydrated tetracalcium aluminate at the surface of the tricalcium aluminate, and hindrance by the tetracalcium compound of metastable direct hydration of the aluminate to the tricalcium hydrate.

Tricalcium silicate hydrolyzes with moderate rapidity to give calcium hydroxide. The hydrolysis continues even in supersaturated solution. Tricalcium silicate is therefore a potent source of reactive calcium hydroxide. The silicate is known to retard the set of tricalcium aluminate and is regarded as a fundamental retarding agent in Portland cement. Gypsum and other calcium compounds may also form reactive calcium hydroxide and thus supplement the action of tricalcium silicate. Slaked lime is a restricted source of reactive calcium hydroxide, and therefore its action as a retarder is limited.

The alkali compounds in cement dissolve rapidly and in solution react with calcium hydroxide to precipitate the insoluble calcium salt. Since the alkali compounds remove calcium hydroxide, they appear to be detrimental as regards the set.

The relative extent of sulfoaluminate and tetracalcium aluminate formation depends on the concentration of calcium hydroxide and calcium sulfate in solution. When sufficient reactive calcium hydroxide is not present, sulfoaluminate appears to be formed rapidly in setting cement. Since the absence of sufficient reactive calcium hydroxide is the condition under which quick set takes place, extensive sulfoaluminate formation accompanies quick set as observed throughout. There is evidence that, besides being indicative of the absence of sufficient reactive calcium hydroxide, formation of sulfoaluminate may be an indirect cause of quickened set. The reason is that, besides formation by reaction between calcium sulfate and tricalcium aluminate the sulfoaluminate may apparently be formed also by reaction between calcium sulfate and tetracalcium aluminate. Any previously formed protective tetracalcium compound may in this way be decomposed and the hydration of the tricalcium aluminate indirectly accelerated.

ACKNOWLEDGMENT

Thanks are due E. P. Partridge for constructive suggestions relating to the presentation, and to A. A. Berk for the analyses of the clinkers (except for the free lime).

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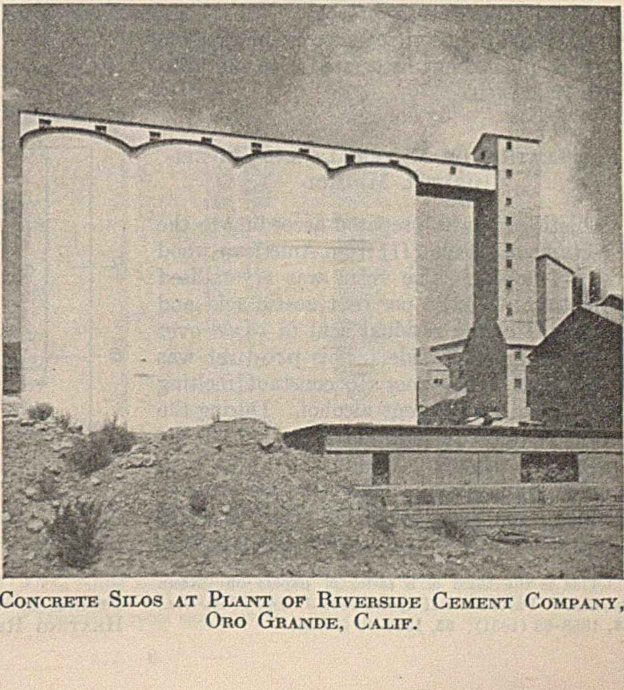

CONCRETE SILOS AT PLANT OF RIVERSIDE CEMENT COMPANY, ORO GRANDE, CALIF.

Pyrolysis of Abietic Acid[1]

W. A. LA LANDE, JR., University of Pennsylvania, Philadelphia, Pa.

l-Abietic acid obtained from American wood rosin by Steele's method is heated for 1-, 3.5-, 8-, and 15-hour periods at 175°, 230°, 275°, 330°, and 385° C. The mechanism of decarboxylation and water production is deduced from the results obtained from the determination of carbon dioxide, carbon monoxide, and water in the gaseous decomposition products. At the lower temperatures anhydride formation is the predominating reaction, although it proceeds concurrently at all the temperatures studied with two different modes of decarboxylation. The isomerization of the acid as evidenced by the change in rotatory power is also discussed.

THE industrial utilization of rosin includes processes in which the rosin is heated at various temperatures up to the distillation point at atmospheric pressures—e. g., in the preparation of metallic rosinates and rosin esters, the blending of rosin with synthetic resins, the purification of rosin by vacuum distillation, and the production of rosin oil. Since abietic acid is remarkably labile at temperatures above its melting point, the problem of the effect of temperature on rosin (and abietic acid) is of obvious importance in technical operations, where the acid function or the characteristic physical properties of rosin are of primary interest, and in the study of the chemistry of the resin acids. The progressive changes which occur as the acid is heated involve, as the temperature rises to the distillation point: isomerization, evidenced by the sharp decrease in melting point and change in optical rotatory power without change in acid or saponification number; loss of water; decarboxylation, with loss of carbon dioxide and monoxide; and finally complex decomposition yielding a large variety of open-chain and ring compounds. Although a considerable amount of data on both phases of the pyrolysis of the acid has accumulated from both industrial research (*5*) and purely scientific investigation (*8*), the information on the predistillation phenomena is especially difficult to correlate because of the unsystematic variation in the experimental conditions and the difference in properties of the rosins or acids used. The present article is offered as a systematic and more complete study of the decarboxylation, dehydration, and isomerization of *l*-abietic acid from American wood rosin between its melting point and distillation temperature during arbitrarily chosen time and temperature intervals. All the experiments were carried out in pure nitrogen to avoid the more complex phenomena associated with the presence of oxygen.

PREPARATION OF MATERIALS AND EXPERIMENTAL METHOD

Abietic acid was prepared according to the directions of Steele (*11*) from American wood rosin (I grade). The rosin was crystallized three times from 98 per cent acetic acid and then freed of the residual acid *in vacuo* over solid sodium hydroxide. This product was crystallized three times (to constant melting point) from 95 per cent alcohol. During the crystallizations the solutions were kept in the absence of oxygen. The material was then dried over anhydrous calcium chloride *in vacuo*. Enough rosin was processed to yield 800 grams of purified acid. Fourteen-gram portions were quickly transferred to tubes which were immediately evacuated and sealed off. In this way about fifty samples were prepared. These were used as required over a period of 9 months. The physical properties were as follows: melting point 158° C., with preliminary softening if the bath was heated from room temperature; acid and saponification number, 185.4; α_D^{20} −75.5 for a 5 per cent solution in ethyl alcohol. No changes were noted in the color, melting point, or rotatory power of the abietic acid thus preserved during the course of the experiments.

Tank nitrogen was passed through alkaline pyrogallol solution, then over solid sodium hydroxide and fused zinc chloride, and finally over hot copper.

Preliminary experiments indicated that fine temperature control was unnecessary. Instead of a more elaborate high-temperature thermostat, a thermometer calibration tank (Figure 1) with both automatic and manual control was used as the heater:

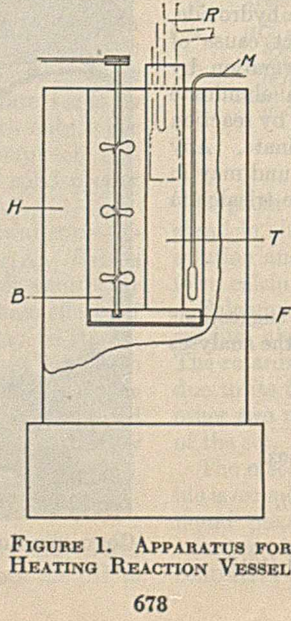

FIGURE 1. APPARATUS FOR HEATING REACTION VESSEL

The tube, *T*, was made from a 14-inch (35.6-cm.) length of 2.25-inch (5.7-cm.) pipe. This pipe was welded, off-center, to the flange blank, *F*, which was machined to fit the bath tank, *B*. *T*, which was kept open at the top, thus served as an air bath and prevented contact of the contents of the reaction tube *R*, with the mixed nitrate bath in case of breakage. By using the proper setting on the manual control, it was possible to obtain a temperature range throughout *T* in which the desired temperature could be closely approximated by slightly raising or lowering *R*. *M*, a gas thermometer, was connected to the automatic control. The space, *H*, contained the heating elements and insulation. The reaction vessel (*R* in Figure 1) is shown in more detail in Figure 2. The thermometer was placed in the neck, *D*. The lower part of the vessel was heated to 400° C. and allowed to cool with nitrogen passing through it before the abietic acid was added through the neck, *A*. *S*, bearing the mercury seal, the stirrer, and the nitrogen delivery tube, *N*, was then quickly replaced with the nitrogen still passing through. The apparatus was thoroughly purged with the gas before being placed in the heater. As soon as the vessel had been transferred to the heater, the flow of nitrogen was adjusted to approximate the rate of flow of gas in a carbon-hydrogen determination. The weighed water and carbon dioxide absorbers and the carbon monoxide apparatus were immediately connected to the tube, *C*, which was lightly plugged with cotton along its length to retain the sublimate which proved troublesome during some of the runs. The stirrer was started and maintained at about 800 r. p. m. as soon as the abietic acid had melted. When a run was completed, the rosin was allowed to cool in the stream of nitrogen, the lower half of *B* was then cut by means of a hot wire, and the product was immediately examined. All the temperatures were constant within ±1.5° C.

The acid and saponification numbers were determined by the usual methods, using 0.2 *N* base for the direct titration of the acid dissolved in warm alcohol, and

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[1] This is the third of a series of papers on "Resin Studies." Parts I and II appeared in *J. Am. Chem. Soc.*, **53**, 1858–68 (1931); **55**, 1536–40 (1933).

0.5 N alcoholic potassium hydroxide for the saponification (2-hour refluxing); for the back titration 0.2 N acid was used.

Dehydrite and ascarite were used in the water and carbon dioxide absorbers, respectively. The weight of water corresponding to the volume of aqueous distillate (estimated to 0.001 ml.) which collected in the graduated condenser tube, G (Figure 2), was added to that retained by the water absorber. The carbon monoxide was determined by a modification of the iodine pentoxide method (*4*). There was no increase in the weight of the water and carbon dioxide absorbers after a 15-hour blank run, but it was necessary to apply a correction factor to the results from the carbon monoxide determinations.

In determining the melting points, the samples, in 1.5-mm. tubes, were heated from room temperature.

MECHANISM OF DECARBOXYLATION OF ABIETIC ACID

Since the saponification number measures the total acidity of a rosin—i. e., unchanged acid plus potentially acid derivatives (e. g., anhydride)—the change in this value is a reliable index of the rate and degree of the destruction of the acid function. The maximum possible acidity of the residue from the thermal decomposition of such material can be calculated from the weight of carbon dioxide and carbon monoxide eliminated, since the only source of these gases is the carboxyl group of the acid or its derivatives. During the complete series at 175° C. and the two shorter periods of heating at 230° there was no evidence of decarboxylation (Table I); however, during the 8- and 15-hour periods at the latter temperature, a slight decrease in the theoretical maximum acidity was noted (Tables I and II), and carbon dioxide but no carbon monoxide was detected. Beginning at 275° C. carbon monoxide appeared in the evolved gases and increased sharply in amount with rising temperature. Thus at 275° the mole ratio of carbon monoxide to carbon dioxide was 1 to 7.2, as compared with 1 to 3.9 at 330° C. and 1 to 0.59 at 385°. The formation of carbon dioxide was undoubtedly due, for the greater part, to direct decarboxylation—i. e., the reaction

$$C_{19}H_{29}COOH \longrightarrow C_{19}H_{30} + CO_2 \qquad (1)$$

while the production of carbon monoxide resulted, in largest measure, from the reaction

$$C_{19}H_{29}COOH \longrightarrow C_{19}H_{28} + CO + H_2O \qquad (2)$$

In Table II the maximum acidity of the residues calculated from the loss in carbon dioxide and carbon monoxide (based only on reactions 1 and 2) are compared with the analytically determined values. The close agreement confirms the predominance of these reactions during decarboxylation. The maximum acidities were calculated from the formula:

$$\text{Maximum acid number} = \frac{185.5(a - b)}{a}$$

where 185.5 = acid number of pure abietic acid
a = CO_2 content of the charge, grams
b = weight of CO_2 evolved + weight of CO × 1.571
1.571 = factor $CO \longrightarrow CO_2$

The formation of carbon dioxide and carbon monoxide during the pyrolysis of abietic anhydride must also be considered in this connection. The anhydride content of the residues increased slowly, reaching a maximum during the 8-hour period at 330°, and subsequently decomposing gradually and incompletely (Table I, Figure 3). Of the two possible paths of decomposition of the anhydride in which carbon monoxide and/or carbon dioxide are produced, the reaction

$$(C_{19}H_{29}CO)_2O \longrightarrow (C_{19}H_{29})_2 \text{ [or } C_{19}H_{28} + C_{19}H_{30}] + CO + CO_2 \qquad (3)$$

appears the more probable since it is supported by the analytical data, while the reaction

$$(C_{19}H_{29}CO)_2O \longrightarrow (C_{19}H_{29})_2CO + CO_2 \qquad (4)$$

is unlikely since the residues gave negative tests with reagents for the carbonyl group. Since it may be assumed that up to and throughout the series at 330° the decomposition of the anhydride was practically nil (Table I, Figure 3), the production of carbon monoxide and carbon dioxide up to this point was due solely to reactions 1 and 2. Subsequently, however, both of these gases were also formed, in relatively small and equivalent amounts, from reaction 3, which was only starting when reactions 1 and 2 were proceeding at their maximum rates. The major part of the carbon dioxide and carbon monoxide produced during the pyrolysis was thus due to these latter reactions.

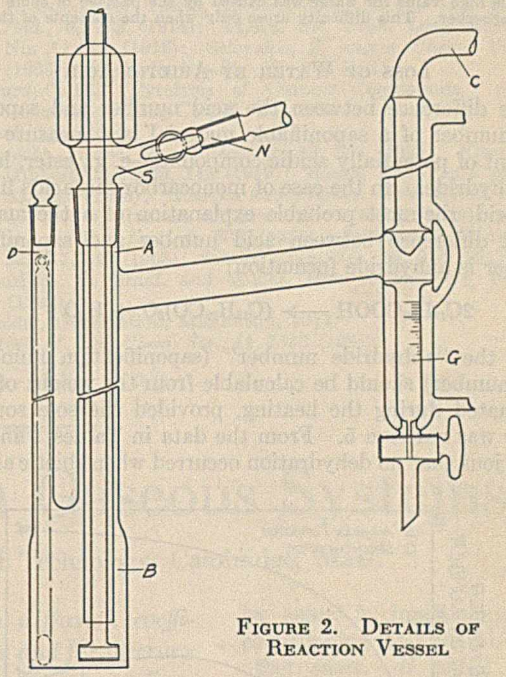


FIGURE 2. DETAILS OF REACTION VESSEL

TABLE I. CHANGE IN MELTING POINT, ACID NUMBER, SAPONIFICATION NUMBER, AND OPTICAL ROTATION OF ABIETIC ACID AT VARIOUS TEMPERATURES

TEMP.	TIME	M. P.[a]	ACID No.	SAPONIFICATION No.	OPTICAL ROTATION[b]
° C.	Hours	° C.			
175	1	158[c]	185.4	185.4	−69.8
	3.5	107; 158	185.4	185.5	−65.6
	8	107; 158	185.4	185.4	−56.0
	15	107; 158	185.5	185.5	−53.3
230	1	112; 150–4	185.5	185.4	−40.0
	3.5	112; 147	182.4	185.2	−38.0
	8	110; 147	177.5	185.0	−34.3
	15	110; 145	172.0	185.0	−31.6
275	1	109; 151	175.0	185.5	−28.5
	3.5	108; 147	162.0	182.0	−18.0
	8	108; 148	146.6	177.1	− 8.6
	15	96	118.3	164.0	+ 8.7
330	1	78; 137	138.6	149.0	+21.7
	3.5	63	100.0	141.5	+47.2
	8	d	65.8	136.0	+57.1
	15	d	59.8	127.2	+51.6
385[e]	1	d	85.0	134.3	+39.3
	3.5	d	48.4	81.0	+38.0
	8	f	17.7	55.0	+38.5
	15	f	12.8	42.0	+33.1

[a] The first number represents the melting point of the amorphous acid, the second the melting point after recrystallization.
[b] For 5 per cent solutions in ethyl alcohol.
[c] The glassy sample crystallized (98° C.) before melting.
[d] Viscous liquids at room temperature.
[e] The initial temperature was 385° C., but after a short time a gentle ebullition began and the temperature gradually dropped to 352° C.
[f] Liquids at room temperature.

Table II. Analytical Data from Pyrolysis of Abietic Acid

(14.00 ± 0.01 gram portions of abietic acid used)

Temp.	Loss in CO_2		Loss in CO		Maximum Acidity		Loss in H_2O			
					Found saponification No.	Calcd. from loss in CO and CO_2	Found	Calculated: From anhydride No. (*a*)	Calculated: From reaction 2 (*b*)	Calculated: Total *a* + *b*
° *C.*	*Gram*	*Mole equivalent*	*Gram*	*Mole equivalent*			*Gram*			
175	None	...	None	...	185.5	185.5	None	....	....	....
230	None	...	None	...	185.0	185.5	0.028	0.0292	None	0.0292
275	0.2062	0.101	0.0181	0.014	165.0	163.9	0.1130	0.1058	0.0116	0.1174
330	0.5096	0.25	0.0811	0.063	128.2	127.4	0.2017	0.1512	0.0521	0.2033
385	0.5711	0.28	0.613	0.474	42.0	45.9	0.5899[a]	0.0431	0.3940	0.4371

[a] This high value for water was caused by the passage of some of the volatile liquid decomposition products (which escaped condensation) into the water absorber. This difficulty arose only when the contents of the reaction vessel were in ebullition and was unavoidable with the apparatus used.

Loss of Water by Abietic Acid

The difference between the acid number and saponification number of a saponifiable material is a measure of the amount of potentially acidic compound—e. g., ester, lactone, or anhydride. In the case of monocarboxylic acids like abietic acid, the most probable explanation of a thermally induced difference between acid number and saponification number is anhydride formation:

$$2C_{19}H_{29}COOH \longrightarrow (C_{19}H_{29}CO)_2O + H_2O \qquad (5)$$

Thus the "anhydride number" (saponification number − acid number) should be calculable from the weight of water eliminated during the heating, provided the sole source of water was reaction 5. From the data in Tables I and II it is obvious that no dehydration occurred when abietic acid was heated for 15 hours at 175° C. A slow elimination of water began after a few hours of heating at 230°. That reaction 5 was the only source of water at this temperature is evidenced by the excellent agreement between the experimentally determined figure and that calculated from the difference between the acid number and saponification number (Table II). For the calculation of the amount of water formed in reaction 5 according to the acid and saponification number data, the following formula was used:

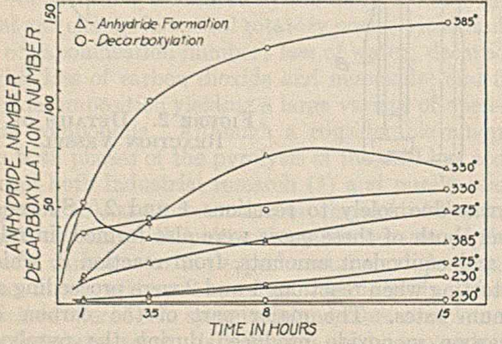


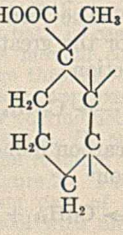
Figure 3. Comparison of Rate and Degree of Anhydride Formation and Decarboxylation

$$\text{Weight of } H_2O = \frac{ab}{191.5} \text{ grams}$$

where *a* = saponification number − acid number
b = weight of water in charge, grams
191.5 = saponification number of abietic anhydride

If reaction 5 had predominated throughout the whole temperature range, the quantity of water eliminated according to calculation would always have closely checked the experimental values. Since, however, the amount of water eliminated at 275°, 330°, and 385° C. was always in excess of that required by anhydride formation, another water-producing reaction was obviously in operation. This second reaction was probably reaction 2 since the water yields calculated from the anhydride number data and the carbon monoxide determinations are in good agreement with the observed values (Table II). These results disagree with those obtained by Rouin (*8*) who pyrolyzed abietic acid at several of the temperatures included in the present study. Rouin concluded, apparently without considering reaction 2, that the source of the water produced when the acid was heated was the dissociation of the compound $4C_{20}H_{30}O_2 \cdot H_2O$, which Dupont, Rouin, and Dubourg (*2*) had observed to be the product when abietic acid was crystallized from the usual solvents. Ruzicka and Schinz (*8*) found, however, that hydration did not occur during crystallization from acetic acid and alcohol, since identical acids were obtained by Steele's method (*11*) and by distillation *in vacuo*.

The rate and degree of anhydride formation and decarboxylation are compared in Figure 3 and Table I. It was unexpected that reaction 5 would be the predominant of the three initially competing reactions (1, 2, 5) at 230°, 275°, and 330° C., and then be superseded by reaction 2, an abnormal mechanism for decarboxylation. The explanation of this behavior undoubtedly lies in the location and mode of attachment of the carboxyl group in the abietic acid structure. In Ruzicka's recently proposed structure for the compound (*9*) the carboxyl group is present in the grouping:



Unfortunately, the action of heat on compounds of known structure containing this type of configuration has not been studied. Decarboxylation of the type illustrated by reaction 1 is generally the primary effect of the action of heat on monocarboxylic acids (*6*). In each of the relatively few cases which have been reported where a monocarboxylic acid forms an anhydride before decarboxylation occurs, there is a substituent in the ortho position to the carboxyl group (*7*).

Problem of the Isomerization of Abietic Acid

The term "isomerization" as used to denote the changes occurring when the resin acids are heated (150° C.) or treated in solution with hydrogen chloride is of vague significance, since both the nature and mechanism of the phenomena involved are unknown. According to Dupont (*1*, *2*) the turpentine acids—i. e., the acids $C_{20}H_{32}O_2$, which are originally present in the untreated oleoresin from various sources—are all (with the exception of *d*-pimaric acid) isomerized to a mixture of isomorphic acids including *l*-abietic acid, which in turn may be converted to a more stable dextrorotatory isomer, pyroabietic acid, by the prolonged action of heat.

As the data in Table I show, isomerization, as indicated by the change in rotatory power, was the single effect of heating only during the complete series at 175° and the first period at 230° C. The decarboxylation and dehydration which proceed concurrently with isomerization under the other conditions naturally affected somewhat the melting points and rotatory power of the reaction products. According to Easterfield and Bagley, however, the optical power of the acid is independent of the presence of the carboxyl group (*3*). In most cases the products of heating were glassy rosins which, when heated in capillary tubes, first sintered, then melted at 107° to 112° C., and then began to recrystallize and finally remelted at 147° to 158° C., both melting points depending on the previous heat treatment. Similar observations were made by Easterfield and Bagley (*3*) and by Seidel (*10*). The change in rotation was very gradual at 175° C., but increased sharply with rising temperature, the greatest change occurring during the first hour of heating. Thus at 230°, 275°, and 330° C. during the first hour when the degree of decarboxylation and anhydride formation was small compared with the extent of these reactions during the longer periods, the change in rotation was 81, 56, and 76 per cent, respectively, of the total change during the longer periods. This indicates that isomerization rather than the rotatory power of decomposition products was the chief cause of the alteration in the optical rotation during these intervals.

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Diffusion Coefficients in Gaseous Systems

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New data are presented on diffusion coefficients for various organic vapors and for mercury in air at one atmosphere at temperatures from 25.9° to 341° C. Data from the literature on diffusion coefficients for a large number of gaseous systems have been collected and plotted. It is found that the data are better correlated by the groups of the original Maxwell equation than by the Sutherland modification, and that the mass of data may be represented within the accuracy of the experimental methods by the Maxwell equation with an empirical constant. The resulting equation is given as Equation 6.

INDUSTRY is exerting ever-increasing pressure upon the engineer to reduce costs. In achieving this, one of the most attractive possibilities is the reduction of the element of fixed charges by increasing the capacity of given equipment. The engineer too frequently fails to appreciate the fact that the limiting factor which constitutes the bottle neck of capacity is not infrequently the diffusion of the reacting substances. The dearth of engineering attention directed to this topic in the past is convincing evidence of the engineer's lack of appreciation of its importance. The time has come to place this matter on an engineering basis which is not only broad but sound.

Two methods of attack are available: the use of empirical experimental data obtained for each individual case, or the development of dependable generalizations which will make possible a sound synthesis of each individual problem. The multiplicity of problems involved is convincing evidence that only the second method of attack is adequate. Thus, one must keep in mind the fact that diffusion is a necessary and frequently a controlling factor in the rate of every interaction between gases in which there is present any nonreacting constituent or in which any substance is synthesized at one point and eliminated from the zone of reaction at the other. Gas diffusion plays its part in the combustion of solid and liquid fuels, in the roasting of sulfide ores, in every acceleration of gaseous reactions by solid or liquid catalysts, in every operation of rectification, in the selective absorption of gases by liquids, in the removal of volatile constituents from the liquids by steam distillation, in the drying of solids by gases, in fundamental air-conditioning and numberless other cases. If sound design must wait until data are available on each individual operation, the engineer will wait till doomsday for the facts he needs. Fortunately, however, the generalizations of the physicist put one in a position to solve these diffusional problems by the use of limited data properly generalized. The purpose of this article is to make an additional contribution in this direction in the special field of gaseous diffusion.

The fundamental differential equations for the diffusion of gases, derived originally by Maxwell (*17*) and Stefan (*24*), must be integrated for the individual situations arising in any given engineering operation.[1] However, the equations contain the diffusion coefficient of the gaseous mixture under consideration and cannot be used without a knowledge of its numerical value. Maxwell, recognizing the importance of this point, proposed the following equation:

$$D = \frac{AT^{3/2}\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{S^2\, P} \qquad (1)$$

where M_A, M_B = ordinary mol. weights of the two gases
P = total pressure
S = distance between the centers of the two unlike molecules at collision (or sum of the radii of the two unlike molecules)
D = diffusion coefficient of the system
T = abs. temp.
A = a constant

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[1] For integrations see Colburn and Hougen (*3*), Hanks and McAdams (*7*), and Lewis and Chang (*13*).

TABLE I. SOURCES OF PUBLISHED DATA FOR VARIOUS SYSTEMS

SYSTEM	TEMP. RANGE ° C.	PRESSURE RANGE Atm.	REFERENCE
	GASES		
Air–H_2	18–22	1	(*23*)
Air–CO_2	0–61	1	(*20, 31*)
Air–O_2	0	1	(*20*)
O_2–H_2	0–61	1	(*4, 9, 20*)
O_2–N_2	12–61	1	(*9, 20*)
O_2–CO	0–61	1	(*20*)
O_2–CO_2	0	1	(*15, 20*)
CO–H_2	0	1	(*15, 20*)
CO–CO_2	0	1	(*15, 20*)
H_2–CO_2	0–61	1	(*4, 15, 20*)
H_2–N_2	0–12	1	(*9, 15*)
H_2–SO_2	0	1	(*15, 20*)
H_2–N_2O	0	1	(*20*)
H_2–CH_4	0	1	(*20*)
H_2–C_2H_4	0	1	(*20*)
CO_2–N_2O	0–61	1	(*20*)
CO_2–N_2	0	1	(*20*)
CO_2–C_2H_4	0	1	(*20*)
CO_2–CH_4	0	1	(*15, 20*)
NH_3–Air	0–25	1	(*27, 23*)
He–A	15	1	(*14, 22*)
Air–H_2O	0–99	0.07–1	(*6, 8, 12, 25, 32*)
H_2–H_2O	18–99	1	(*6, 32*)
CO_2–H_2O	18–99	1	(*6, 32*)
	ORGANIC ESTERS		
Air–methyl formate	11–99	1	(*5, 21*)
Air–methyl acetate	10–51	1	(*5, 21, 32*)
H_2–methyl acetate	20–46	1	(*32*)
CO_2–methyl acetate	20–46	1	(*32*)
Air–ethyl formate	11–50	1	(*21, 32*)
H_2–ethyl formate	20–46	1	(*32*)
CO_2–ethyl formate	20–46	1	(*32*)
Air–methyl propionate	15–70	1	(*5, 21, 32*)
H_2–methyl proprionate	46–67	1	(*32*)
CO_2–methylproprionate	46–67	1	(*32*)
Air–ethyl acetate	10–70	1	(*21, 32*)
H_2–ethyl acetate	46	1	(*32*)
CO_2–ethyl acetate	46	1	(*32*)
Air–propyl formate	20–80	1	(*21, 32*)
H_2–propyl formate	46–67	1	(*32*)
CO_2–propyl formate	46–67	1	(*32*)
Air–methyl butyrate	22–99	1	(*21, 32*)
H_2–methyl butyrate	67–92	1	(*32*)
CO_2–methyl butyrate	67–92	1	(*32*)
Air–methyl isobutyrate	12–80	1	(*21, 32*)
H_2–methyl isobutyrate	49–67	1	(*32*)
CO_2–methyl isobutyrate	49–67	1	(*32*)
	ORGANIC ESTERS (*continued*)		
Air–ethyl propionate	10–92	1	(*21, 32*)
H_2–ethyl propionate	67–90	1	(*32*)
CO_2–ethyl propionate	67–90	1	(*32*)
Air–propyl acetate	10–99	1	(*21, 32*)
Air–isobutyl formate	25–85	1	(*21*)
Air–methyl valerate	45–100	1	(*21*)
Air–ethyl butyrate	42–100	1	(*21, 32*)
H_2–ethyl butyrate	67–96	1	(*32*)
CO_2–ethyl butyrate	67–96	1	(*32*)
Air–ethyl isobutyrate	59–100	1	(*21, 32*)
H_2–ethyl isobutyrate	67–96	1	(*32*)
CO_2–ethyl isobutyrate	67–96	1	(*32*)
Air–propyl propionate	53–100	1	(*21, 32*)
H_2–propyl propionate	96	1	(*32*)
CO_2–propyl propionate	96	1	(*32*)
Air–butyl acetate	50–100	1	(*21, 32*)
H_2–butyl acetate	67–98	1	(*32*)
CO_2–butyl acetate	67–98	1	(*32*)
Air–amyl formate	37–99	1	(*21*)
Air–isoamyl formate	49–100	1	(*21*)
Air–ethyl valerate	50–99	1	(*21, 32*)
H_2–ethyl valerate	98	1	(*32*)
CO_2–ethyl valerate	98	1	(*32*)
Air–propyl butyrate	50–100	1	(*21, 32*)
H_2–propyl butyrate	98	1	(*32*)
CO_2–propyl butyrate	98	1	(*32*)
Air–propyl isobutyrate	56–100	1	(*21, 32*)
H_2–propyl isobutyrate	97	1	(*32*)
CO_2–propyl isobutyrate	97	1	(*32*)
Air–isopropyl isobutyrate	50–100	1	(*21*)
Air–isobutyl propionate	66–100	1	(*21, 32*)
H_2–isobutyl propionate	98	1	(*32*)
CO_2–isobutyl propionate	98	1	(*32*)
Air–propyl valerate	70–100	1	(*21, 32*)
H_2–propyl valerate	98	1	(*32*)
CO_2–propyl valerate	98	1	(*32*)
Air–isobutyl butyrate	75–100	1	(*21, 32*)
H_2–isobutyl butyrate	98	1	(*32*)
CO_2–isobutyl butyrate	98	1	(*32*)
Air–isobutyl isobutyrate	75–100	1	(*21, 32*)
H_2–isobutyl isobutyrate	98	1	(*32*)
CO_2–isobutyl isobutyrate	98	1	(*32*)
Air–isobutyl valerate	80–100	1	(*21, 32*)
H_2–isobutyl valerate	98	1	(*32*)
CO–isobutyl valerate	98	1	(*32*)
Air–amyl butyrate	50–100	1	(*21*)
Air–amyl isobutyrate	84–100	1	(*21, 32*)
H_2–amyl isobutyrate	98	1	(*32*)
CO_2–amyl isobutyrate	98	1	(*32*)

Numerous rederivations and modifications of Maxwell's original equation have been proposed. Jeans (*10*) gives the same relation but with a slightly different constant, $8/3\pi$ times that given by Maxwell. Chapman's derivation (*2*) leads to a constant three-fourths as large as that obtained by Maxwell. This type of equation predicts no variation of the diffusion coefficient with the relative amounts of the two gases present. Meyer (*18*) has proposed an equation which indicates large variations in D as the relative percentages of the two gases are varied. The work of Lonius (*14*), Schultze (*23*), Jackman (*9*), and Deutsch (*4*) indicate that such variations are very slight, and probably within the experimental accuracy; consequently the Maxwell type of equation is used in preference to that of Meyer.

The most important modification of the Maxwell equation is due to Sutherland (*26*), who introduced the factor $(1 + C/T)$ in the denominator of the right-hand side of Equation 1:

$$D = \frac{A'T^{3/2}\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{S^2P\left(1 + \frac{C}{T}\right)} \qquad (2)$$

The Sutherland constant, C, for the system depends only on the natures of the two kinds of molecules and is obtained from the individual values of C for each gas, which are in turn obtained preferably from viscosity data on the pure gases. Methods of estimating C for any gas system are discussed by Arnold (*1*).

The radii of the molecules may be obtained in several ways (e. g., viscosity data, x-rays, etc.); but, since data from these sources are rather limited, it seems better to use the empirical relation developed by Titani who found that the molal volume of a liquid at its normal boiling point is proportional to the cube of the radius of the molecule. Equations 1 and 2 then become:

$$D = \frac{BT^{3/2}\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P(V_A{}^{1/3} + V_B{}^{1/3})^2} \qquad (3)$$

$$D = \frac{B'T^{3/2}\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{(V_A{}^{1/3} + V_B{}^{1/3})^2\,P\left(1 + \frac{C}{T}\right)} \qquad (4)$$

where V_A, V_B = molal volumes at the normal boiling point
B, B' = constants

The constants in the Equations 3 and 4 can be calculated as has been done by Arnold (*1*); but, since these calculations involve the use of Titani's empirical constant, it seems better to compare the groups suggested by the above equations with the actual experimental data to obtain the most suitable values of B and B'.

Several hundred determinations of experimental diffusion coefficients have been reported in the literature. The principal methods of obtaining these coefficients are briefly as follows:

EVAPORATION OF LIQUIDS IN NARROW TUBES. One of the two components, in the liquid state, is placed in a small glass tube,

TABLE I (*Continued*)

SYSTEM	TEMP. RANGE °C.	PRESSURE RANGE Atm.	REFERENCE
	ORGANIC ACIDS		
Air–formic	65–85	1	(*32*)
H_2–formic	65–85	1	(*32*)
CO_2–formic	65–85	1	(*32*)
Air–acetic	62–99	1	(*21, 32*)
H_2–acetic	66–99	1	(*32*)
CO_2–acetic	66–99	1	(*32*)
Air–propionic	51–99	1	(*21, 32*)
H_2–propionic	93–99	1	(*32*)
CO_2–propionic	93–99	1	(*32*)
Air–butyric	75–100	1	(*21, 32*)
H_2–butyric	99	1	(*32*)
CO_2–butyric	99	1	(*32*)
Air–isobutyric	78–100	1	(*21, 32*)
H_2–isobutyric	98	1	(*32*)
CO_2–isobutyric	98	1	(*32*)
Air–valeric	82–100	1	(*21*)
Air–isovaleric	71–100	1	(*21, 32*)
H_2–isovaleric	99	1	(*32*)
CO_2–isovaleric	91	1	(*32*)
Air–caproic	82–100	1	(*21*)
Air–isocaproic	82–100	1	(*21*)
	ALCOHOLS		
Air–methyl	10–50	1	(*30, 32*)
H_2–methyl	25–50	1	(*32*)
CO_2–methyl	25–50	1	(*32*)
Air–ethyl	10–67	1	(*12, 30, 32*)
H_2–ethyl	40–67	1	(*32*)
CO_2–ethyl	40–67	1	(*32*)
Air–propyl	10–84	1	(*21, 30, 32*)
H_2–propyl	67–84	1	(*32*)
CO_2–propyl	67–84	1	(*32*)
Air–isopropyl	15–60	1	(*21*)
Air–butyl	60–100	1	(*21, 32*)
H_2–butyl	99	1	(*32*)
CO_2–butyl	99	1	(*32*)
Air–isobutyl	60–99	1	(*21, 32*)
Air–*tert*-butyl	21	1	(*21*)
Air–*n*-amyl	99	1	(*32*)
H_2–*n*-amyl	99	1	(*32*)
CO_2–*n*-amyl	99	1	(*32*)
Air–methyl ethyl ethanol	99	1	(*32*)
H_2–methyl ethyl ethanol	99	1	(*32*)
Air–*n*-hexyl	99	1	(*32*)
H_2–*n*-hexyl	99	1	(*32*)
CO_2–*n*-hexyl	99	1	(*32*)
	MISCELLANEOUS		
Air–propylbenzene	52–99	1	(*21*)
Air–isopropylbenzene	60–99	1	(*21*)
Air–mesitylene	60–100	1	(*21*)
Air–ethylbenzene	50–100	1	(*21*)
Air–*o*-xylene	50–100	1	(*21*)
Air–*m*-xylene	50–100	1	(*21*)
Air–*p*-xylene	20–100	1	(*21*)
Air–chlorobenzyl	84–99	1	(*21*)
Air–ethyl ether	10–42	1	(*5, 17, 21, 32*)
H_2–ethyl ether	10–20	1	(*17, 32*)
CO_2–ethyl ether	10–20	1	(*32*)
Air–chlorobenzene	42–67	1	(*12*)
Air–diphenyl	25	1	(*16*)
Air–aniline	25	1	(*16*)
Air–naphthalene	25	1	(*16*)
Air–anthracene	99	1	(*16*)
Air–CS_2	16–33	1	(*17, 32*)
H_2–CS_2	20–33	1	(*32*)
CO_2–CS_2	20–45	1	(*32*)
Air–benzene	20–67	1	(*12, 32*)
H_2–benzene	20–45	1	(*29, 32*)
O_2–benzene	23	1	(*29*)
CO_2–benzene	20–45	1	(*32*)
Air–toluene	25	1	(*16*)
Air–*n*-octane	25	1	(*16*)
Air–benzidine	99	1	(*16*)
H_2–CCl_4	23	1	(*29*)
Air–propyl bromide	21–63	1	(*21*)
Air–isopropyl bromide	20–52	1	(*21*)
Air–propyl iodide	31–100	1	(*21*)
Air–isopropyl iodide	50–79	1	(*21*)
Air–safrole	77–100	1	(*21*)
Air–isosafrole	63–100	1	(*21*)
Air–eugenol	86–99	1	(*21*)
Air–isoeugenol	85–99	1	(*21*)
Air–*n*-butylamine	61–63	1	(*21*)
Air–isobutylamine	19–62	1	(*21*)
Air–diethylamine	10–51	1	(*21*)
N_2–mercury	19	0.00259–0.00745	(*19*)
N_2–iodine	19	0.0087–0.018	(*19*)
Air–iodine	0–30	1	(*11, 16, 28*)
Air–*o*-chlorotoluene	65–98	1	(*21*)
Air–*n*-chlorotoluene	65–98	1	(*21*)
Air–*p*-chlorotoluene	60–100	1	(*21*)

filling the tube within 1 to 5 cm. of the top. The tube and liquid are held at constant temperature, and the second gas is passed over the top of the tube. The rate of diffusion is obtained by measuring the rate of fall of liquid in the tube. This technic, devised and developed by Stefan, is perhaps the best and most widely used of the experimental methods. It is limited, however, to a fairly narrow temperature range for any one system, since one of the components must be liquid, and the precision is poor at very low or very high vapor pressures. This method has been used by Stefan (*24*), Griboiedow (*5*), LeBlanc and Wuppermann (*12*), Vaillant (*30*), Trautz and Ries (*29*), and extensively by Winkelmann (*32*) and Pochettino (*21*).

UNSTEADY-STATE INTERDIFFUSION OF TWO GASES. The two gaseous components are placed in separate sections of a tube, and diffusion is allowed to take place by removing the partition separating the sections. After a definite time interval the gas from various portions of the tube is analyzed and the results are compared with an integrated form of the following diffusion equation:

$$\frac{\delta p}{\delta \Theta} = D \frac{\delta^2 p}{\delta x^2} \qquad (5)$$

This method has been widely used for systems of the permanent gases but gives results somewhat less reliable than those obtained by the first method. Von Obermayer (*20*), Lonius (*14*), Schultze (*23*), Jackman (*9*), Deutsch (*4*), Loschmidt (*15*), Waitz (*31*), Toepler (*27*), and Wintergest (*33*) were the principal users of this method.

MISCELLANEOUS METHODS. Diffusion coefficients for iodine in air have been obtained by measuring the rate of evaporation of a small sphere of iodine suspended in air. It seems probable that convection currents in the air make this method unreliable. Mullaly and Jacques (*19*) placed iodine and mercury, respectively, at the two ends of a tube filled with nitrogen at low pressures. The diffusion coefficient of both iodine and mercury were calculated from the measured amount, composition, and location of the deposit of mercurous and mercuric iodides formed. Special methods of this type are useful only for special types of systems.

TABLE II. DIFFUSION COEFFICIENTS DETERMINED EXPERIMENTALLY

(Barometric pressure, 1 atmosphere)

SYSTEM	TEMP. °C.	D_{760} Sq. cm./sec.
Air–water vapor	25.9	0.258
	39.4	0.277
	59.0	0.305
Air–*n*-butyl alcohol	25.9	0.087
	39.4	0.092
	59.0	0.104
Air–toluene	25.9	0.086
	39.4	0.092
	59.0	0.104
Air–*sec*-butyl alcohol	25.9	0.089
	39.4	0.096
	59.0	0.108
Air–ethyl acetate	25.9	0.087
	39.4	0.094
	59.0	0.106
Air–*sec*-amyl alcohol	25.9	0.071
	39.4	0.076
	59.0	0.086
Air–chlorobenzene	25.9	0.074
	39.4	0.079
	59.0	0.090
Air–aniline	25.9	0.074
	39.4	0.079
	59.0	0.090
Air–diphenyl	218	0.160
Air–mercury	341	0.473
Air–isopropyl alcohol	25.9	0.099
	39.4	0.107
	59.0	0.121

The published results collected total some five hundred determinations, covering the various systems indicated by Table I. In addition, experimental determinations were made on a number of vapors including diphenyl and mercury

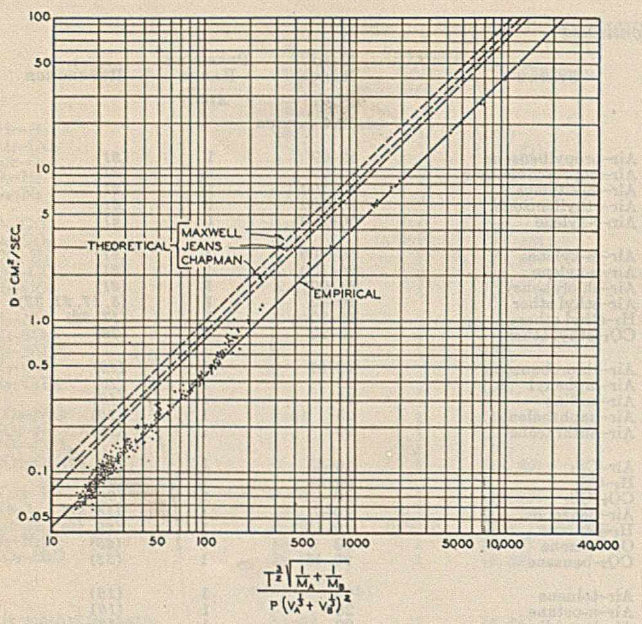

FIGURE 1. DIFFUSION COEFFICIENT *vs.* GROUP SUGGESTED BY EQUATION 3

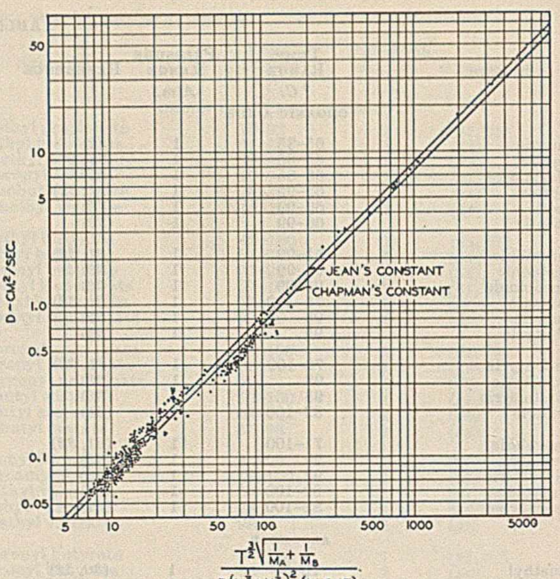

FIGURE 2. DIFFUSION COEFFICIENT *vs.* GROUP SUGGESTED BY EQUATION 4

at elevated temperatures in air, using the evaporative technic. These new data are summarized in Table II.

The experimental apparatus was similar to that used by previous investigators (*12*, *21*, *24*, *32*). Small glass tubes 2 mm. in diameter and 10 cm. long were etched in millimeter divisions and filled within 1 to 5 cm. of the top with the liquid to be tested. Tubes containing the liquid were placed vertically in a constant-temperature bath, and air at the temperature of the bath was passed slowly across the top open ends of the tubes. The heat requirements were small since the rate of evaporation was low. In the low-temperature experiments a thermostatically controlled water bath was used; this was replaced by a condensing vapor bath when operating at higher temperatures. The liquid level in the tubes was recorded at equal time intervals, and the diffusion coefficient calculated from the ordinary integrated form of the Stefan equation.

The data from the literature, together with the new data of Table II, are plotted in Figures 1 and 2 using as abscissa the groups suggested by Equations 3 and 4, and the experimentally observed diffusion coefficients as ordinates. In calculating the group plotted as abscissa in Figure 2, the values of C were obtained as suggested by Arnold (*1*), using values of C for the pure gases obtained from viscosity determinations, or, where those were lacking, values estimated from the empirical relation:

$$C = 1.47\,T_b$$

where
T_b = normal boiling point, ° K.

Each plot shows a wide band of points, with considerable deviation from a mean line. This is to be expected from the rather poor precision obtained by the experimental methods so far developed for obtaining diffusion coefficients. There is, however, no definite trend with molecular weight or with pressure, both of which were varied over wide ranges in the data plotted. Comparison shows Figure 1 to give better correlation than Figure 2. The temperature range covered was narrow, being only from 0° to 100° C., except for a few points, so that it is not possible to show whether the poorer correlation with the Sutherland group is due to the temperature function being incorrect, or to the use of the incorrect value of C in calculating the groups plotted. Without discarding some of the experimental data, it would be difficult to obtain a much better correlation than that of Figure 1, as the percentage deviations in this figure are of the same order of magnitude as the deviations in the actual experimental data as obtained by the different investigators for the same systems under similar conditions. In obtaining an empirical relation, the first plot is the more satisfactory from a practical point of view, since it not only shows a better correlation of the data but is simpler to use and does not involve the uncertain quantity, C. Figure 1 shows the empirical constant to be 0.0043, and the relation is, therefore:

$$D = \frac{0.0043T^{3/2}\sqrt{\dfrac{1}{M_A}+\dfrac{1}{M_B}}}{({V_A}^{1/3}+{V_B}^{1/3})^2P} \tag{6}$$

where D = diffusion coefficient, sq. cm./sec.
T = abs. temp., ° K.
P = total pressure, atm.

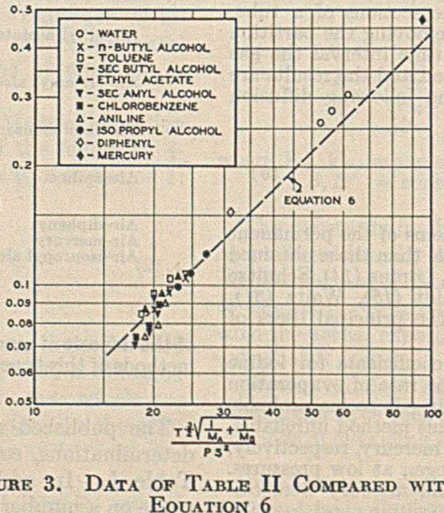

FIGURE 3. DATA OF TABLE II COMPARED WITH EQUATION 6

Figure 3 shows the data of Table II compared with Equation 6.

Sutherland (*26*), on analyzing certain of von Obermayer's data for several pairs of gases, found a greater variation in B' than in B. For six pairs of gases he found B to vary from 0.0038 to 0.0047. Lines corresponding to the calculated constants of Maxwell, Jeans, and Chapman are drawn in Figures 1 and 2.

In using Equation 6, values of V should be obtained in the same way as were those employed in preparing Figure 1. For this plot the values of V were obtained using Kopp's law of additive columns, with the rules and values for each element given by LeBas, as outlined by Arnold (*1*). These values and rules are summarized for convenience in Table III.

Equation 6 is recommended for use in estimating values of *D* where no good experimental data exist. Reliable experimental data are, of course, to be preferred to an estimation obtained from such an empirical equation.

TABLE III. SUMMARY OF VALUES AND RULES

ELEMENT	ATOMIC VOL.
Carbon	14.8
Chlorine	24.6
Iodine	37.0
Hydrogen	3.7
Bromine	27.0
Sulfur	25.6
Oxygen in:	
Aldehydes and ketones	7.4
Methyl esters	9.1
Methyl ethers	9.9
Higher esters and ethers	11.0
Acids	12.0
Nitrogen:	
Double-bonded	15.6
In primary amines	10.5
In secondary amines	12.0

Deduct 15 for benzene ring formation; deduct 30 for naphthalene ring formation. For example: Molar volume of $C_2H_6 = 2 \times 14.8 + 6 \times 3.7 = 51.8$.

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Solder

Effect of Impurities on Its Appearance and Microstructure

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THE solder industry has for a long time judged the quality and purity of 50-50 tin-lead solder by the physical appearance of a poured bar. Many contend that a smooth, shiny bar is indicative of quality, and that the presence of metallic impurities is reflected in a generally rough or frosty looking bar. One aim of the solder manufacturer is to produce a bar which is clean and smooth, and the occasional persistent roughness which sometimes prevails is always the source of much concern. This roughness is variously attributed to antimony, copper, nickel, arsenic, or other impurities whose effects have never been experimentally demonstrated. Needless to say, conclusions in these cases are based largely on whim, fancy, or tradition rather than on experimental evidence.

At first thought it would appear that such points could easily be settled by chemical analysis. Very often, however, an exhaustive chemical investigation on samples of smooth and rough bars fails to reveal any essential differences. It is the purpose of this investigation to determine the effects of small amounts of common known impurities on the physical appearance and the microstructure of 50-50 bar solder.

The first publication of an investigation of the surface appearance of solders seems to have been by Bannister and Tabor in 1909.[1] These authors, however, did not emphasize the practical significance of the influence of extremely small amounts of impurities such as concern the manufacturer of high-quality solders. In most cases such a manufacturer is concerned with traces of impurities which defy chemical detection in routine analytical work. In view of the many diverse and contradictory opinions held on this subject, it was thought advisable to investigate this question a little further, repeating at the same time much of the work of Bannister and Tabor.

TESTS ON SOLDER

When tin and lead are fused together in equal proportions by weight and poured into an iron mold of appropriate thermal capacity, there results a smooth, shiny bar of solder which has a slight contraction crack extending down the center of the bar and throughout the greater part of its length. In best grades of commercial 50-50 bar, which totals usually from 0.03 to 0.07 per cent impurity, there is always a faint, rough line extending along the contraction crack or portion which freezes last. For the following work the total impurity content of the metal, which is the purest commercially obtainable, was approximately 0.03 per cent, and in the resulting 50-50 bar, the faint "frost line" was practically negligible.

Alloys of known impurity content were made by alloying such solder with known amounts of different elements, and a bar was made from each alloy. Each bar was then examined visually for frost, roughness, etc.; a short cross section about a centimeter long was then taken from the bar for metallurgical examination. After carefully filing the

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[1] *J. Inst. Metals*, 2, No. 2 (1909).

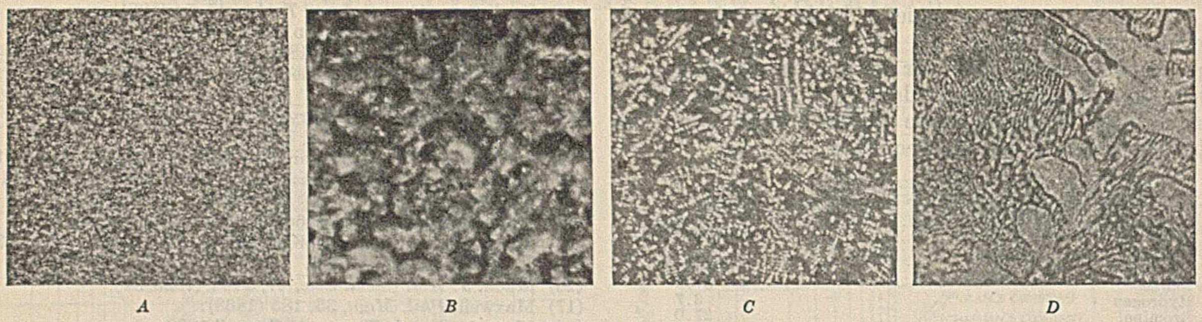

FIGURE 1. MICROSTRUCTURE OF PURE 50-50 TIN-LEAD BAR SOLDERS

A. × 50 *B.* × 500 *C.* Poured too cold; × 50 *D.* Poured hot and cooled too slowly; × 220

rough sawed end, the cross section was polished successively on No. 1, 0, 00, 000, and 0000 emery paper; then on French broadcloth with moist, levigated alumina; and finally, after washing and drying, on soft flannel. The sample was then etched for 1 to 2 minutes in 15 per cent ferric chloride at room temperature.

First, it was found that the ratio of solder mold to bar was an important factor. Certain statements appearing in technical literature to the effect that the appearance of solder bars is improved by decreasing the cooling rate could not be confirmed. By using a small, prewarmed mold about twice as heavy as the solder bar, an extremely rough, frosty bar was obtained by the resultant slow rate of cooling. When the cooling rate was speeded up by using a mold eight times as heavy as the solder, a smoother, less frosty bar was obtained, particularly, in the case of the lower tin alloys. It was found that an extreme in either direction is to be avoided and best results are obtained by adjusting the thermal capacity of bar and mold to the point where hot solder will just run freely to the end of the mold before partial solidification begins. In this work a mold was used which gives a solder bar approximately 4 inches long and 5/8 inch square, whose mass is about eight times that of the bar which it produced.

Pure 50-50 solder is preferably poured at 525° to 575° F. At higher temperatures there is undue oxidation of the metal, and at lower temperatures the appearance of the bar is unsatisfactory. The contraction crack down the center of the bar is practically free from frost, and the bar is smooth and shiny. When pure solder is prepared under these conditions, the microstructure at 50 magnifications appears exceedingly uniform, homogeneous, and free from dendrites (Figure 1*A*). At higher magnifications one can detect the light eutectic and the dark mixture of lead and solid solution (Figure 1*B*).

Just as in the case of other metals, the microstructure of pure solder depends largely on the manner in which it is treated. If pure solder is poured into a mold at too low a temperature so that the solder does not flow freely to the end of the mold, the bar will be frosty and the microstructure at 50 magnifications will reveal many dendrites (Figure 1*C*). If, on the other hand, the metal is poured into a hot mold and allowed to cool slowly, the microstructure will again reveal large dendrites of lead and solid solution and the beautifully laminated structure of the eutectic (Figure 1*D*). Ac-

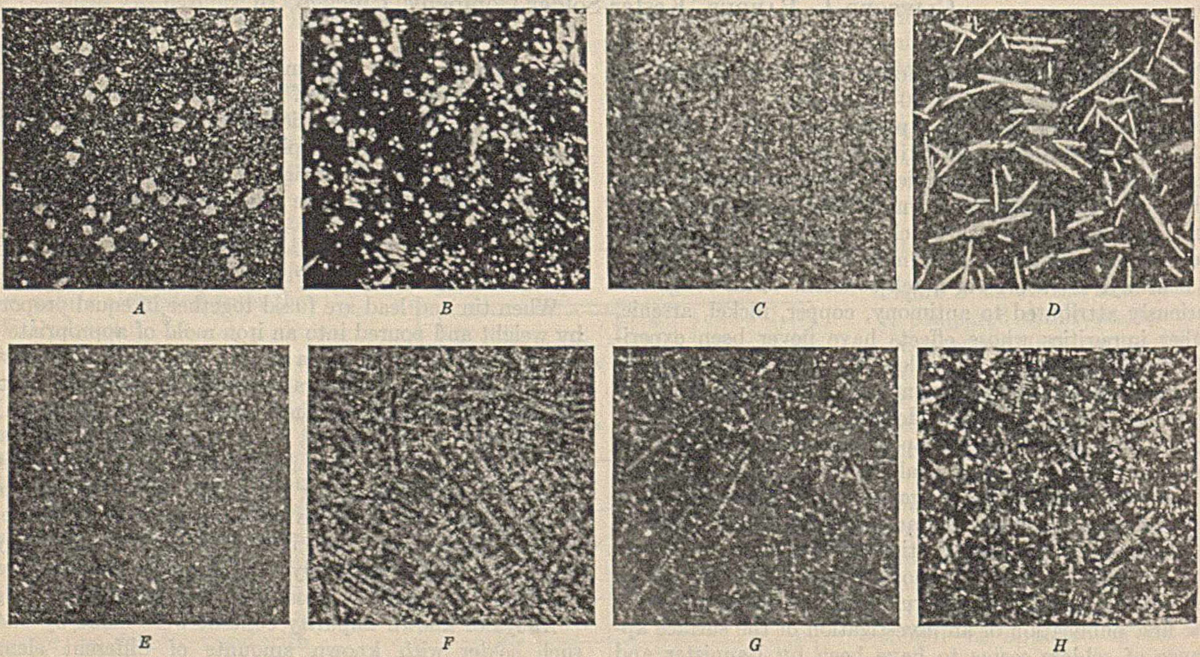

FIGURE 2. MICROSTRUCTURE OF COMMERCIAL BAR SOLDERS (× 50)

A. 48.5 per cent tin; 48.5, lead; 3, antimony
B. 49.5 per cent tin; 49.5, lead; 1, copper
C. 50-50 solder containing 0.25 per cent nickel
D. 49.5 per cent tin; 49.5, lead; 1, arsenic
E. 50-50 solder containing 0.10 per cent arsenic
F. 50-50 bar solder containing 0.001 per cent zinc
G. 50-50 bar solder containing 0.01 per cent aluminum
H. 50-50 bar solder containing 0.01 per cent cadmium

tual commercial 50-50 bar solder, however, is not produced under either of these extreme conditions and, as actually made, the microstructure appears as in Figure 1*A* and *B*.[2]

EFFECT OF IMPURITIES

The following observations on appearance and microstructure are confined to 50-50 bar solder as actually produced in the solder industry:

Antimony up to 2 per cent has no effect on the appearance or the microstructure of 50-50 alloys. Only at higher concentrations are there obtained the curious raised, round spots or "cooling spots," thought to be characteristic of antimony, which form as the alloy cools. The presence of these spots is not reflected in the microstructure of the alloy. On low-tin alloys such as 45-55, the addition of 0.5 to 1 per cent antimony actually produces a bar as smooth and free of frost as pure 50-50. Microscopic investigation of antimonial solder reveals the characteristic square, unetched crystals of SbSn only when the antimony content reaches 3 per cent or more (Figure 2*A*).

Bismuth up to 3 per cent has no effect on the appearance or the microstructure of solder.

Copper in amounts as high as 0.5 per cent does not alter the appearance or the microstructure of solder. Only when the copper content approaches 1 per cent does the solder bar become rough and frosty; in such an alloy the characteristic needles of Cu_3Sn are clearly distinguishable under the microscope (Figure 2*B*).

Silver at 0.05 per cent produces no local frost line or cooling spots, but does produce a general or pronounced "velvety" appearance on the entire surface of the bar in contrast to the bright finish of pure 50-50 solder; the microstructure is unaltered.

Nickel in amounts ranging from 0.03 to 0.25 per cent gives rise to countless cooling spots, but no frost line. The microstructure of a 0.10 per cent nickel alloy is identical with that of pure solder. When the nickel content reaches 0.25 per cent, microscopic examination reveals long, unetched, needle-like or occasionally star-shaped portions which are quite similar in physical appearance to Cu_3Sn (Figure 2*C*).

Arsenic is similar to nickel, causing in amounts as low as 0.03 per cent many cooling spots, but no frost, even at 0.25 per cent. Microscopic investigation of a 1 per cent arsenic alloy reveals long, unetched needles, similar in all respects to the constituent observed in the cases of copper and nickel (Figure 2*D*). This constituent persists down to 0.10 per cent arsenic (Figure 2*E*).

When zinc is added to solder in amounts as low as 0.001 per cent, there results an extremely rough, frosty bar with the frost line covering almost its entire surface. Such a bar can be poured only at temperatures 150° to 200° F. higher that that required for pure solder. Such a bar, although containing 1 part of zinc in 100,000 parts of solder, reveals at 50 magnifications a beautiful, crystalline network of fine dendritic needles distinctly different from the homogeneous appearance of pure bar solder (Figure 2*F*). The dendrites, however, do not appear to be directly connected with zinc, and the influence of the latter appears to consist in altering the temperature at which the solder is mobile.

Aluminum, like zinc, requires a high pouring temperature, and produces in amounts as low as 0.01 per cent much roughness and a wide and prominent frost line. The microstructure of such a bar is a dendritic network similar to that of the zinc (Figure 2*G*).

Cadmium has the same effect as zinc or aluminum, causing at 0.01 per cent an extremely rough, frosty bar and a highly dendritic microstructure (Figure 2*H*). Aluminum and cadmium are, however, much less active than zinc in causing frost and altering the microstructure of solder.

CONCLUSIONS

1. The frostiness on bar solder is largely influenced by the relative thermal capacities of the solder mold and a given poured bar. Satisfactory results may be obtained by using a mold whose total mass is about six to eight times that of the bar which is produced.
2. Antimony, bismuth, copper, silver, nickel, and arsenic have no part in the frostiness which appears on bar solder. In amounts in which these elements are ordinarily present in solder, none (with the possible exception of arsenic) can be detected by microscopic investigation.
3. The round, raised, cooling spots usually attributed to antimony, are really caused by arsenic or nickel which are about one hundred times more active in producing this curious effect.
4. Zinc in amounts as low as 0.001 per cent, and aluminum and cadmium in amounts as low as 0.01 per cent produce a noticeable roughness and frostiness on bar solder. These elements also produce a distinct change in microstructure, giving rise to a dendritic network in contrast to the uniformly velvety appearance of pure bar solder when properly made. The influence of these elements doubtless consists largely in altering the mobility and fluidity of solder, and the dendritic structure may be merely associated with the fact that the poured bar is necessarily frosty. The persistent frostiness which occasionally prevails on apparently "pure" solder is undoubtedly traceable to one or more of these elements.

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[2] It has been observed that in the case of eutectic (63-37) bar solder, the aminated eutectic structure can hardly be observed if the bar has been properly made. In case the bar is poured either too hot or too cold, so that it is either frosty or oxidized, the microstructure will be highly laminated.

European Nitrogen Agreement

At a meeting in Paris, the existing agreement of European synthetic-nitrogen producers for regulating the international trade, which expires June 30, 1934, was extended for a year to June 30, 1935. It is reported, according to the Department of Commerce, that the conditions of the existing agreement remain unchanged and the proposal for prolongation was adopted unanimously by all the representatives present. Producers in nine European countries are embraced in the pact, and in addition to the so-called Triple Cartel of producers in Germany, Great Britain, and Norway, it includes France, Belgium, the Netherlands, Poland, Czechoslovakia, and Italy.

The renewal of the pact this year is notable because of the early date at which it has been signed and the apparent ease at which agreement was reached. In past years, agreement was usually not reached until late in the fertilizer year, or around the beginning of the new fertilizer year dating from July 1; moreover, the preliminary negotiations were long drawn out and were accompanied by considerable difficulties. The dispatch with which the renewed pact was agreed upon this year indicates an appreciation of the benefits accruing to the producers from peaceful conditions in the international trade.

The Chilean natural nitrate industry remains outside of the pact, as heretofore, and it is suggested in trade circles that a reason for the early date of the agreement among the synthetic producers this year is the desire to make a renewed effort to bring Chile within the pact; it is stated that the British group, the Imperial Chemical Industries, in particular, favors an understanding with Chile.

Diatomaceous Earth

Equilibrium and Rate of Reaction in the System Hydrated Lime–Diatomaceous Silica–Water

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The conditions of equilibrium and of the rate of reaction in the system lime–diatomaceous earth–water, with diatomaceous earth present in excess, are studied. At equilibrium the liquid phase contains silica and lime in solution in the molecular ratio of 1.5. This corresponds to the formula $2CaO{\cdot}3SiO_2$. The solid phase under these conditions consists of unreacted diatomaceous earth and, presumably, of a hydrated calcium silicate. The latter has a molecular ratio of silica to lime of 1.2 corresponding to the formula $5CaO{\cdot}6SiO_2$.

The rate of reaction between diatomaceous silica and lime solution is characterized by rapid reaction during the first few minutes. This is followed by a "period of inhibition" during which the rate of reaction over a period of several hours is relatively low. A period of higher rate of reaction which continues to equilibrium then follows.

Applications of the data obtained are indicated.

IN CONSIDERING the reactivity of the various forms of silica, it has been recognized that the amorphous or hydrous varieties are more soluble and reactive than are the crystalline forms. This is particularly true as regards the reactivity of the silicas with basic solutions. However, few published data are available on the reactivities of the naturally occurring amorphous silicas, and particularly of diatomaceous silica which in recent years has become a material of considerable economic importance.

A study of the system hydrated lime–diatomaceous silica–water is of importance to a fundamental understanding of the nature and properties of diatomaceous earth, particularly with respect to its chemical reactivity and the nature of the chemical reactions between diatomaceous silica and basic substances in general. The reaction between hydrated lime and diatomaceous silica is likewise of importance in the use of diatomaceous earth in the manufacture of lime-bonded insulating materials, in its use as a filtering medium, as a filler, as an admixture for improving the workability of mortars and concrete, and as an absorptive medium.

Nature of Diatomaceous Silica

Diatomaceous silica is composed of the microscopically minute remains of marine or fresh water diatom plants. In past geological periods residues of these organisms were deposited under water and compacted into beds. The forms and shapes of the fossil diatoms making up diatomaceous earth are of great variety and infinite beauty. A photomicrograph of earth from the Celite deposit at Lompoc, Calif., is shown in Figure 1. The individual frustules of diatoms are ordinarily very thin walled and frequently of rather complex structure, which gives a high specific surface. The great liquid-absorbing capacity and low bulk density are two of the most striking physical characteristics of diatomaceous earth and are due to the physical structure of the diatom particles. On the other hand, the true adsorptive capacity of diatomaceous earth is relatively low.

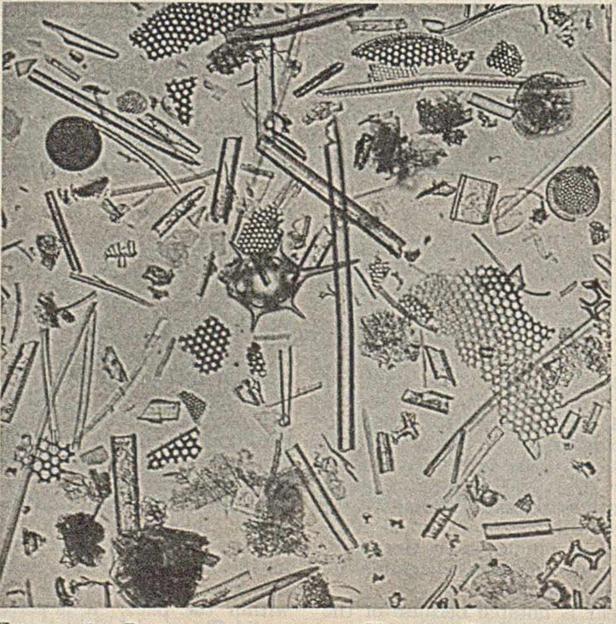

Figure 1. Photomicrograph of Typical Diatomaceous Earth from Celite Deposit, Lompoc, Calif.

In chemical composition, pure diatomaceous earth is essentially hydrous or opaline silica containing 3 to 7 per cent of combined water. It is an amorphous substance as shown by the customary methods of crystallographic examination. The commercial grades of diatomaceous silica contain 1 to 10 per cent of impurities, mostly iron oxide, alumina, alkaline earths, and sodium compounds. In the presence of water, diatomaceous silica reacts readily with basic substances, such as lime, to form hydrated basic silicates. These hydrated silicates are initially gels. Their formation can be greatly accelerated by heat and pressure. It is the purpose of the present investigation to determine the nature of and the rate of the reaction between hydrated lime and diatomaceous silica under certain carefully controlled conditions, and to indicate the significance of the results obtained in some of the major uses of diatomaceous earth.

Methods of Study

The investigation of this system was carried out at 30° C. ± 0.01° in a large, modified type of the Clark constant-temperature air bath (*1*). The apparatus is illustrated in Figure 2. For obtaining equilibrium in the mixtures of lime, diatomaceous silica, and water reported, a mechanical shaker was devised. This consisted of a box-like apparatus holding four one-liter Pyrex glass bottles. A motor in the rear of the air bath rotated the box, causing the bottles to turn end over end at a slow rate, thus thoroughly agitating the contents. The bottles were paraffin-coated on the inside to prevent reaction between the lime and the glass. Electrical leads passed from the inside of the air bath through small openings to accessory equipment about the laboratory. This constant-temperature equipment proved very satisfactory for the purpose, as it was accurate, clean, convenient, and not subject to electrical leakage.

The accessory equipment connected with the air bath permitted the reasonably accurate determination of the hydrogen-ion concentration of the solutions by electrometric methods and of the ionic conductivity of the solutions by electrical methods.

The apparatus for hydrogen-ion determination consisted of a tank of hydrogen piped through the wall of the air bath by means of 0.25-inch (0.635-cm.) copper tubing. The usual assortment of gas wash bottles within the air bath purified the hydrogen and brought it to the desired temperature. The electrical equipment was a Leeds and Northrup hydrogen-ion potentiometer with galvanometer and an Eppley standard cell, all conveniently wired. The calomel cells and platinum electrodes were of the usual types.

The conductivity equipment consisted of a Leeds and Northrup students' type potentiometer and slide wire bridge, a 1000-cycle audio oscillator as a source of alternating current, and a 10,000-ohm resistance box capable of being varied by one ohm from zero to its maximun resistance. The conductivity cell was of the dip cell type especially designed and constructed for this work so that measurements of conductivity could be made without removal of solution or other changes in the system. The cell was properly standardized over the range of concentration for which it was used.

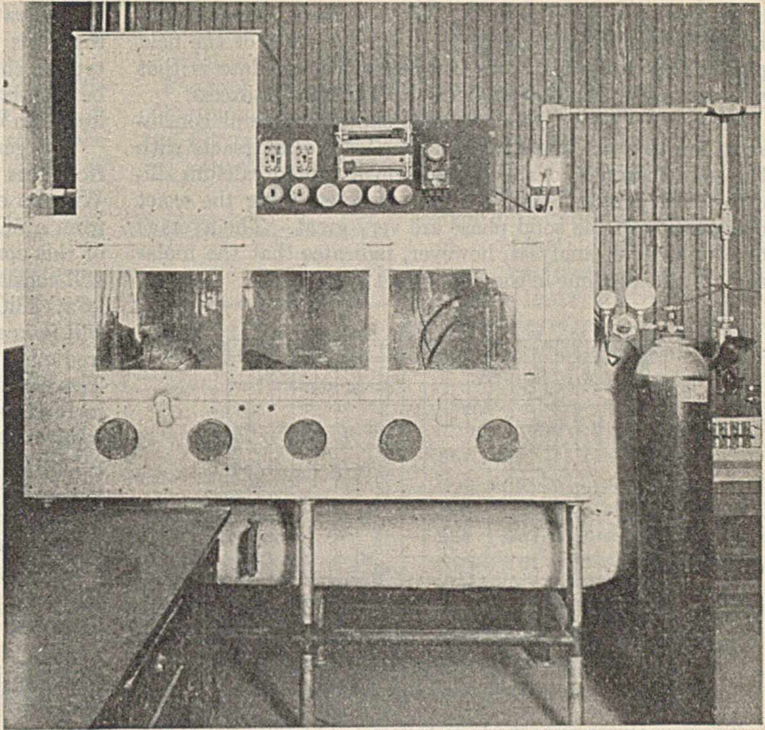

FIGURE 2. CONSTANT-TEMPERATURE AIR BATH FOR EQUILIBRIUM AND RATE-OF-REACTION MEASUREMENTS

The method of procedure was as follows:

A saturated lime solution was prepared from calcined Iceland spar, and exactly one-liter portions were transferred to one-liter Pyrex glass bottles, placed in the shaking device within the air bath. The solutions were shaken until constant temperatures were obtained. The concentrations of the lime solutions were then determined by measuring their conductivities. The milled samples of diatomaceous earth were prepared by washing them free of electrolytes with conductivity water, drying at 105° C., and brushing repeatedly through a 100-mesh screen to break up all small aggregates. The requisite quantities of the dried earth were then weighed out and transferred to the lime solutions. The conductivities of the lime solutions were determined at the end of 1, 2, 10, and 30 minutes, and then correspondingly longer periods until equilibria were attained. By difference the degree of combination between the lime in the solutions and the diatomaceous earth samples were calculated. At equilibrium the hydrogen-ion concentrations of the solutions were determined and the requisite analyses made.

The use of the conductivity method for determining the rate of combination of lime and diatomaceous silica proved very successful, since a measurement required only 30 seconds. By this procedure the rates of combination in the very early stages of the reactions were accurately followed. This procedure was dictated by the need for information on the very early states of the reaction in connection with some of the uses of diatomaceous earth. For example, when these products are employed as filter aids or for improving the workability of concrete, the extent of reaction which occurs within 10 minutes or less is the period of the reaction which is of most importance.

EQUILIBRIUM IN THE LIME-SILICA-WATER SYSTEM

The following hypothetical reactions are presented to show possible stages in the reactions between the lime-silica compound which contains the highest proportion of lime (tricalcium silicate) at the one extreme and hydrated silica plus calcium hydroxide at the other:

$$\begin{array}{lclcl} (CaO)_3\cdot SiO_2 & \leftrightarrows & 3Ca^{++} & + & SiO_5^{---} \\ & & + & & + \\ 6H_2O & \leftrightarrows & 6OH^{-} & + & 6H^{+} \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & 3Ca(OH)_2 & & H_6SiO_5\ (SiO_2\cdot aq.) \end{array} \tag{1}$$

The above equilibria indicate the extremes of the reaction. Possible intermediate stages are:

$$\begin{array}{lclcl} (CaO)_3\cdot SiO_2 & \leftrightarrows & Ca^{++} & + & Ca_2SiO_5^{--} \\ & & + & & + \\ 2H_2O & \leftrightarrows & 2OH^{-} & + & 2H^{+} \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & Ca(OH)_2 & & Ca_2SiO_4 + H_2O\ [(CaO)_2\cdot SiO_2\cdot aq] \end{array} \tag{2}$$

$$\begin{array}{lclcl} (CaO)_2\cdot SiO_2 & \leftrightarrows & Ca^{++} & + & CaSiO_4^{--} \\ & & + & & + \\ 2H_2O & \leftrightarrows & 2OH^{-} & + & 2H^{+} \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & Ca(OH)_2 & & CaSiO_3 + H_2O\ (CaO\cdot SiO_2\cdot aq.) \end{array} \tag{3}$$

$$\begin{array}{lclcl} CaO\cdot SiO_2 & \leftrightarrows & Ca^{++} & + & SiO_3^{--} \\ & & + & & + \\ 2H_2O & \leftrightarrows & 2OH^{-} & + & 2H^{+} \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & Ca(OH)_2 & & H_2SiO_3(SiO_2\cdot aq.) \end{array} \tag{4}$$

Studies on these systems in the fields of geology, soils, and Portland cement, as well as the investigations of this laboratory, undertaken from divergent viewpoints and under greatly varying conditions, indicate that with water and an excess of silica present and at ordinary temperatures and pressures, equilibrium in this system lies in the region represented by Equations 3 and 4. At equilibrium the composition of the solid phase, and therefore of the system, is defined by the hydroxyl-ion concentration of the solution phase (the concentration of calcium hydroxide in solution). By decreasing or increasing this concentration, the equilibrium can be shifted as desired within limits. From these facts it is apparent that beginning with any given mixture of water, calcium silicates, and/or calcium hydroxide and silica the equilibrium established will depend on the ratio of the three components: lime, water, and silica. The sum total of all the work done, both here and elsewhere, is insufficient to define this system completely. The portion of the field particularly investigated in this laboratory to date is that in which silica (diatomaceous earth) is present in excess.

From the results obtained the following general conclusions are drawn: The hydrated lime in solution reacts with the solid diatomaceous earth to form hydrated calcium silicate. The difficulties in the way of determining the exact composition of the solid phase are very great. The average of a number of analyses, however, indicates that the molar ratio of silica to lime in the solid phase is nearly 1.2.

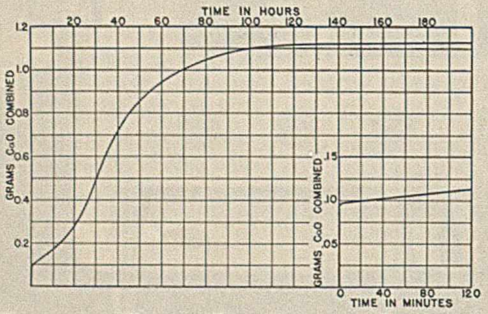

FIGURE 3. TYPICAL TIME-REACTION CURVE FOR DIATOMACEOUS SILICA AND LIME

(10 grams diatomite plus 1 liter saturated lime)

These analyses were made as follows: The solid phase was filtered and washed twice. It was then repeatedly extracted with separate portions of dilute hydrochloric acid until extraction was complete. The undissolved residue was considered to consist of unreacted diatomaceous earth. Microscopic observation confirmed this assumption. The dissolved portion was found to consist of silica, lime, and a trace of alumina. The ratio of silica to lime equal to 1.2 corresponds roughly to a composition represented by the rather complex formula of $5CaO \cdot 6SiO_2$. Variations from this formula were rather in the direction of higher silica content than otherwise. The composition of the solid phase when silica is present in excess is clearly higher in silica than is represented by the simple formula $CaO \cdot SiO_2$.

The solution phase consists of calcium hydroxide, of a soluble calcium silicate, or of mixtures of the two. Above a pH of about 11.0 the solution phase consists almost exclusively of calcium hydroxide. This is indicated by the following values:

CaO per Liter in Soln. Conductivity method	CaO per Liter in Soln. Chem. analysis	pH (Electrometric Method)	SiO_2 in Soln. (Chem. Analysis)
Gram	*Gram*		
0.820	..	..	0.006
0.714	0.6915	12.1	0.003
0.300	0.297	11.5	0.006
...	0.148	10.0	0.083
...	0.112	9.6	0.178

Below a pH value of about 11.0, the calcium silicate begins to be appreciably soluble in the presence of calcium hydroxide.

At equilibrium in the presence of a limited quantity of water and with silica in excess the solution consists of a saturated solution of slightly hydrolyzed calcium silicate.

In the following table, data are given for the equilibrium solution under the conditions described above:

In Soln. per Liter (Chem. Analysis) CaO	In Soln. per Liter (Chem. Analysis) SiO_2	pH	Molar Ratio SiO_2/CaO	Conductivity of Equilibrium Soln.
Gram	*Gram*			*Mho*
0.1120	0.1785	9.6	2.975/2.000	3.83×10^{-4}
0.1105	0.1780	9.6	3.012/2.000	3.83×10^{-4}

The analyses indicate that, for the conditions shown above, the soluble calcium silicate has the composition $2CaO \cdot 3SiO_2$. Consideration of the conductivity and pH values indicate that this calcium silicate is rather highly ionized for this type of compound (the exact percentage of ionization cannot be calculated from the data on hand), but the compound is less than one per cent hydrolyzed.

The general conditions for the equilibrium, as deduced from this study, are as follows for a temperature of 30° C.: With an excess of diatomaceous silica over that required to form a $5CaO \cdot 6SiO_2$, the solid phase will consist of a silicate of this composition plus unreacted silica. The liquid phase will consist of a saturated solution of the molar composition $2CaO \cdot 3SiO_2$. With increasing lime ratio, the solid phase will increase in calcium silicate content, while decreasing in free silica content until all of the free silica is combined. The liquid phase meanwhile will remain unchanged. With increasing proportions of calcium hydroxide, the pH of the solution will increase above a pH value of 9.6, which is the pH of the saturated calcium silicate solution. The solution will be composed of decreasing proportions of calcium silicate and increasing proportions of hydrated lime as the pH increases until at a pH of about 11.2 the calcium silicate will practically have disappeared from solution. At pH values of 11.2 and above, the solution will consist principally of hydrated lime. While the composition of the liquid phase was studied over the range of 9.4 to 12.4 (the pH of saturated lime solution), the composition of the solid phase was studied only for the equilibrium condition where silica was in excess. Shaw and MacIntire (*4*), however, have studied the compositions obtained in both solid and liquid phases where mixtures of silica gel and solid hydrated lime have been caused to react in the presence of water over a considerable range of compositions.

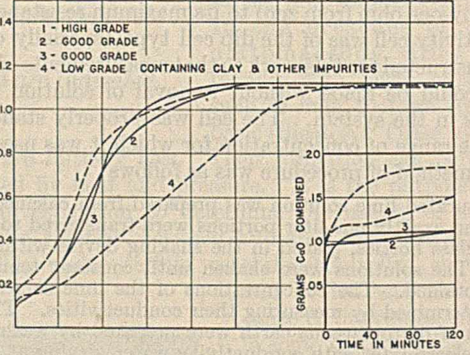

FIGURE 4. TIME-REACTION CURVES FOR DIFFERENT GRADES OF LOMPOC DIATOMACEOUS SILICA

RATE OF REACTION IN THE LIME-SILICA-WATER SYSTEM

In the rate-of-reaction studies the combination of lime with the diatomaceous earth was determined by means of the electrical conductivity of the solution. As a preliminary step, therefore, it was necessary to standardize a special conductivity cell of the dip type and with it to determine the relation of the electrical conductivity of solution against concentration of calcium hydroxide from saturation to a low concentration. This was done, and a curve representing the relationship plotted on large-scale coördinate paper. From these data the concentration of lime in any solution could be determined accurately and with extreme rapidity by determining the conductivity of the solution. By difference the lime combined with diatomaceous earth was calculated. By this method the rate of combination between hydrated lime and diatomaceous silica (where the silica was in excess) was studied over the whole range of reaction from the beginning to practical equilibrium. This method is highly accurate over the earlier range of the reaction. As equilibrium is approached (when most of the lime is removed from solution), however, silica becomes appreciably soluble and the conductivity measured is due to the remaining calcium hydroxide in solution plus (presumably) the effect of the soluble and ionized lime silicate. When silica becomes appreciably soluble, however, the curve (Figure 3) is approaching equilibrium asymptotically, and the presence of the soluble silicate does not materially alter the nature of the curve of reaction.

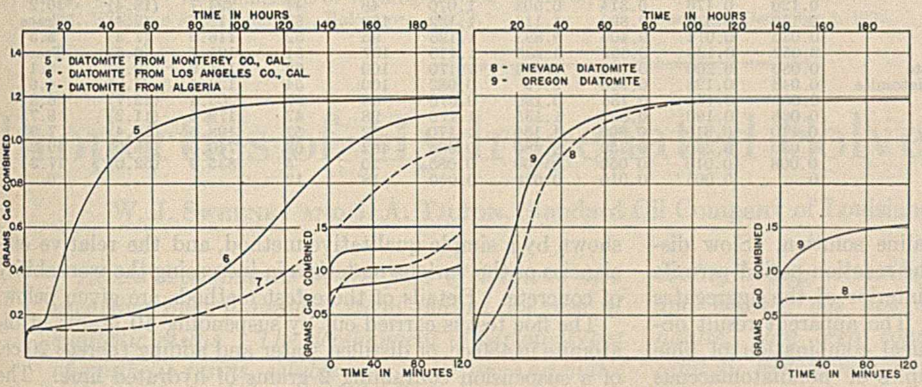

FIGURE 5. TIME-REACTION CURVES FOR VARIOUS DIATOMITES

Figure 3 represents a typical time-reaction curve. In this case 10 grams of a good grade of diatomaceous earth were allowed to react at 30° C. with one liter of saturated lime solution containing approximately 1.19 grams of lime. The data are plotted on a relatively small scale for a period of 200 hours which shows the general trend of the entire reaction. In the lower right-hand corner the early stages of the reaction are plotted on an enlarged scale showing the initial stages of the reaction. Figure 3 is representative of the technic and quantities of reacting materials used throughout this investigation (Figures 3 to 7).

The results indicate that there is an initial, extremely rapid reaction between diatomaceous silica and hydrated lime. This is believed to represent a process in which a coating of highly hydrated calcium silicate gel is formed on the surface of the diatom particles. A very large increase in the volume of the mass of diatomaceous earth and a flocculation of the dispersed diatomaceous particles occur simultaneously with this initial rapid reaction. It is recognized that adsorption effects may account for the removal of some of the lime from solution at the start of the reaction. It is not possible to distinguish between the amounts of lime removed by adsorption and by chemical reaction, although it is believed that the chemical reaction is responsible for most of the lime removed. Following the very rapid initial reaction, there is a period of "inhibited reaction" which usually continues for several hours and during which very little further combination occurs. There is evidence to indicate that the period of inhibited reaction is due to the presence of a hydrated calcium silicate coating on the surface of the diatoms which retards access of the dissolved lime to the underlying opaline silica and prevents further reaction at the extremely rapid rate characterizing the early part of the reaction. Following the period of inhibited reaction, the reaction proceeds at an increasingly rapid rate for a time. It then gradually tapers off, going more and more slowly, as the lime concentration in the solution decreases and equilibrium is approached. The reason for this intermediate increase in rate of reaction is not known. That it is characteristic, however, is indicated by the fact that a great variety of diatomaceous earth samples obtained from numerous sources and subjected to different preliminary treatments all react in the same general manner indicated in Figure 3.

Figure 4 shows the time-reaction curves for several grades of diatomite obtained from Lompoc, Calif., deposits. Sample 1 is a typical high-quality crude, almost entirely free from clay, quartz, organic matter, and other natural impurities. Its high quality is reflected in a high initial and rapid final rate of combination with hydrated lime. Samples 2 and 3 are from slightly lower grades of crude. Their rates of reaction are similar and somewhat lower than sample 1. Sample 4 is a low-grade diatomite from a stratum high in clay and other natural impurities. Its low rate of reaction is probably due to the fact that the clay, organic matter, and similar impurities are capable of adsorbing or combining with lime to some extent.

Figure 5 shows the rate of reaction of diatomites obtained from a wide variety of sources. Their rates of reaction are widely different. The species of diatoms composing the different samples also vary greatly. There is some evidence to support the idea that the chemical composition of the siliceous residues formed by different species of diatoms may differ slightly. The opinion is held that at least a part of the differences noted in the rates of reaction is due to inherent differences in the chemical composition of the diatomites. The degree of hydration of the silica and its physical state of aggregation would also be expected to influence the reactivity. Likewise, the structural configurations of the diatom particles, reflected in surface differences, probably also have some effect. The impurities, present in all of these samples as indicated by chemical and microscopical analyses, are of minor importance (except sample 4, Figure 4).

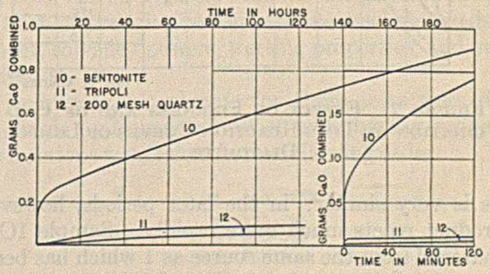

FIGURE 6. TIME-REACTION CURVES FOR SILICEOUS NONDIATOMACEOUS MATERIALS

Figure 6 shows the time-reaction curves for several nondiatomaceous materials. Bentonite is a highly colloidal, claylike material. Tripoli is a cryptocrystalline form of silica, whereas quartz is a definitely crystalline form of silica. These two samples of crystalline silicas have low rates of reaction which differentiate them from the more reactive amorphous, opaline silica of diatomite. The high initial degree of combination of lime with bentonite is probably due to the high adsorption and base exchange properties of the claylike material. The slow, continued combination of bentonite with lime may be explained as follows: Upon placing bentonite in an aqueous solution, there is a tendency for it to form small aggregates of the individual bentonite particles. The aggregated particles swell at the surface, thus sealing off and protecting the interior of the aggregated

TABLE I. CORRELATION OF THE REACTIVITY WITH OTHER PROPERTIES OF VARIOUS DIATOMACEOUS EARTH PRODUCTS AT DIFFERENT TIME INTERVALS

SAMPLE No.	DESCRIPTION OF SAMPLE	REACTION WITH LIME 10 min.	10 hr.	30 hr.	70 hr.	150 hr.	VOL. OF FLOC	IMPROVEMENT IN WORKABILITY OF CONCRETE	LOOSE WEIGHT		RESIDUE ON 200-MESH SIEVE
		Gram CaO combined					*Cc.*	*%*	*Kg./cu.m.*	*(Lb./cu. ft.)*	*%*
1	Lompoc, Calif., diatomite	0.127	0.262	0.730	1.002	1.086	130	88	115.3	(7.2)	4.9
2	Lompoc, Calif., diatomite	0.090	0.174	0.470	1.000	1.108	113	67	136.2	(8.5)	6.6
3	Lompoc, Calif., diatomite	0.098	0.170	0.480	1.045	1.130	118	64	132.9	(8.3)	5.2
4	Lompoc, Calif., diatomite	0.120	0.176	0.314	0.603	1.070	48	44	294.7	(18.4)	10.2
1F	Fines from No. 1	0.150	0.336	0.890	1.118	1.132	160	83	118.5	(7.4)	Trace
1C	No. 1 calcined	0.030	0.074	0.400	0.883	1.126	95	52	116.9	(7.3)	5.5
1FC	Fines from No. 1 calcined	0.052	0.128	0.602	0.935	1.110	137	51	105.7	(6.6)	Trace
5	Monterey Co., Calif., diatomite	0.080	0.200	0.716	1.074	1.170	100	62	156.9	(9.8)	3.1
6	Los Angeles County, Calif., diatomite	0.046	0.128	0.166	2.79	0.982	100	54	126.5	(7.9)	4.6
7	Algerian diatomite	0.082	0.132	0.136	0.180	0.670	68	37	203.4	(12.7)	6.3
8	Nevada diatomite	0.068	0.190	0.830	1.135	1.170	98	47	179.4	(11.2)	8.7
9	Oregon diatomite	0.110	0.319	0.890	1.130	1.170	82	57	198.6	(12.4)	7.9
10	Bentonite	0.080	0.250	0.350	0.480	0.680	462	68	740.0	(46.2)	10.2
11	Tripoli	0.008	0.018	0.050	0.060	0.085	20	5	835.9	(52.0)	17.3
21	200-mesh quartz	0	0.005	0.010	0.029	0.060	18	12	....	....	0

particles from contacting the alkaline solution. Slow dispersal of these aggregates during the reaction period permits the unreacted particles from the interior of the aggregates to react in their normal manner. The apparent result observed is a slow continuous chemical combination of lime with bentonite. All of the samples of nondiatomaceous materials show decidedly different types of time-reaction curves from those which are characteristic of the diatomites.

Figure 7 shows the effect of fineness and of heat treatment upon the reactivity of diatomite. Sample 1 is a typical high-grade diatomite; sample 1F is the air-separated fines from this material. The initial degree of reaction of these two samples is very similar; in the later periods, however, the finer product reacts much more rapidly. Sample 1C represents material from the same source as 1 which has been subjected to calcination at 982° C. (1800° F.). During calcination most of the water of hydration of the opaline silica is removed, although the calcination is not carried to the point where marked crystallization or inversion of the silica has taken place. The removal of water of hydration reduces the reactivity of the diatomaceous silica, as is indicated by the low initial degree of combination of this sample and the slower rate of reaction at later periods. Sample 1FC represents very fine material from the same source as the other three samples of this series which has been calcined. Its rate-of-reaction curve lies intermediate between sample 1C and the uncalcined samples. This is as would be expected.

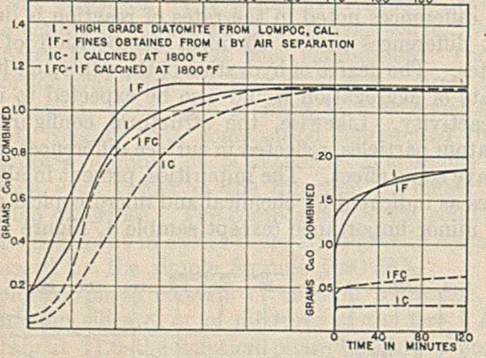

FIGURE 7. EFFECT OF FINENESS AND OF CALCINATION ON TIME-REACTION CURVES OF LOMPOC DIATOMITE

In Table I are given reaction values at different time intervals on the rate-of-reaction curves for the several samples of diatomites studied. These results are compared with the results of other tests made upon the same samples. These other tests give the comparative degrees of fineness of the powders, their bulk densities, their reactivities with lime as shown by a simple qualitative method, and the relative efficiencies of the various materials in increasing the workability of concrete. Details of these test methods are given below.

The floc test is carried out by suspending 10 grams of diatomite in 480 cc. of distilled water and adding thereto 20 cc. of a suspension containing 2 grams of hydrated lime. The mixture is contained in a 500-cc., glass-stoppered graduated cylinder. When the floc formed has settled to a constant volume, the value is recorded. The floc test is a rapid test which has been found to give a fair indication of the purity of the diatomite and of its value for certain purposes, particularly for improving the workability of concrete and mortar.

The effectiveness of the various materials in increasing the workability of concrete was obtained by means of the penetration workability apparatus (*2*, *3*, *5*, *6*) developed first at the Bureau of Standards and extensively investigated at this laboratory.

The bulk density is the weight per cubic foot of the dry powder shaken through a sieve into a cubical container. Fineness is expressed as the percentage retained on the standard Tyler 200-mesh sieve.

Comparison of the results presented in Table I warrant several conclusions:

1. Diatomites react much more vigorously with lime than do nondiatomaceous products of the types represented.
2. Among the diatomites, fineness, heat treatment, and type of diatom affect the rate of combination with lime.
3. The "volume of floc" correlates in a general way with the extent of combination with lime at 10 minutes. Samples 1FC, 4, 7, and 9 depart somewhat from this general relationship. In each case, however, this departure may be explained by some peculiarity of the sample, such as the presence of impurity, the effect of preliminary treatment, etc. This fact renders the floc test of possible value as a rapid method of indicating the quality of diatomite crudes for certain purposes. Very fine samples of diatomite tend to give an unusually high floc test. Bentonite forms a voluminous floc with lime which is in line with its well-known capacity for swelling in the presence of electrolytes.
4. With some exceptions which may be explained similarly to the above, the improvement in the workability of concrete obtained by the use of these samples as admixtures shows a general linear relationship with the extent of combination with lime in 10 minutes. This indicates that the calcium silicate gel formed on the surface of the diatom during the period of mixing and placing of concrete (about 10 minutes) is one of the factors playing a part in the over-all workability effect. A second factor is probably physical; i. e., the heterogeneously sized diatom particles of favorable and very fine particle-size distribution function as a "mechanical lubricant" in the concrete mix thus favoring greater workability of the mass.
5. The ease and rapidity of reaction between the typical base, lime, and diatomaceous silica with the corresponding change in properties of the diatomaceous earth indicates some of the possibilities and limitations in the use of these materials as abrasives, fillers, filter aids, etc., where they come in contact with alkaline solutions.

ACKNOWLEDGMENT

Acknowledgment is made to G. A. Smith, who supervised all determinations of the effect of the various materials on the workability of concrete.

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Properties of Hydrogenated Solvent Naphthas

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Recent developments in the field of lacquers and varnishes show a decided trend toward the use of synthetic resins. The development of various types of synthetic resins, soluble only in the more aromatic hydrocarbon solvents, such as the coal-tar solvents, toluene, xylene, and high-flash coal-tar naphtha, created demands on petroleum refiners to improve the solvency of their products. Among the processes for the manufacture of higher solvency petroleum naphthas, the catalytic high-pressure hydrogenation of naphthenic type petroleum fractions has demonstrated decided possibilities.

Petroleum fractions, such as the extracts obtained from sulfur dioxide treatment of virgin kerosene cuts during the improvement of the latter in burning quality and cracked gas oils of refractory and aromatic nature, have been converted by high-temperature catalytic hydrogenation to lower boiling distillates. These can be separated by distillation into fractions of various boiling ranges and solvency characteristics. Data are presented dealing with the properties of a representative line of such solvents of a wide range of evaporation rates, all of which were finished from the same hydrogenated distillate. These data indicate that this line of hydrogenated solvents possesses sufficiently high solvency powers for satisfactory use with most synthetic resins and offers a wide variety of evaporation rates.

THE widespread use of synthetic resins—for example, the phenol-formaldehyde and the alkyd, or Glyptal, types—has created demands for naphthas of higher solvency than the common run of petroleum solvents marketed in the past. In the early development of these resins a tendency toward the use of the aromatic coal-tar solvents was natural. While the coal-tar solvents such as toluene and high-flash naphtha possess high solvency powers, they have certain objectionable properties, in particular poor odor.

In order to furnish suitable high-solvency petroleum naphthas to comply with the new demands of the lacquer and varnish industries, the refiner has had to devise means of production other than the simple fractionation of even the most aromatic types of natural petroleum naphthas. Pyrolysis of petroleum fractions from naphthenic-base crudes, and pyrolysis followed by extraction are among the recent developments by the petroleum technologists toward producing higher solvency petroleum naphthas. Catalytic hydrogenation of petroleum for lubricating oil improvement, antiknock gasoline production, etc., has been discussed elsewhere (*1A*, *6–9*, *11*). This process may also be applied after selection of suitable conditions of temperature and hydrogen partial pressure to the reforming of petroleum fractions of the type referred to above into naphthas of almost any solvency and boiling range desired. These conditions are high temperature and low hydrogen partial pressure, which favor the production of aromatic or ring-type molecules according to the well-known equilibrium relations between the various types of hydrocarbons. At the same time, impurities such as sulfur, oxygen, and nitrogen are converted to and eliminated as hydrogen sulfide, water, and ammonia. The finishing of these products is accordingly simplified and their degree of purity enhanced.

To view the possibilities of naphthas produced by the hydrogenation process, a critical study of their properties was required. Included in a survey of the general properties of hydrogenated solvents is the application of tests commonly used in both the oil industry and the varnish and lacquer industry to show the relative merits of these solvents—degree of refinement, solvency powers, wetting properties, and evaporation rates.

The hydrogenated solvents for these tests were distilled from a single hydrogenated oil of wide boiling range. The solvent fractions were taken in the following order:

Hydrogenated solvent	1	200–275° F. boiling range
	2	275–365
	3	365–419
	4	419–460

These fractions were made with the aim of covering a wide range of naphthas for practical solvent purposes.

TESTS APPLIED TO HYDROGENATED SOLVENTS

Most of the tests determined on the hydrogenated solvent fractions find general application in either or both the oil and the varnish and lacquer industries. The gravity, color, doctor, copper-strip corrosion, aniline point, distillation, and lamp sulfur are tests that are widely used in the oil industry. Directions for these tests are to be found in an A. S. T. M. report (*1*).

In cases where the aniline point of solvents was below the freezing point of C. P. aniline (21.2° F.), three blends were made—25, 50, and 75 per cent—in an oil of high aniline point. The aniline point values of the blends of solvent and oil were extrapolated to obtain a value for the solvent alone. The accuracy of this method is of course limited; however, by

TABLE I. INSPECTION OF

SOLVENT	GRAVITY	SP. GR. (60/60° F.)	ANILINE POINT[a]	COLOR (SAYBOLT)	DOCTOR TEST	CORROSION (CU STRIP)	CORROSION (HG)	SULFUR (LAMP)	ODOR	FLASH (TAG CLOSED TESTER)	DIMETHYL SULFATE VALUE	DILUTION RATIO
	°A. P. I.		° F.					%		° F.	%	
Hydrogenated solvent naphtha:												
Solvent 1 (200–275° F.)	50.6	0.777	52	+25	Pass	Pass	Pass	0.038	Sweet and slightly aromatic	<60	24.0	1.9
2 (275–365° F.)	34.0	0.855	−1	+23	Pass	Pass	Pass	0.040		61	62.0	2.8
3 (365–419° F.)	26.2	0.897	−10	+23	Pass	Pass	Pass	0.040		135	87.0	2.6
4 (419–460° F.)	19.6	0.937	−33	0	Pass	Pass	Pass	0.042		190	100.0	2.4
Coal-tar solvents, commercial grade:												
Toluene	32.0	0.865	−70	+30	Slightly off	Pass	Pass	0.078	Characteristic	<50	100.0	2.7
High-flash coal-tar naphtha	32.0	0.865	−20	+26	Off	Pass	Pass	0.059	Characteristic	93	100.0	2.5
DATA PUBLISHED BY CLEVELAND PAINT CLUB (*3*)												
Company A:												
Solvent 1	..	...	61	..	......	..	..	...	......	..	34	...
2	..	...	<14	..	......	..	..	...	......	..	49	...
3	..	...	25	..	......	..	..	...	......	..	42	...
3	..	...	52	..	......	..	..	...	......	..	36	...
5	..	...	<14	..	......	..	..	...	......	..	49	...
6	..	...	50	..	......	..	..	...	......	..	32	...
7	..	...	48	..	......	..	..	...	......	..	26	...
8	..	...	<14	..	......	..	..	...	......	..	40	...
Company B:												
Hydrogenated solvent 1	..	...	50	..	......	..	..	...	......	..	31.5	...
2	..	...	25	..	......	..	..	...	......	..	42	...
3	..	...	<14	..	......	..	..	...	......	..	73	...
Company C:												
Solvent 1	..	...	<14		......	..	..	...	......	..	38	...
Company D:												
Solvent 1	..	...	..	..	......	..	..	...	......	..	...	...
2	..	...	..	..	......	..	..	...	......	..	...	...

[a] All aniline points below 21.2° F. extrapolated from values of three blends in a high-aniline-point burning oil.

[b] Kauris calculated from 50/50 blend of solvent in Kahlbaum benzine of 31.5 kauri-butanol value.

extrapolation, relative aniline points can be obtained for the high-solvency naphthas.

The dimethyl sulfate test (*10*) is carried out by mixing together 100 cc. (3.4 fluid ounces) each of dimethyl sulfate and the oil to be tested. The dimethyl sulfate value is taken as the amount of the oil miscible with this amount of the reagent. This test is used as a rough measure of the combined olefins and aromatics present in a solvent.

The gum kauri–butanol test (*10*) is frequently utilized by both the oil refiner and the trade for evaluating solvent naphthas. This test consists essentially of titrating 20 grams (0.7 ounce) of a standard gum kauri solution[1] in a 200-cc. (6.8-fluid-ounce) Erlenmeyer flask with the solvent to be tested. The end point is reached when normally clear liquid acquires a slight turbidity. This is determined by placing a printed page (10-point print) beneath the flask, and noting when the print, as viewed through the solution, just becomes blurred. The number of cubic centimeters of solvent required to produce this end point is called the "kauri-butanol value" of the solvent. With a properly standardized solution the kauri-butanol value of C. P. benzene is 100. In the case of the highest boiling hydrogenated solvent, the kauri-butanol value when determined by the above method is considerably in excess of 100, and it is very difficult to obtain a definite end point. Owing to this fact, alterations were made in the test by blending the high-solvency naphthas with an equal amount of paraffinic petroleum benzine of known kauri-butanol value, and determining the kauri-butanol value of the blend. The kauri-butanol value of the solvent was calculated arithmetically from the kauri-butanol value of the blend. It is recognized that the blended kauri-butanol values are not the true values for a solvent, but the results are reproducible with a greater degree of accuracy and can be used satisfactorily for comparative purposes.

The dilution ratio (*4*) or "cotton tolerance" has widespread applications where solvents are to be used in protective coating prepared with nitrocellulose. A 25 per cent solution of $^1/_2$-second nitrocellulose is prepared with butyl acetate. Ten grams (0.35 ounce) of this solution are agitated by mechanical stirring with successive additions of the solvent to be tested. The ratio, in volumes of solvent per volume of butyl acetate when the nitrocellulose is precipitated from solution, is the dilution ratio. At the end of the test the amount of nitrocellulose in solution should be around 8 per cent. Otherwise, necessary modifications for the base solution are made to give the proper amount of nitrocellulose in solution when the end point is obtained.

The evaporation rates were determined with a Hart evaporation balance (*5*). All of the tests were run at about the same room temperature. Surface tensions were determined against air on a du Noüy surface tension apparatus (*5*).

Gardner-Holt viscosity numbers (*5*) on mixtures of solvents with resins, (*a*) Rezyl 1102 and (*b*) Rezyl 110, were converted from the viscosity in seconds Saybolt Universal determined at 77° F. The viscosity of solvent-resin mixtures measures to an extent the solubility of the resin in the naphtha. The greater the viscosity of the mixture, the less soluble the resin.

PROPERTIES OF HYDROGENATED SOLVENTS

Table I gives the data for the hydrogenated solvents together with the properties of commercial toluene and high-flash coal-tar naphtha. Also, for the purpose of comparison similar results on petroleum solvents as published by the Cleveland Paint Club (*3*) are included. In Figure 1 the evaporation rates for the hydrogenated and coal-tar solvents are shown.

By the standard petroleum tests the hydrogenated solvents demonstrate a high degree of refinement. The low sulfur content and ability to pass the corrosion tests, both copper

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[1] The standard gum kauri solution is made by dissolving 100 grams (3.5 ounces) of gum kauri in 500 grams (17.6 ounces) of *n*-butanol.

Gum Kauri-Butanol Value	Surface Tension at 80° F.	Miscibility with Blown Castor Oil (Baker's 15)	Preformed Glass-Dish Gum	A. S. T. M. Distillation: Initial	10% off at:	20% off at:	30% off at:	40% off at:	50% off at:	60% off at:	70% off at:	80% off at:	90% off at:	95% off at:	Final	Recovery	Residue	Evaporation Rate (Hart Balance): 25%	50%	75%	100%	Gardner-Holt Viscosity No. of Resin Mixtures: Rezyl 1102 (25% in mixture)	Rezyl 110 (50% in mixture)
	Dynes/cm.			° F.												%	%	Minutes					
55.2	24.5	∞	0.0	168	198	206	212	220	228	237	248	260	279	298	322	98.5	1.0	0.75	1.75	2.75	4.25	Too Hy.[d]	B
75.6	29.1	∞	0.0	270	293	299	305	312	317	324	332	342	358	367	397	99.0	0.9	2.5	5.5	9.75	21.25	C	C
77.3[b]	32.3	∞	0.6	352	368	372	376	380	383	387	393	400	412	422	438	99.0	0.8	17.5	35	53	80	C	E
85.7[b]	34.6	∞	3.0	410	423	426	429	432	434	437	442	448	458	465	489	99.0	0.9	180	622	1870	...	A	F
90.1[b]	29.7	∞	0.0	223	228	228	228	228	229	229	229	229	230	230	259	99.5	0.5	3.75	7.5	13	24.5	A	A
72.6[b]	30.4	∞	3.2	294	307	311	315	319	323	328	333	340	352	362	392	99.0	0.5	12.5	26.5	54	92	A	A
59	..	..	...	204	208	213	216	219	222	226	230	236	249	268	271	..	...	2	4	6	11	Too Hy.	F
76	..	..	...	215	218	220	222	223	223.5	224	224.5	226	232	240	240	..	...	5	8	14	25	D	C
66	..	..	...	269	271	272	273	274	274.5	275	276	278	280	284	286	..	...	10	25	44	90	S	T
67	..	..	...	289	295	300	304	308	314	322	330	342	360	378	382	..	...	9	20	30	65	Z-4	D
76	..	..	...	284	302	310	318	325	331	336	342	350	358	370	376	..	...	15	30	53	120	W-X	E
64	..	..	...	312	324	332	340	348	355	362	370	378	390	397	406	..	...	44	72	286	645	Z-6	K
67	..	..	...	364	370	373	375	378	380	384	388	392	400	412	415	..	...	245	435	540	[c]	Too Hy.	N
79	..	..	...	367	372	374	378	380	384	387	391	396	404	412	418	..	...	245	435	540	[c]	T-U	I
55.5	..	..	...	132	161	176	192	206	218	230	242	256	275	278	278	..	...	0.75	1.75	3.25	5.5	Too Hy.	L
63	..	..	...	213	218	224	228	231	235	240	246	255	270	294	296	..	...	1	2.5	4.25	6.5	W	E
78	..	..	...	316	324	331	334	340	346	351	357	366	380	405	405	..	...	12	27	48	79	A	C
68	..	..	...	300	306	310	314	318	322	326	332	340	352	369	377	..	...	13	23	36	52	Z-4	G
..	..	..	...	218	229	235	241	249	255	263	270	281	300	322	334	..	...	2	4	6.5	11	....	..
..	..	..	...	335	340	343	346	349	354	358	362	368	378	387	394	..	...	23	47	72	127[c]	....	..

[c] Oily residue.

[d] Resin and solvent miscible but viscosity is above limits of Gardner-Holt viscosity number scale.

strip and mercury, meet the requirements for high-grade solvent naphthas. The odor, often a criterion in judging solvents, in case of the hydrogenated solvents is mild and inoffensive. The flash test shows that hydrogenated solvents 2, 3, and 4 can be used with relative safety. The hydrogenated solvent 1, owing to its low boiling range, shows a low flash point and appears less desirable from a safety point of view than the others.

One apparent feature of hydrogenated solvents is high evaporation rate for a given mid-boiling point. For instance, hydrogenated solvent 1 with a mid-boiling point of 228° F. shows a total time for evaporation of 4.25 minutes as compared to toluene with a mid-boiling point of 229° F. and a total time for evaporation of 24.5 minutes. This occurs in spite of the fact that toluene is a narrow-boiling fraction with an end point 63° F. lower than hydrogenated solvent 1. Differences of this type exist throughout the entire line of hydrogenated solvents. The probable explanation for this phenomenon is the greater glass-wetting power of the hydrogenated solvent. As a result, a given quantity of hydrogenated solvent on a watch crystal has more exposed surface than an equivalent amount of coal-tar solvent. Using a nickeled surface in place of a glass surface did not change the evaporation rates of the solvents to any appreciable extent. It appears that on certain surfaces the hydrogenated solvents have a marked wetting power. These data confirm the findings of the Cleveland Paint Club (*3*) and certainly point out the difficulty of judging the evaporation rate of a solvent by its distillation curve.

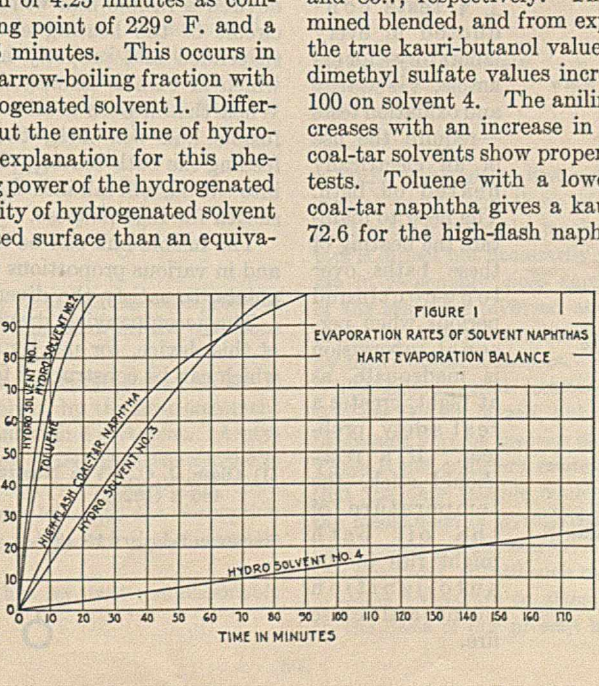
FIGURE 1
EVAPORATION RATES OF SOLVENT NAPHTHAS
HART EVAPORATION BALANCE

Brunkow (*2*) has pointed out that Varnish Makers' and Painters' naphtha, when added to castor oil, forms a turbid mixture and requires a third component such as toluene, butanol, or butyl acetate to give a clear solution. However, the full line of hydrogenated solvents are miscible in all proportion with Baker's number 15 blown castor oil.

As judged by the kauri-butanol values, the dimethyl sulfate values, and the aniline point test, the solvency powers of hydrogenated solvents increase with the boiling range. For example, the kauri-butanol values on solvents 1, 2, 3, and 4 with progressively higher boiling ranges are 55.2, 75.6, 77.3, and 85.7, respectively. The latter two values were determined blended, and from experience are probably lower than the true kauri-butanol values of the solvents. Likewise, the dimethyl sulfate values increase from 24 on solvent 1 up to 100 on solvent 4. The aniline points show corresponding decreases with an increase in the solvent boiling range. The coal-tar solvents show properties of the opposite type by these tests. Toluene with a lower boiling range than high-flash coal-tar naphtha gives a kauri-butanol value of 90.1 against 72.6 for the high-flash naphtha.

This increase in solvency with increasing boiling range seems to hold true also for the solvency of fractions of any individual cut, indicating that during evaporation the solvency of the unevaporated portion will increase progressively. As a corollary it may be that smoother lacquer finishes will result when solvents having this characteristic are used.

The dilution ratio shows an increase from hydrogenated solvent 1 to 2, then a slight decrease for solvents 3 and 4. The values are 1.9, 2.8, 2.6, and 2.4, respectively. Davidson and Reid (4) concluded from dilution ratios on cracked and straight-run gasoline fractions that lower boiling fractions of a given gasoline are better diluents than higher boiling fractions. It is clear from the above dilution ratios that this is not altogether true in the case of hydrogenated solvent naphthas.

Viscosity tests were made on mixtures of each of the four hydrogenated solvents with Rezyl 1102 (25 per cent) and with Rezyl 110 (50 per cent). It will be remembered that the ordinary solvency tests (kauri-butanol value, dimethyl sulfate value) indicate that the solvency of the hydrogenated fractions increases with boiling range. It might be supposed, therefore, that the viscosities of hydrogenated solvent-resin mixtures would decrease with increasing boiling point of the hydrogenated solvent. However, this is not a universal run. For example, the solvent mixtures with Rezyl 1102 decrease in viscosity with an increase in boiling range (hence, kauri-butanol value), whereas the opposite is true with solvent mixtures of Rezyl 110.

The two coal-tar solvents tested—namely, toluene and high-flash coal-tar naphtha—give low-bodied mixtures with both Rezyl 1102 and Rezyl 110. With the latter the high-flash coal-tar naphtha shows a Gardner-Holt viscosity number A. Hydrogenated solvent 4 mixed with the same resin shows a Gardner-Holt viscosity number F. Yet the kauri-butanol value of hydrogenated solvent 4 is 85.7 *vs.* 72.6 for the high-flash coal-tar naphtha. Also, both solvents show dimethyl sulfate values of 100, and aniline points of −33° and −20° F. for hydrogenated solvent 4 and the high-flash coal-tar naphtha, respectively. With Rezyl 1102 both solvents give Gardner-Holt viscosity number A. Here again it is clearly shown that the solvency tests are not reliable in all instances. These facts apparently point out the necessity for practical trials of solvents for their intended purposes unless by experience the lacquer or varnish maker knows the particular test that applies to his work.

The surface tensions of the hydrogenated solvents increase in the order of their boiling ranges. The results determined on a du Noüy tensiometer range from 24.5 dynes per centimeter for hydrogenated solvent 1 to 34.6 dynes for hydrogenated solvent 4. The surface tensions of the hydrogenated solvents compare favorably with the results obtained for toluene and high-flash coal-tar naphtha. The latter are known to have excellent wetting properties.

Thus the above tests indicate that hydrogenated solvents surpass the usual petroleum solvent naphtha in solvency power, and compare favorably with commercial coal-tar solvent naphthas.

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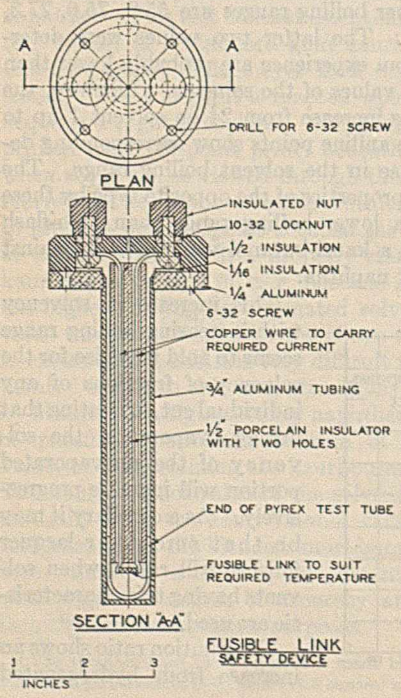
RECEIVED October 4, 1933. Presented before the Division of Paint and Varnish Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Preventing Overheating of Oil Baths

HARRY LEVIN AND RAYMOND LANARI, Beacon Laboratory, The Texas Company, New York, N. Y.



FUSIBLE LINK SAFETY DEVICE

NUMEROUS tests conducted in every laboratory—for example, viscosity and oxidation tests—require the use of an electrically heated oil bath. The need to maintain the heating of these baths over long-continued periods when personal supervision is inadequate, as at night, creates a real safety problem. If a relay should stick, the temperature of the oil bath might rise to the auto-ignition point and cause fire.

In order to prevent such occurrence, the authors have devised a fusible link which is incorporated in the electrical circuit of the heating element of the bath. This link is suspended and properly insulated in a thin metal sheath, which in turn is immersed in the oil bath to be protected. When the oil bath attains a predetermined temperature the fusible link will melt, thus breaking the electrical circuit feeding the bath heater. The molten link, instead of falling into the oil, will fall into the glass tube contained in the metal sheath for that purpose.

The fusible link can be made of numerous components (*1*) and in various proportions to yield alloys of different melting points, to satisfy the diverse needs as regards temperature.

The accompanying drawing illustrates a convenient form of this device, for use by vertical insertion in an oil bath, which can be constructed for approximately five dollars.

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RECEIVED February 15, 1934.

CORRESPONDENCE

Mechanism of Formation of Aromatic Hydrocarbons by Pyrolysis

SIR: In the paper by H. P. A. Groll on "Vapor-Phase Cracking" [IND. ENG. CHEM., 25, 784–98 (1933)], certain conclusions were drawn from our previously published researches on the pyrolysis of hydrocarbons. We are unable to concur with those conclusions.

The mechanism suggested by us for the formation of aromatic hydrocarbons from gaseous paraffins and olefins is criticized and the conclusion arrived at that propylene and not ethylene is the essential intermediate in the formation of aromatics. The statement is then made that ". . . propylene forms aromatic hydrocarbons more readily and with higher yields than ethylene or butylene, an observation which can also be made from Wheeler's experiments, though he did not arrive at this conclusion. According to Dunstan and Wheeler's theories one would expect just the opposite."

Briefly, the points we would make are:

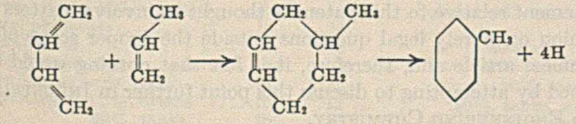
1. The yield of aromatic hydrocarbons obtainable from the olefins, expressed in gallons per 1000 cubic feet of gas, increases as the series is ascended. The yield from propylene is not greater than that from the butylenes.

2. The weight conversions to liquid hydrocarbons (to which, presumably, Groll refers) are with propylene 40.6 per cent and with the butylenes 39.6 per cent. These figures give the total oil obtained, and it should be stressed that, since the temperature gap between two consecutive experiments was not less than 50° C., and no effort was made to obtain the true optimum conversions, any conclusions based on the difference between 40.6 and 39.6 per cent are worthless.

3. When the production of motor benzene is considered, the corresponding conversions by weight for propylene, 1,2-butylene, and 2,3-butylene are 20.4, 23.6, and 25.8 per cent, respectively. Here the advantage is in favor of the butylenes.

4. That ethylene, and not propylene, is an essential intermediate in the formation of aromatic hydrocarbons is supported by the following experimental result: Under suitable conditions, with ethylene at 750° C., a conversion by weight to liquid hydrocarbons as high as 65 per cent, expressed on the ethylene decomposed, is attained; with propylene and the butylenes a conversion of 42 per cent, expressed similarly, is not surpassed.

5. We have observed that the ratio of toluene to benzene in the aromatic liquids obtained by pyrolysis is greater with propylene than with the other olefins, and, by analogy with the mechanism suggested for benzene formation, we have:



In support of this mechanism it may be stated that the presence of methyl cyclohexenes has been indicated in the fractions obtained from the pyrolysis of propylene.

6. Acetylene is not so reactive as Groll states. This is shown both by Davidson[1] and ourselves, by the heat treatment of synthetic mixtures of gaseous paraffins and acetylene. Acetylene was invariably detected in the exit gases from the synthetic mixtures but not, under similar temperature conditions, from the pure paraffins. Groll is therefore left with the conception of "nascent" acetylene $H\underset{|}{C}{=}\underset{|}{C}H$ as the parent of the aromatic hydrocarbons. Having proceeded thus far, is it not reasonable to postulate, with a certain amount of experimental evidence, the existence of the radicals $-CH_3$, $=CH_2$, and $\equiv CH$ and from these to construct any hydrocarbon?

7. When gaseous hydrocarbons are decomposed by heat under mild conditions, the liquids obtained contain large quantities of unsaturated hydrocarbons including cyclohexene, methyl cyclohexenes, and some cyclohexenes. We believe that these hydroaromatic hydrocarbons are the forerunners of the aromatic hydrocarbons found to predominate when conditions are more drastic. The presence of these hydrocarbons cannot readily be explained by the polymerization mechanism suggested by Groll.

8. Our experiments indicate that the primary reaction of ethylene is a true polymerization to butylene, followed by secondary reactions involving the formation of butadiene and hydrogen in one case, and propylene and methane in the other. Our work does not confirm the statement made by Groll that above 500° C. propylene prevails increasingly over butylene in the products obtained by the heat treatment of ethylene.

It was from our work with the paraffin hydrocarbons that ethylene was concluded to be the essential intermediate in the formation of aromatic hydrocarbons. It should be manifest that in the pyrolysis of the olefins the mechanism need not follow the exact lines indicated for the paraffins, and that butylene for the synthesis need not be produced by the polymerization of ethylene. Thus, with propylene the primary products of decomposition are ethylene and butylene, followed by the secondary formation of butadiene from the ethylene. Decomposition of butylene produces butadiene, ethylene, and propylene. It follows that, if butadiene is regarded as the keystone, the following reactions, with the olefins present, may occur:

a. With ethylene to give cyclohexene and thence benzene.
b. With propylene to give methylcyclohexene and thence toluene.
c. With 1,2-butylene to give ethylbenzene and thence styrene.
d. With 2,3-butylene to give dimethylcyclohexene and thence *o*-xylene.

Evidence of the occurrence of these reactions is forthcoming.

E. N. HAGUE
R. V. WHEELER

UNIVERSITY OF SHEFFIELD
SHEFFIELD, ENGLAND
February 3, 1934

. . . .

SIR: Although at first sight it may appear that my experimental results and those of Hague and Wheeler lead to conflicting theories on the mechanism of pyrolysis of hydrocarbons, this is in fact not necessarily the case. Our experimental results are in reasonably close agreement considering the complexity of the reactions involved and the difficulty of securing experiments by different conditions for reactions which are influenced by many different factors.

The experimental results obtained not only by Hague and Wheeler and by myself, but also by other workers, may be used to support various theories of mechanism according to preference. There is not sufficient evidence for any finality, and it is likely that the only reliable evidence will arise from examination of the mechanism of pyrolysis by exact physical methods such as have recently been started by workers in our own laboratories and elsewhere. Until such methods have been further expanded, it seems premature to attempt to build theories of mechanism on the basis of our present knowledge of the accumulative end

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[1] J. IND. ENG. CHEM., 10, 901 (1918).

products of a complex series of reactions. However, it is believed that the formation of free radicals and their participation in a series of ensuing chain reactions will undoubtedly play an important part in the formation of aromatics as of other products of pyrolytic change.

A point-by-point answer to Hague and Wheeler's argument would only lead to controversy which could be of little value because the experimental evidence is not sufficient to support it. Therefore I limit the following to three essential points based upon recent experiments in this laboratory:

1. When checking the experiments of Davidson[1] I found to my surprise that acetylene is always formed when propylene, propane, or any other hydrocarbon is cracked in the vapor phase. Its occurrence is always coincidental with tar formation; i. e., with propane or propylene it will be found from about 600° C. upward, as follows:

GAS	ACETYLENE IN EXIT GAS AT:				
	600° C.	650° C.	700° C.	750° C.	800° C.
	%	%	%	%	%
C_3H_8	Trace	0.03	0.08	0.19	0.32
C_3H_6	0.01	0.04	0.20	0.23	0.36
95% C_3H_8 + 5% C_2H_2, turbulent flow by use of baffles					0.66
95% C_3H_8 + 5% C_2H_2, laminary flow					1.08

The results show that at 800° C. the remnant acetylene from propane containing 5 per cent acetylene is nearly as low as from pure propane,[2] provided the experiment is carried out in such a manner that no considerable portion of the gas can pass through the tube without ever coming near the hot walls.

2. By adding up Hague and Wheeler's equations in the same manner as had been done in my paper, the following summary equation is found,

$$C_nH_{2n} \longrightarrow \frac{n}{6} C_6H_6 + \frac{n}{2} H_2 \qquad \text{(A)}$$

as against Equation 11 of my paper

$$C_nH_{2n} \longrightarrow \frac{n}{9} C_6H_6 + \frac{n}{3} CH_4 \qquad \text{(B)}$$

Equation A would call for a yield of 93 per cent aromatics and Equation B for a yield of 62 per cent. Formation of aromatics with aliphatic side chains should increase the yield according to (B) more than according to (A). By considering the amount of unchanged olefin, the actual yields obtained by any investigator agree much closer with Equation B than with A.

3. When cyclohexene is subjected to pyrolysis, rupture of the ring occurs more readily than dehydrogenation;[3] therefore we question the soundness of considering cyclohexene as an essential intermediate to the formation of aromatic compounds. According to experiments in this laboratory, cyclohexene at 800° C. does not form more aromatic hydrocarbons than any other olefin, while the gas formed as always contains 3 or more parts methane to 1 part hydrogen. Consequently the theory of Hague and Wheeler does not find such support in the behavior of its last intermediate compound, cyclohexene, as do the theories of Berthelot, Haber, and others whose last intermediate, acetylene, gives an excellent yield of aromatic hydrocarbons.

Considering the relative ease with which, according to Lenher[4] and others, the lower olefins are changed into one another, no considerable difference in the yield of aromatic hydrocarbons from any olefin should be expected, provided conditions are arranged so that no excessive amounts of olefin remain unchanged.

Up to the present all investigators, including Hague and Wheeler, have reported lower yields of aromatic hydrocarbons from ethylene than from its higher homologs because more of this hydrocarbon remained unchanged in the usual single-pass experiments. The high yield of 65 per cent quoted in Hague and Wheeler's letter differs so widely from any published result that in the absence of any experimental details it is difficult to make useful comment.

H. P. A. GROLL

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIF.
April 3, 1934

Colloidal Bentonite-Sulfur

SIR: In the March, 1934, issue of INDUSTRIAL AND ENGINEERING CHEMISTRY (Vol. 26, pp. 340–5) an excellent article on "Colloidal Bentonite-Sulfur, A New Fungicide" by A. S. McDaniel appeared. The world looks to this journal for the continuous record of the progress in industrial chemistry, and to maintain this high and authoritative position it is essential that articles of this kind should be accurate and as complete as is practicable.

This article is incomplete in that it fails to make any mention of U. S. Patent 1,742,472 (issued to the writer in 1930) which is the dominating patent in the field of sulfur-bentonite mixtures. The Sherwin-Williams Company, the present owner of this patent, has licensed the Niagara Sprayer Company to operate under the same, and the sulfur-bentonite mixtures which they are so successfully marketing lie within the scope of this patent.

On page 341, the last sentence in the third paragraph from the end of the first column, reads as follows: "Incidentally, attempts to produce a so-called dry lime sulfur had not proved satisfactory." If the reader of this understands that this refers merely to attempts on the part of the Niagara Sprayer Company, there is no harm done, but if he should be misled into accepting it as a general statement of fact, a great injustice would be done to those dry lime sulfurs which have met with so much success in the insecticide and fungicide fields.

E. C. HOLTON

THE SHERWIN-WILLIAMS COMPANY
CLEVELAND, OHIO
March 15, 1934

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SIR: The primary purpose of the article referred to by Holton was to discuss the properties, etc., of the new product made by absorbing fluid (preferably liquefied) sulfur into dry bentonite. Since this product or method is not described in U. S. Patent 1,742,472, it was not cited in the literature references.

In so far as Holton's statement refers to the existence of a license agreement under U. S. Patent 1,742,472, it is, of course, true, and this fact is freely admitted. The remainder of Holton's statement relative to this patent is thought to involve matters of opinion on purely legal questions outside the proper scope of a technical article and, therefore, it is felt that nothing would be gained by attempting to discuss this point further in INDUSTRIAL AND ENGINEERING CHEMISTRY.

With reference to the statement in the article about dry lime sulfur, which Holton quotes, attention is called to the fact that this statement clearly refers to the situation at the time, several years ago, when colloidal bentonite-sulfur was being considered for commercial development and represents only the opinion of the author of the paper on the situation as it then existed, and not necessarily that of anyone else. Each reader is entitled, of course, to his own views on the facts within his knowledge on the situation as it now exists with respect to dry lime sulfur, which was not discussed.

A. S. MCDANIEL

NIAGARA SPRAYER AND CHEMICAL COMPANY, INC.
MIDDLEPORT, N. Y.
April 4, 1934

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[2] The main factor which may obscure the presence of acetylene is its high solubility in the tar. For instance, it is not found if the tar is removed by excessive cooling or by absorption on charcoal. The acetylene was determined according to Schuftan, "Gasanalyse in der Technik," p. 44, S. Hirzel, Leipzig, 1931.

[3] Schmidt, O., *Z. Elektrochem.*, **39**, 975 (1933).

[4] *J. Am. Chem. Soc.*, **53**, 3752 (1931).

MARKET REPORT—MAY, 1934

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, MAY 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

NEWER CHEMICALS

Acetaldehyde, drums, lc-l., wks.	lb.	.16
Acetaldol, 50-gal. drums	lb.	.27
Acetamide, drums	lb.	.40
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.07
Adipic	lb.	.72
Furoic, tech., drums	lb.	.35
Linoleic	lb.	.16
Naphthenic, drums	lb.	.10
Sebacic, tech.	lb.	.58
Ammonium linoleate, drums	lb.	.12
Ammonium oleate	lb.	.10
Aroclors	lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	.65
Calcium furoate, tech., drums	lb.	.25
Capryl alcohol, tech.	lb.	.85
Pure	lb.	2.50
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Crotonaldehyde, 50-gal. drums, c/l.	lb.	.26
Dichloroethyl ether, 50-gal. drums, c/l.	lb.	.21
Diethylene glycol, drums	lb.	.14
Monobutyl ether, drums	lb.	.26
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.26
Dimethylamine, pure 25 & 40% sol. —100% basis, drums	lb.	1.20
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.15
Ethyl acetoacetate, 110-gal. drums	lb.	.37
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 phthallate	lb.	.26
Glycol stearate	lb.	.18
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
Phosphorus oxychloride, 175 cyl.	lb.	.20
Potassium abietate	lb.	.06
Sodium abietate	lb.	.06
Sodium alginate	lb.	.50
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.15
Distilled	lb.	.40
Tetrachloroethane, 50-gal. drums	lb.	.08½
Trichloroethylene, 50-gal. drums	lb.	.09½
Triethanolamine, 50-gal. drums	lb.	.35
Trihydroxyethylamine linoleate	lb.	.40
Trihydroxyethylamine stearate	lb.	.35
Vinyl chloride, 16-lb. cyl.	lb.	1.00
Zinc perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

CHEMICALS PREVIOUSLY QUOTED

Acetanilide, U. S. P., powd., bbls.	lb.	.26
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks., c/l.	lb.	.11
Acetphenetidin, bbls.	lb.	1.30
Acid, acetic, 28%, c/l., bbls.	100 lbs.	2.91
56%, c/l., bbls.	100 lbs.	5.50
Glacial, c/l., bbls.	100 lbs.	10.02
Glacial, U. S. P., c/l., carboys	100 lbs.	10.52
Acetylsalicylic, bbls.	lb.	.70
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb.	.40
Boric, bbls.	lb.	.04
Butyric, 100% basis, cbys.	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.04½
Chromic, 99%, drums	lb.	.15½
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.28
Cresylic, pale, drums	gal.	.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.	1.45
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, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.10½
Denatured, No. 5, comp. denat., c/l., drums	gal.	.34
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	.75
Isopropyl, ref., drums	gal.	.50
Propyl, ref., drums	gal.	.75
Wood, *see* Methanol		
Aldol, 95%, drums, c/l.	lb.	.21
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.33

Alum, ammonia, lump, bbls., wks.	100 lbs.	3.00
Chrome, casks, wks.	100 lbs.	7.00
Potash, lump, bbls., wks.	100 lbs.	3.00
Soda, bbls., wks.	100 lbs.	4.00
Aluminum, metal, N. Y.	100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.04
Aluminum stearate, 100-lb. bbl.	lb.	.17
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.35
Iron-free, bags, wks.	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks.	lb.	.04½
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.15¼
Bromide, bbls.	lb.	.39
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.50
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	4.30
Nitrate, tech., cryst., bbls.	lb.	.08½
Oxalate, kegs	lb.	.24
Persulfate, cases	lb.	.20
Phosphate, dibasic, tech., bbls.	lb.	.08½
Sulfate, bulk, wks.	ton	25.00
Amyl acetate, tech., from pentane, tanks, delivered	lb.	.135
Aniline oil, drums	lb.	.16½
Anthracene, 80–85%, casks, wks.	lb.	.75
Anthraquinone, subl., bbls.	lb.	.45
Antimony, metal	lb.	.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.	1.30
Bismuth, nitrate, 25-lb. jars	lb.	1.20
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.55
Blanc fixe, dry, bbls.	ton	70.00
Bleaching powder, drums, wks.	100 lbs.	1.90
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.018
Bordeaux mixture, bbls.	lb.	.10½
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butyl acetate, drums, c/l.	lb.	.11
Cadmium bromide, 50-lb. jars	lb.	1.25
Cadmium, metal, cases	lb.	.55

Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	1.85
Calcium acetate, bags	100 lbs.	3.00
Arsenate. bbls	lb.	.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.	.53
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.	8.50
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
Dianisidine, bbls	lb.	2.35
Dibutylphthalate, drums, wks	lb.	.20½
Diethylaniline, drums	lb.	.52
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.29
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, tech., drums	lb.	.17
Dinitrochlorobenzene, bbls	lb.	.14½
Dinitronaphthalene, bbls	lb.	.34
Dinitrophenol, bbls	lb.	.23
Diphenylamine, bbls	lb.	.31
Diphenylguanidine, bbls	lb.	.36
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.75
Ether, conc., drums	lb.	.09
Ethyl acetate, tanks, c/l	lb.	.07½
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylenechlorohydrin, anhyd. drums	lb.	.75
Glycol, c/l., wks	lb.	.26
Feldspar, bulk	ton	10.00
Ferric chloride, tech., bbls	lb.	.05
Ferrous chloride, cryst., bbls	lb.	.06
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls	100 lbs.	1.10
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, c. p., drums	lb.	.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.	4.00
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls	lb.	.08
Oxide, litharge, bbls	lb.	.06¾
Peroxide, drums	lb.	.20
Red, bbls	lb.	.07¾
Sulfate, bbls	lb.	.06
White, basic carb., bbls	lb.	.06½
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.,	280 lbs.	1.70
Limestone, ground, bags, wks	ton	4.50
Lithopone, bbls	lb.	.04½
Magnesite, calcined, 500-lb. bbls., wks	ton	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	76.50
Meta-nitroaniline, bbls	lb.	.67
Meta-phenylenediamine, bbls	lb.	.82
Meta-tolylenediamine, bbls	lb.	.67
Methanol, pure, synthetic, drums, delivered, c/l	gal.	.37½
Tanks, delivered	gal.	.35½
Methyl acetone, drums	gal.	.54½
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls	lb.	2.50
Naphthalene, flake, bbls	lb.	.06
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.11½
Double, bbls	lb.	.11½
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.09
Oil, castor, No. 1	lb.	.10¼
China wood, bbls	lb.	.08⅞
Coconut, Ceylon, tanks	lb.	.02⅜
Cod, N. F., bbls	gal.	.48
Corn, crude, tanks, mills	lb.	.04⅝
Cottonseed, crude, tanks	lb.	.04
Linseed, bbls	lb.	.101
Menhaden, crude, tanks	gal.	.20
Neat's-foot, pure, bbls	lb.	.12
Oleo, No. 1, bbls	lb.	.06
Olive oil, denat., bbls	gal.	.88
Foots, bbls	lb.	.07
Palm, Lagos, casks	lb.	.03⅞
Peanut, crude, tanks	lb.	.05⅛
Perilla, bbls	lb.	.09
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-toluidine, bbls	lb.	.56
Paris Green, 250-lb. kegs	lb.	.23
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.52
Phenylethyl alcohol, 1-lb. bot	lb.	3.75
Phosphorus, red, cases	lb.	.45
Phosphorus trichloride, cyl	lb.	.18
Phthalic anhydride, bbls	lb.	.14½
Platinum, metal	oz.	36.00
Potash, caustic, drums	lb.	.07¼
Potassium acetate, kegs	lb.	.27
Bicarbonate, casks	lb.	.07½
Bichromate, casks	lb.	.08⅛
Binoxalate, bbls	lb.	.14
Bromide	lb.	.35
Carbonate, 80-85%, calc., casks	lb.	.07
Chlorate, kegs	lb.	.09
Chloride, crystals, bbls	lb.	.04¾
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.10½
Muriate, fert., bulk	ton	35.55
Permanganate, drums	lb.	.18½
Prussiate, red, casks	lb.	.39
Yellow, casks	lb.	.18
Titanium oxalate, bbls	lb.	.32
Pyridine, drums	gal.	1.25
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P.	lb.	.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.	.32⅞
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.23
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.60
Sodium acetate, bbls	lb.	.05
Benzoate, bbls	lb.	.45
Bicarbonate, bbls	100 lbs.	1.85
Bichromate, casks	lb.	.06½
Bisulfite, bbls	lb.	.03
Bromide, bbls., U. S. P	lb.	.35
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls	lb.	.07½
Metallic, drums, 12¼-lb. bricks	lb.	.19
Metasilicate, cryst	100 lbs.	3.25
Metasilicate, gran., bbls	100 lbs.	2.65
Naphthionate, bbls	lb.	.52
Nitrate, crude, 200-lb. bags, N. Y.	100 lbs.	1.315
Nitrite, bbls	lb.	.07¼
Perborate, bbls	lb.	.17
Peroxide, cases	lb.	.20
Phosphate, trisodium, bbls.	100 lbs.	2.50
Phosphate, disodium, bags	100 lbs.	1.90
Picramate, kegs	lb.	.67
Prussiate, bbls	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.80
Silicofluoride, bbls	lb.	.05
Stannate, drums	lb.	.35
Sulfate, anhyd., bbls	100 lbs.	2.20
Sulfide, cryst., bbls	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls	lb.	.30
Thiosulfate, reg., cryst., bbls.	lb.	.02½
Tungstate, kegs	lb.	.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.	.55⅛
Tin tetrachloride, anhydrous, drums, bbls	lb.	.26
Oxide, bbls	lb.	.57
Titanium dioxide, bbls., wks	lb.	.17¼
Toluene, tanks	gal.	.30
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls	lb.	.37
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.15
Whiting, bags	ton	7.00
Xylene, 10°, tanks, wks	gal.	.29
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	4.35
Zinc ammonium chloride, bbls	lb.	.05
Chloride, granulated, drums	lb.	.05⅜
Oxide, Amer., bbls	lb.	.06¾
Stearate, bbls	lb.	.18
Zinc dust, bbls., c/l	lb.	.0640

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† 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.