

Industrial *and Engineering* Chemistry



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Letting the Consumer Do It

THE establishment of the joint laboratory for the testing of textiles, to be maintained primarily by cleaners, dyers, laundry owners, garment and textile product producers, and retail merchants, and having in affiliation certain fiber and fabric manufacturers, seems to us another case where an industry is content to let the consumer undertake the research. This may be expected ultimately to give the consumer a better knowledge than many of the manufacturers have of the facts underlying the industry. It is obvious that no manufacturer should be content to know less than anyone else about his business, and particularly the scientific facts underlying it. This is not to be mistaken as taking exception to the establishment of the joint laboratory, of which the Better Fabrics League is the sponsor, for we believe the public will be the direct beneficiary. We are simply impatient with the great textile industry of the country, which has been so indifferent as a whole to what it should do in these days of theoretical and applied science. We are not forgetting the very short list of notable exceptions.

The statement is made that the people in the United States today spend a billion dollars annually for the care of garments and other textiles. This means the frequent cleansing of all classes of fabrics, some of which are so unserviceable that they do not stand the normal process of cleaning. Others have hidden defects which appear only after the process of laundering or cleaning. These two sorts of weakness cause fifty million dollars a year to be paid out by laundry and cleaning establishments in reimbursing their customers.

The new laboratory is to center attention on the practical wear and maintenance of apparel and household goods. The research will be confined to the fibers themselves or to single features of the fibers or fabrics. The laboratory, while operated on a non-profit basis, will charge non-members commercial rates, and in testing fabrics for buyers and others will have as its first aim the determination of the serviceability which the goods will yield consumers. The laboratory also hopes to prepare definite instructions for laundries and cleaners, so that wearing apparel made from new fabrics and fibers can be given proper attention without in any wise becoming damaged. While the laboratory will not condemn any fabric, it will approve the better fabrics.

This new project, established in the interests of the consumer, does not relieve the textile industry from serious consideration of the several plans that have been constantly urged before it. In contrast with what is not being done in the United States, a note from the American commercial attaché at Paris with respect to the interest of the Soviet Government of Russia in textile research is interesting. In Russia there has been established an institute for textile research which will utilize the laboratories in educational institutions at the start and later expects to establish special experiment stations. Studies will be devoted to the different fibers now existing in the Union of Soviet Socialist Republics, paying attention to their chemical, physical, and technologic

properties. Methods for the treatment of such fibers, standards of raw materials, research for the discovery of new fibers, and the perfection of both the mechanical and chemical processes now employed by the Soviet textile industries with a view to lowering costs, together with the study of different phases of production, are a part of the important program.

Our textile industry at times has shown some increase of interest in science, but there is still lacking, so far as we are aware, any strong united effort looking to the support of a really adequate program.

Danger Signals

MANY clever and reliable devices, designed to give an automatic and prolonged signal in case of approaching danger, are to be found in manufacturing establishments. If a tank threatens to overflow, bells ring and lights flash. Similar signals indicate too low a level in such tanks. Electricity is automatically switched off when overheating is imminent, and now the televox promises to reach the stage where impending dangers will be reported.

Some such persistent and automatic danger signal which will continue its warning until the danger has been averted seems to be needed in these days of quantity production and high-pressure methods. We are using many raw materials at a prodigious rate and taking no thought for their continued supply, though exhaustion can be forecast. We sympathize with the point of view that rarely can one predict the requirements of the next generation, but we shall not have to wait for the next generation to see embarrassment in some raw materials, if no early steps are taken to supplement them.

To cite a specific instance, what do the tanners propose to do when a time of famine comes for tanning materials? This famine is seen by specialists as a reality within fifteen or twenty years. It will be due partly to the increased demand for vegetable tanning materials and, more particularly, to the destruction of our chestnut forests by chestnut blight. It is paradoxical that at the moment we have an abundant supply of tanning extracts. But do not be misled. This abundance in itself marks the passing of our chestnut trees, for much tannin is obtained from the bark and wood of dead trees and this source for several years to come will yield a considerable supply. In order to obtain as much as possible from the dead trees, the extraction is going on at a more rapid rate than normal. Obviously, this is a resource of the most temporary nature.

It is none too early to begin on research work which, it may be hoped, will make available an equivalent when the need arises. Already research men have called attention to the situation, but those in authority are complacent with present supplies and perhaps feel that a magician will appear when the time arrives and definitely shake from his sleeve the perfect formula for the ideal equivalent. Technical

men know it is not done that way. Research programs on tanning materials should be laid down now and supported under able leadership, adequately and continuously, until a satisfactory future program is known to have been evolved.

Welcome, British Chemists

LATE this month a larger number of the chemists of Great Britain will enter our country in a body than has come to us for many years—certainly not since the Eighth International Congress of 1912. Our colleagues come for two meetings—the annual one of the Society of Chemical Industry and a joint gathering with the American Institute of Chemical Engineers. While the two groups will convene separately—the former in New York the first week in September and the Institution of Chemical Engineers with the American Institute of Chemical Engineers at Niagara Falls, August 24 and 25—they will join on some occasions and will participate in an industrial tour of eastern Canada and the United States.

As this is written, the number of visitors from overseas is uncertain, but it will probably approach two hundred and will include many whose names are familiar to American chemists.

These visitors with whom we have so much in common are heartily welcome. It is hoped that what has been planned for them will prove interesting and instructive and that the several programs arranged may not prove too strenuous or tiring. It is regretted that time does not make possible a more extended tour westward both in Canada and in the United States, for far too few of our visitors from abroad have an opportunity to acquire a real idea of what the North American Continent and its people are. We should be glad if the entire English party could join with the AMERICAN CHEMICAL SOCIETY at its annual meeting in Swampscott, though we fear that the necessity of early return home may make this impossible for some of our visitors. Wherever the party finds itself, we are confident there will be American chemists, whether members of the visiting organizations or not, who will welcome the opportunity to have a part in the entertainment, show with care and courtesy whatever may be of interest locally, and do everything within their power to send our colleagues home again with nothing but pleasant recollections of their experiences.

The American Institute

THE American Institute of the City of New York for nearly one hundred years has been the chief patron of various industrial fairs in the city of New York. In the early days its principal activity was to show the city all that was new in horticulture, industry, agriculture, and commerce, but of late specialized exhibits offered at various times of the year have taken the place of these older displays.

The officials of the Institute have decided that it must take up new activities and, as we are pleased to note, have decided to concentrate on service to science through the encouragement of fundamental research. It plans to do this by becoming an intermediary between scientists and the people in an effort to bring about better understanding and appreciation, which is so necessary for the advancement of scientific work. The lecture platform has been chosen as the chief means for interpreting contemporary research. Motion pictures are to be used, the radio will not be neglected, and eventually the research student's work may be further popularized through the medium of dramatization.

The chemist knows better than most scientists how difficult is the task and how great the reward in the humanizing of science. The laborers in this field have been comparatively few. It is therefore heartening to be able to welcome as a recruit an institute founded in 1828 in answer to Henry Clay's plea that something be done to ameliorate the internal condition of the country. The new work will answer Clay's plea even more satisfactorily than the initial enterprises.

Shall the Sulfur Tolerance Be Raised?

THERE are many examples of failure to put to proper use knowledge established through the work of science. But there is seldom justification for it. The suggestion made in this issue that we should now refine petroleum with respect to the temperatures at which the gasoline is to be used is a case in point. If, as the author of that article maintains, it has been established that the corrosion caused by sulfur in gasoline which occurs below an outside atmospheric temperature of 32° F. is negligible, then it would seem criminal to continue wasting a non-replaceable raw material at the rate of \$35,000,000 per annum. If those competent to judge agree with the soundness of the position taken, then such changes in refinery practice should not be left merely to the discretion of the refiners. They should be made mandatory.

However, the burden does not fall entirely upon the refiner. Is it not time that the public be taught the advantages of modern motor design and be educated to the point where it will demand adequate crankcase ventilation and perhaps thermostatic controls and facilities for maintaining the crankcase at an optimum temperature, just as the engine block is now maintained? At least one great motor corporation has taken a prominent part in the research underlying such improvements and has incorporated the results of finished investigations in the designs of motors. As such facts are established, the public should decline to buy those cars in which factors contributing to the satisfactory service life of the motor have been neglected.

Not only is the knowledge of corrosion being disregarded by many, but there continues to be extravagant use of lubricating oil—again because many fail to put established data to practical use. We are informed that lubricating oil as now made by at least one refiner contains but a small part which carbonizes and that a proper filter, mounted on the engine, will remove this carbon and the dust and dirt which gain access during operation, thereby multiplying manyfold the useful life of the oil. Here, again, adequate crankcase ventilation is the other controlling factor.

There will be a number of objections raised to any change in specifications for sulfur in gasoline. It may be pointed out that the motorist runs the risk of paying a high penalty if, for any reason, he endeavors to use at temperatures below 32° F. gasoline refined for use at a higher temperature. Two or three weeks' continuous operation with a gasoline of high sulfur content might cause sufficient corrosion to require extensive repairs and replacements in the motor; provided, of course, it is one of the old type without proper crankcase ventilation. It will also be pointed out that some dealers cannot be relied upon to discontinue the sale of the higher sulfur fuels with the advent of cooler weather and that the refiner does not necessarily exercise control over the time the gasoline he sells will be distributed to the user. The large number of older cars which were built without due regard to motor fuels and which will continue in service for years to come seriously complicate the question. There might also

be a few motor operators with unjust claims for damage alleged to be due to corrosion from high sulfur but actually from other causes.

Much depends here, as in every transaction, upon the honesty of those involved and the desire of every good merchant to build his business on fair dealing and integrity. If a motorist buys an unknown gasoline from an unknown dealer, he may fall into more difficulties than merely that of high sulfur. As a matter of fact, there is nothing to prevent an unscrupulous refiner from placing upon the market a fuel higher in sulfur than present specifications tolerate. We can see no justification for any motor manufacturer today putting a single car upon the road lacking a properly ventilated crankcase, an oil filter, and whatever else is in the interest of the automobile owner and operator. We believe the public, through experience in this country where there is a motor car to every five inhabitants, has reached the place where necessary added costs for such service-prolonging equipment can be explained and that they will be gladly accepted. We cannot with justice or with proper regard for public economy continue to throw away annually \$35,000,000 worth of motor fuel. While that figure is but a fraction of the total value of the cars involved and of the gasoline sold, nevertheless it is an indication of what our failure to do as well as we know means.

Changes and improvements such as have been suggested must be found acceptable to those who write federal specifications, if widespread adoption is to be expected. It will also require intelligent coöperation on the part of motor operators, as well as the direct aid of motor manufacturers and, more particularly, of those who sell the modernized automobile. Undoubtedly the average salesman stresses the points in which the average buyer has the greatest interest—the upholstery, the speed, the design, and the color scheme. Should not more appeal be made to the practicalities of motor operation and to explaining engine refinements which are of real economic importance to the prospective purchaser?

We shall be glad to devote space in our Notes and Correspondence to a discussion of the proposal. Obviously the objective is of general interest as well as of scientific import.

The Bundle of Sticks

IN OUR grade readers there was the familiar story of the man who called his seven sons together, gave them a bundle of sticks, and bade them break them. All failed, but when the father separated the bundle into individual sticks he could snap them with ease.

Our American chemical industry has so far been a group of individual units organized more or less successfully along lines of special interest. The desirability of forming some sort of federation to include all branches and individual elements of the chemical industry has been the subject of numerous editorials. The matter has again come to the surface and it is to be hoped that this time something will be accomplished.

While Americans are notoriously independent in their actions, emergencies serve to unite them for a common purpose. A real emergency may not exist at the present time, but there is surely an abundance of questions of mutual interest. Foreign loans, the progress of strong foreign chemical consolidations, the possibility of tariff revision at the next session of Congress, and a uniform policy in export business are some of the things which appeal to all parts of our industry. There is certain to be objection to any plan raised by associations which consider themselves so well es-

tablished as to need no assistance, and perhaps officered by some who look with apprehension upon any project which might tend toward a personal eclipse. Others may feel that, after all, the industry is not closely knit together, and yet other industries possessing units with far less in common have succeeded in setting up their own effective national chambers of commerce or bodies under different names but having a similar object. The chemical industry might include among the purposes of such a nation-wide organization the objects of the recently formed Rubber Institute, Inc.:

To promote in the industry a mutual confidence and a high standard of business ethics; to eliminate trade abuses; to promote sound economic business customs and practices; to foster wholesome competition; to provide ultimately an opportunity for individual efficient business management operating independently to do business with an adequate return; and thus generally to promote the service of the industry to the public welfare.

We sincerely hope that the more recent efforts to bring the industry into one strong group will be entirely successful and pledge the support of INDUSTRIAL AND ENGINEERING CHEMISTRY.

An Industrial Bulwark

OF THE quarter of a million manufacturing concerns in the United States, the great majority remain unconverted to scientific research as the best insurance against many types of disaster. And yet it is quite clear that, but for the products of science, it would be almost hopeless to find other lines of profitable activity when circumstances require. Our readers know that the modern trend is toward a larger share for science in business activities. The deeper and more widespread the penetration of science in industry, the greater and more complete are the changes in industry. These changes make dependence upon research more certain, for we know that it is research which both creates and helps to meet the competition of the day.

The most rapid progress has been made by those industries which are based primarily on science. The growth and achievements in the electrical industry, as well as in the chemical industry, emphasize this point when a comparison is made with older activities where knowledge has been gained slowly and expensively over generations of experience and where, in consequence, we are likely today to find the greatest resistance to modernizing influences.

Our point is illustrated in the field of dry battery manufacture. The advent of the battery eliminator caused reductions in the payrolls in the plants of battery manufacturers, approaching a million dollars a year in at least one establishment. A new line of products had to be devised to keep employed otherwise idle capital and manufacturing facilities. Later came the A C tubes which, while as yet imperfect and easily subject to destruction, are nevertheless so serviceable that they have made their impression upon the eliminator business and have caused further and substantial reductions in payrolls. The older devices possess advantages which enable them to hold a certain portion of the business, but it is a picture where continued research leads to new developments which more nearly approach the ideal than their predecessors and consequently gradually take their place.

The rewards of industry go to the best trained organizations where the scientific staff is adequately supported. In these days of the new competition the manufacturer remains a competitor if he makes science his handmaiden. He disappears from the roster of manufacturers if he turns a cold shoulder to what she has to offer.

Experimental Oil-Shale Plant of the Bureau of Mines¹

Martin J. Gavin

PETROLEUM OFFICE, U. S. BUREAU OF MINES, SAN FRANCISCO, CALIF.

THE experimental oil-shale plant of the Bureau of Mines includes the mine and retorting plant at Rulison, Colo., and the experimental refinery and research laboratory at the University of Colorado, Boulder, Colo. The plant at Rulison was constructed and operated until July 1, 1927, under two congressional appropriations: the first appropriation of \$90,000 was made available on March 4, 1925, and the second, of \$89,000, July 1, 1926. The experimental refinery was constructed with funds provided through the cooperation of the state of Colorado, and its staff was supplied by the bureau. The research laboratory is maintained jointly by the bureau and the state, both of which provide its staff. Construction of the plant was begun in October, 1925, and the first shale was retorted on September 17, 1926. The plant was closed down on July 1, 1927, through failure of an appropriation measure providing for its continued operation; however, early in 1928 appropriations were granted to continue the work until June 30, 1929. Experimental operation was resumed in May, 1928, following improvement and alteration of plant equipment.

The experimental oil-shale mine or quarry is situated in Colorado, on Naval Oil-Shale Reserve No. 1, at an elevation of 8000 feet; it is about 2½ miles northwest of Rulison station. Rulison is on the main line of the Denver & Rio Grande Western Railroad, 9 miles west of the town of Rifle. The experimental plant is 2400 feet below and approximately 1 mile southeast of the mine, and is on Naval Oil Shale Reserve No. 3 (Figure 2). The mine and plant are connected by a 3-mile trail and a 5800-foot aerial tramway.

Mine

The mine is a bench quarry opened on the richest 60-foot zone of oil shale in the Green River formation. In this zone shales ranging in richness from only a few gallons to over 65 gallons of oil per ton are available. Table I is a log of the section worked at the quarry and shows that a continuous vertical section of 69.1 feet yields oil at the rate of 30.47 gallons per ton. Almost any desired selection or mixture of shales can be made without difficulty. During 1927 a short drift was driven in the richest section of the zone, and in 1928-29 probably most of the shale will be mined by underground methods. Mine buildings and machinery include the bunk house, mess house, machinery building and shop, gasoline-engine-driven air compressor, forge, and tramway machinery and bins. A cook is provided for the mine camp, and all supplies, including water, are hauled by tramway. Figure 1 gives a close view of the shale, the upper terminal of the tramway, and one end of the quarry floor.

¹ Received June 5, 1928. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Light jack-hammer machine drills with cross-point bits were used for drilling the shale, air at 90 pounds pressure being furnished by the compressor at the mine. Air-operated auger drills were tried, but were ineffective. Good drilling speed was made in the quarry; for example, ten 6-foot holes were drilled in 90 minutes by one man with one machine, using 2-foot steel changes. So far the work has indicated that the drill should be a high-speed machine which strikes a relatively light blow and has ample air capacity for blowing the hole free of cuttings. Incidentally, the drill cuttings are relatively coarse; very little fine dust is formed. The cuttings can be collected easily and serve as satisfactory control samples. Enough dust is formed, particularly from the leaner shales, however, to indicate that wet-drills will be necessary for underground work.

The shale was shot from the bench faces with 35 per cent gelatin dynamite. Powder of this strength seemed most effective for work in the quarry, while the work in the drift indicated that powder of lower strength would be more satisfactory. Powders ranging in strength from 25 to 70 per cent have been used in the study. All shots were fired electrically, except

mudcapping or bulldozing shots on the quarry platform. Powder consumption averaged approximately 0.5 pound per ton of shale.

The shale was loaded into mine cars on the quarry floor; trammed down a slightly favorable grade to the tramway loading terminal; weighed; and dumped into the loading bin.

Tramway

The tramway installed in 1926 was a single-bucket reversible type, driven by a gasoline engine at the upper terminal. The tram structures were so designed that the system could be readily changed to a two-bucket reversible gravity type, and this change has been made for operating in 1928. The slope length of the tramway is 5800 feet, and the carrier descends 2175 feet in this distance. Track rope is 1-inch plow steel and traction rope 0.5-inch. There are only two towers on the tramway, except for the terminal structures; the upper tower is 63 feet and the lower tower, 73 feet high. The span between these towers is 4200 feet. The maximum capacity with the single carrier was 2.5 tons of shale per hour—five trips. Normally the tramway was operated for 12 hours a day, and usually two or three loads of supplies were taken to the mine each day. The loaded bucket gravitated to the lower terminal, tripped automatically, and was pulled back to the upper terminal by the gasoline engine. Breaking of power and idling shafts at the upper terminal interfered several times with the retorting schedule, but the two-bucket system now being installed will probably eliminate this source of trouble. Single loads weighing up to 1100

A description is given of the experimental oil-shale plant operated by the United States Bureau of Mines at Rulison, Colo., during 1926 and 1927. The oil-producing equipment consists of two retorts, a standard Pumpherson retort of the type in commercial use in Scotland and a N-T-U retort similar to the units used by the N-T-U Company at Casmalia, Calif. Analyses of the oils produced by both retorts are given. The results obtained thus far have demonstrated the utility of both retorts as large-scale units and the work is to be continued until June 30, 1929, with some modifications in retort design and methods of operation to make the process more suitable for American shales and to establish the economic capacities of the two methods.

pounds have been hauled from the plant to the mine over this cableway.

At the discharge terminal is an 80-ton two-compartment storage bin, which is now being enlarged to 120-ton capacity.

Table I—Assay Log of Oil-Shale Section in Garfield County, Colo. (A) Experimental Mine

(Samples are cuttings from vertical holes, drilled down with air-operated jack hammer)

DISTANCE ABOVE BASE OF "SANDSTONE MARKER"	SECTION	YIELD	SP. GR. OF OIL	COKING ^a OF CHAR-ACTER	REMARKS
Feet	Feet	Gallons per ton			
19.8	2.0	23.3	0.905	0	
17.8	2.0	17.6	0.902	0	
15.8	1.3	15.6	0.907	0	
14.5	2.0	24.0	0.908	0	
					Contains two oil-bearing sandstone members: upper 1 inch thick; lower 3 to 6 inches thick, yielding 19.6 gallons oil per ton
12.5	2.0	27.0	0.904	0	
10.5	1.0	35.2	0.905	1-	
9.5	2.0	37.2	0.896	1	
7.5	2.0	25.5	0.898	0	
5.5	1.5	19.2	0.908	0	
4.0	2.0	20.9	0.905	0	
2.0	1.5	20.1	0.902	0	
"Sandstone marker"	0.5	5.6	...	0	
Below marker					
1.5	1.5	10.9	0.900	0	
3.5	2.0	16.2	0.910	0	
4.7	1.2	44.8	0.900	2	
6.7	2.0	24.6	0.897	0	
8.3	1.6	25.7	0.898	1-	Light and dark gray streaks of limestone cells
9.5	1.2	27.9	0.893	1-	Black and dark gray
11.3	1.8	37.1	0.890	0	Black and dark gray
12.3	1.0	67.5	0.882	8	Black, waxy, contains 1 to 2-inch compressed waxy seam
13.3	1.0	48.6	0.883	6	Black, not so waxy
14.3	1.0	78.0	0.881	10	Black, waxy with thin gray streaks
15.3	1.0	66.5	0.880	9-10	Black, waxy with fewer gray streaks
16.3	1.0	52.5	0.891	4-5	Black, not so waxy, zone of "alum" pockets
17.9	1.6	44.8	0.887	4-5	Black, not waxy
19.6	1.7	46.9	0.905	2+	Black, not waxy
21.0	1.4	22.6	0.924 (?)	0	Black and dark gray streaks, resists erosion
22.6	1.6	19.9	0.899	1-	Tan and gray, erodes rapidly
24.7	2.1	35.7	0.899	1	Black and gray, resists erosion
27.4	2.7	20.4	0.904	0	Tan and gray with 1-inch sandstone, erodes rapidly
29.4	2.0	45.8	0.890	1+	Hard black
31.4	2.0	45.1	0.884	1+	Hard black
33.4	2.0	34.4	0.884	1-	Brown, erodes to gray and tan
34.6	1.2	25.7	0.877	0	Black
36.6	2.0	27.1	0.893	0	
38.5	1.9	22.7	0.899	0+	
39.7	1.2	36.6	0.903	2	
40.9	1.2	12.2	0.901	0	
42.3	1.4	16.4	0.889	0	
44.3	2.0	36.3	0.878	2-	Black with small hard cells
47.3	3.0	30.0	0.885	1	Black with gray bands—hard
49.3	2.0	33.7	0.884	1-	Hard black—small cells
Yield of total section	Feet	Gallons per ton			
Yield of section below marker	69.1	30.47			
Yield of section above base of marker	49.3	33.29			
Yield of section below marker, excluding top 3.5 feet	19.8	23.45			
	45.8	34.77			

^a Relative coking tendency is shown by an arbitrary numerical scale in which 0 indicates no coking tendency, and 10 indicates coking so strong that the assay charge forms one solid mass, shrinks to less than half its original volume, and adheres tenaciously to the retort walls. Shales having a coking number greater than 3 have so far always given trouble in both experimental retorts.

Experimental Plant (Figures 3 and 4)

Below the lower-terminal bin is the shale crusher which has a capacity of 7 tons per hour, and is belt-driven by a gasoline engine. The crusher is of the single-roll type with feed opening 18 by 16 inches, and has given entirely satisfactory results. From the crusher the shale drops either into a crushed-shale storage bin of 20-ton capacity or directly

into a steel chute which leads to the retorts. This chute is now being replaced by a trestle leading from a bin below the crusher to the top of the Pumpherson retort. End-dumping cars will haul shale from the bin over the trestle to the top of the Pumpherson retort and dump directly into this retort or into a chute leading to the N-T-U retort. The retorts and their auxiliary equipment are described below. Other equipment consists of the boiler plant with two coal- or oil-fired 35-horsepower oil-field type boilers; a 40-horsepower gas producer which supplies fuel for the Pumpherson retort; a 5-kilowatt turbogenerator set which supplies electricity for plant and camp lighting and for laboratory apparatus; machine shop with facilities for making minor repairs, store room, etc.; steam-heated laboratory and office building completely equipped; and water-supply system. Water for the plant is pumped through a 2-inch line from a well on the bank of the Colorado River, 1.25 miles southeast of and 600 feet lower than the plant, to storage tanks above the retorts. Water-cooling and recirculating equipment for the gas producer, and condensers for the turbines, now being installed will materially reduce water consumption and improve the quality of the boiler feed water.

The camp buildings include mess and bunk houses and smaller dwellings for some of the technical staff.

Retorts

Two retorts (Figure 4) comprise the oil-producing equipment of the plant. Selection of retorts for the plant was based largely on the results of laboratory study carried on since 1920 in the Coöperative Oil Shale Laboratory at Boulder, Colo., supplemented by field study of retorts proposed for use, and in use, in this and other countries. The retorts selected were a standard Pumpherson experimental retort, of full commercial size and of the type in commercial use in Scotland for twenty-five years, and a N-T-U retort of approximately 25-ton charging capacity, somewhat more than half as large as the units used by the N-T-U Company at Casmalia, Calif., for the previous three years. Both retorts are mechanically simple, operate on principles demonstrated by laboratory study to be fundamentally sound, and are easily adapted to experimental study. Moreover, both types had been operated for a period long enough for their limitations and methods of control to be fairly well established and the engineering problems of construction and operation to be reasonably well worked out. Both retorts are provided with indicating and recording instruments necessary for experimental operation.

Figure 5 shows horizontal and vertical sections of the Pumpherson retort erected at the experimental plant. The retort, except for minor points, is an exact duplicate of that in use at the Pumpherson works of the Pumpherson Oil Co., Ltd., of Scotland, and is really a full-sized commercial unit. All the metal parts and specially shaped brick for this retort were purchased in Scotland by the writer, and the retort was erected under the direction of an experienced construction foreman loaned by a Scottish retort-manufacturing company. Space does not permit a full description of this retort. It is, however, adequately described in publications of the Bureau of Mines.²

The Scottish retort is a continuously-operating, externally-heated, vertical retort. Attention here is called to the constructional feature of the retort which permits the retort proper to expand and contract independently of the side walls, and to the use of steam in the retorting process. Steam, which may be exhaust from the power plant, is admitted to the spent shale hopper in direct contact with the shale and serves the following purposes:

² Gavin, Bur. Mines, Bull. 210, p. 69 (1924).

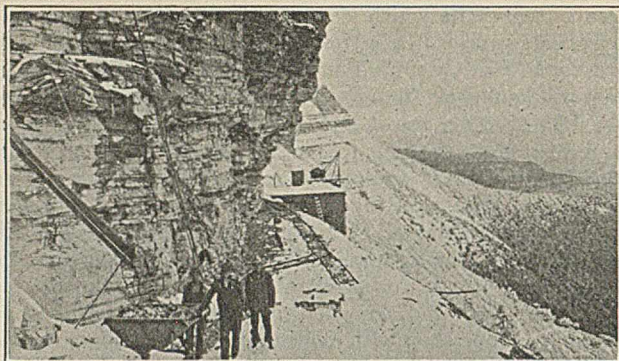


Figure 1—View from East End of Quarry Platform, Showing Oil-Shale Strata and Upper Tramway Terminal

1—Steam cools the spent shale and itself is superheated; rising through the shale charge, it gives its heat to the distilling charge.

2—It distributes the heat from the spent shale and from the side walls uniformly through the charge.

3—It reacts with the fixed carbon of the spent shale, producing a mixture of hydrogen, carbon dioxide, and carbon monoxide which eventually becomes part of the fuel supply for the retort.

4—It prevents undue decomposition of the oil by increasing the velocity of the oil vapors through the retort.

5—It increases the production of ammonia from the nitrogen of the shale.

At the experimental plant, vapors and gases from the retort pass in series through a three-stage atmospheric condenser (Figure 3), a water-cooled condenser of conventional design; a water scrubber for removal of dust and ammonia remaining in the gases; and an exhaustor which draws the vapors and gases from the retort, through the condensing system (the suction on the retort off-take is 0.10 to 0.20 inch of water), forces the gas through an oil scrubber to recover light gasoline, and finally delivers it to the return-gas burner. The retort is heated by the return gases, supplemented when necessary by producer-gas made from petroleum coke.

The oil and water condensing in the system are trapped off at four points: a trap is provided for each header of the atmospheric condenser and for the outlet header of the water-cooled condenser. These traps are of original design and serve also as water separators. From the traps the oil flows to 25-barrel run tanks and thence to a 250-barrel storage tank.

N-T-U Retort

Figure 6 shows the essential features of the N-T-U retort. This retort is of the internally-heated, intermittent, vertical type. The bottom of the shell containing the grates is supported on wheels which run on I-beams and can be moved from under the retort when the spent shale is to be discharged. Raw shale is charged at the top, with the grate in place, and

when the retort is filled a wood fire is started at the top. An exhaust fan meanwhile draws combustion and distillation products downwardly through the shale charge and through the condensers, then forces them through a cyclone separator and out the waste stack. As soon as the shale charge is satisfactorily ignited, the retort charging door is closed. Part of the combustion and distillation gases are then returned to the top of the retort, while a regulated quantity of air is admitted at the top through ports around the gas nozzles.

Distillation may be conducted either by maintaining gaseous combustion in the dome of the retort, the hot products of combustion passing down through the distilling charge, or by so regulating return gas and air that a combustion zone travels down through the charge, burning out the fixed carbon of the spent shale, while a distillation zone precedes the combustion zone. Four thermocouples in the bottom of the retort, just below the grates, indicate a temperature of approximately 140° F. throughout the greater part of the run.

As the combustion zone reaches the bottom of the retort, the temperatures of one or two of these couples rise more or less rapidly, depending on the proportions and volumes of air and return gas being used. When any one of the thermocouples indicates a temperature of approximately 1000° F., the air ports at the top of the retort are closed, thus stopping combustion, and the return gas valves are opened wide. The return gas is superheated by the hot spent shale in the top of the retort and serves to complete the distillation of the shale just above the grates without subjecting the grates to destructive temperatures. When the

lowest indicated temperature reaches 650–700° F., the exhaust fan is stopped, the gas off-take valve closed, the retort bottom pulled back by a small steam engine operating through a reduction gear and worm, and the spent shale drops from the retort.

Oil is trapped off from the condenser, from the discharge of

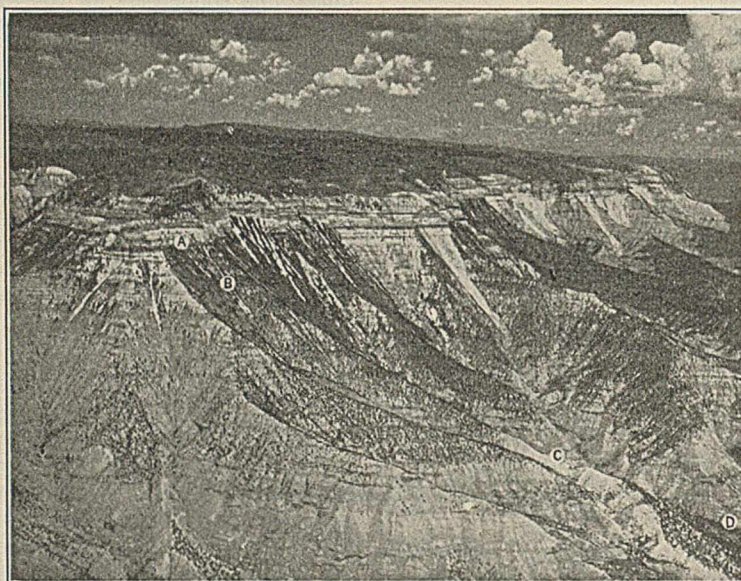


Photo by U. S. Navy Air Service

Figure 2—Site of Bureau of Mines Oil-Shale Experimental Plant and Mine, near Rullison, Colo.

A—Mine site; B—Location of tramway tower No. 1; C—Location of tramway tower No. 2; D—Plant site below this ridge in canyon to right



Figure 3—General View of Plant Tramway and Mine Site
Mine is on first escarpment in upper right center

the exhaust fan, from the cyclone, and from the lower end of the 8-inch waste-gas line, which runs 270 feet up the hillside back of the retort on a slope of 35 degrees and terminates in a 30-foot vertical stack. The oil flows to traps and water separators, similar to those used with the Pumpherston retort, thence to run tanks, and finally to storage.

Operation of Pumpherston Retort

The Pumpherston retort, after a long preliminary heating, was first charged with shale on September 17, 1926. From this date until July 1, 1927, 1341 tons of shale were put through the retort and 23,700 gallons of crude shale oil were produced. In addition, tests indicated that in this period 435 gallons of light naphtha might have been obtained by scrubbing the retort gases. (The plant oil-absorption system was not used during this period.) The total amount of oil recovered and recoverable by scrubbing the gases was thus 24,135 gallons, or an average yield of 17.9 gallons per ton. Shales varying in richness from 11 to 43 gallons of oil per ton have been retorted. The highest yield from the retort was at the rate of 42.5 gallons per ton of shale retorted. The low average yield is due to long periods of operation in which shale was discharged not completely spent and to operation in which the shale was permitted actually to burn within the retort. The latter procedure is evidently poor practice, but information as to results of operating in this manner was desired. The retort was idle from November 15 to December 15 because of a broken crusher gear, and also from December 17 to 28 because temperatures had dropped too low for good operation after a sudden cold snap froze the main water line and caused a water shortage for two days. From December 30, 1926, until March 17, 1927, the retort operated continuously without giving the slightest trouble; in this period the retort handled shale yielding from 11.6 to 42.5 gallons of oil per ton, including charges which were wet and contained much fine, low-grade, and dirty surface shale. On March 17 the shale hung up in the retort; this marked the beginning of trouble caused by coking shale, which continued periodically until June 15. From June 15 until July 1 operation was smooth, and splendid results were obtained.

The only trouble experienced with the Pumpherston retort was that caused by coking shale; but whether the difficulty was due primarily to the type of shale used or to leakage of air and hot combustion products into the retort through a crack in the inner wall has not yet been determined. The crack was not noticed until after the retort had been cooled down in July, 1927, and the time of its formation is not known, but its position with respect to the location at which coke adhered to the retort walls suggests strongly that coking may have been induced by leakage through the crack. The crack may have been caused by an explosion in the combustion flue during the preliminary heating period, or by strains transmitted through the structure from the shale chute support mounted on the top of the retort (Figure 4). The operators are now so experienced in operating the retort that explosions in the combustion flue are not likely to occur again; and, as has been noted, the shale chute has been replaced by a trestle which places no stresses on the retort proper. The crack was repaired for the resumed operations.

Certain oil shales, particularly the richer varieties (Table I), have strong coking tendencies and probably will give trouble in any type of retort. The shale which caused the first hang-up in the Pumpherston retort was a mixture of coking and non-coking varieties which yielded 42 gallons of oil per ton, but possibly such a mixture may be handled successfully with all air leaks stopped. Before this original hang-up, mixtures of coking and non-coking shale yielding as much as

35 gallons of oil per ton were retorted without trouble, but afterward such mixtures hung up frequently. The later difficulties were probably caused by incomplete removal from the walls of coke formed in the first hang-up. Finally, on May 28 efforts to retort mixtures containing coking shale were abandoned, and a 30-gallon, non-coking shale from a lower level in the quarry was charged for the first time. This material several times packed in the retort at the location of the previous hang-ups, but from June 15 on it was handled without difficulty.

After the retort had cooled, inspection of the interior showed that coke, evidently formed in March, April, and May, had built up to such an extent that the taper of the retort was practically reversed for a short distance. This accumulation was suspected, but could not be observed, as inspection within the retort was not possible when the retort was hot; nor could the coke be removed by poking from the top or bottom hoppers. The coke has now been removed, and the work will be resumed and continued on a relatively rich non-coking shale until early in 1929, when an attempt will again be made to retort mixtures containing coking material.

The work in 1926-27 has given good preliminary data on the influences of certain variables of retorting, and has convincingly shown the Pumpherston retort

to be an excellent apparatus for large-scale experimentation. Its capacity is to a material extent determined by the quality of shale retorted. For five consecutive days in June the throughput exceeded 7.5 tons per day, and on two of these days the throughput was over 8 tons. At this time the retort was handling shale which assayed 29 gallons of oil per ton, was discharging the shale completely oil-spent, and the oil recovery was ranging from 93.2 to 100.1 per cent of the assay value of the shale. The gas yield ranged from 3380 to 4210 cubic feet per ton, varying inversely with the throughput rate and directly with the amount of steam supplied. During the five days the gas produced was sufficient for heating the retort during the warmer hours of the day. With the inner walls of the retort free from coke, the throughput rates will probably be higher. Actual heat balances have not yet been calculated, but attention is directed to the fact that the single experimental retort was almost self-supporting as regards fuel at the throughput rates given above. When the retorts are built in battery, heat economy will be greater, and unquestionably other means can be taken to improve materially the heat economy of the equipment.

High throughput rates are not favorable for the production of ammonia, but the writer has assumed that the production of ammonia from American oil shales is of minor importance in comparison with oil production.

The oil produced varies in quality with the nature of the shale used and with the conditions of retorting. The two

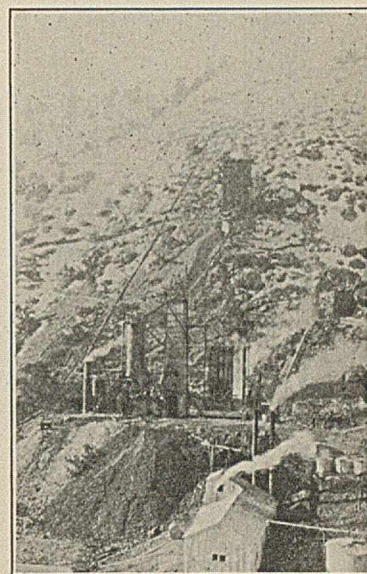


Figure 4—Both Retorts in Operation; N-T-U Retort to Left; Pumpherston to Right

Note waste-gas line from N-T-U retort and spent shale dump

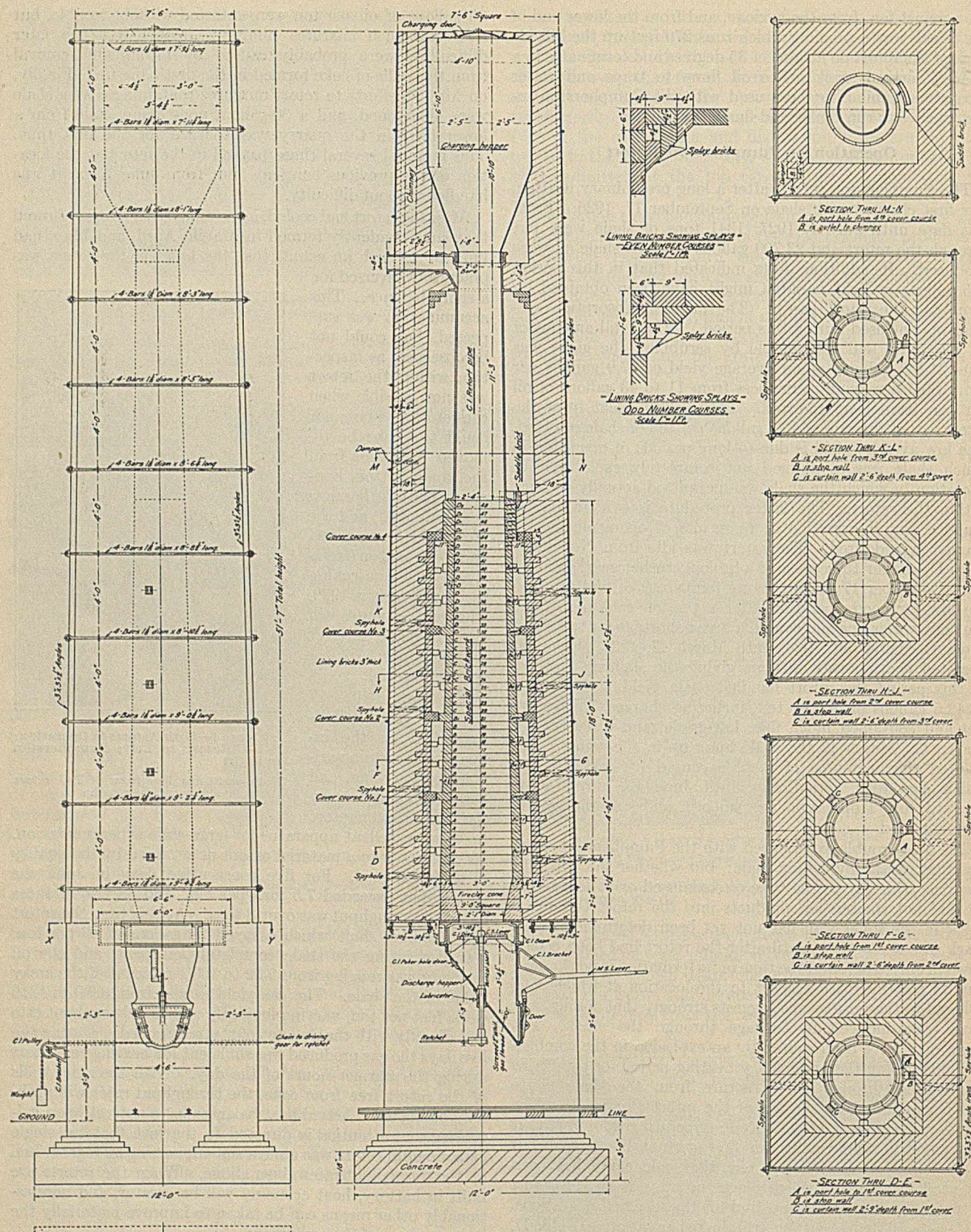


Figure 5—Pumpherson Experimental Oil-Shale Retort

distillation analyses given (p. 789) are of two typical oils made from shales of the same quality and with nearly the same throughput rates, the variable being the amount of steam supplied to the retort. These crudes do not contain the scrubber naphtha recoverable by scrubbing the retort gases.

The quantity and composition of the gas produced by the Pumpherson retort also depend on the nature of the shale retorted and the retorting conditions. This fact is shown by Table II. Retort temperatures were very nearly the same for the five days on which data were obtained.

Table II—Composition and Heating Value of Gas Produced by Pumpherson Retort
(Heating values calculated from analyses)

Date	June 4	June 12	June 18	June 22	June 26
Throughput rate, tons per day	4.76	5.23	7.00	8.07	7.56 ^a
Assay value of shale, gallons per ton	27.0	33.1	35.2	26.6	29.1
Steam flow rate, gallons per 24 hours	220	300	375	425	425
Gas yield per ton of shale, cubic feet	4220	6100	3890	3380	4210
Total gas yield, cubic feet	20,100	31,900	27,200	27,300	31,800
Gas composition, per cent:					
Hydrogen sulfide	0.8	1.5	1.8	1.7	1.7
Carbon dioxide	18.0	31.8	32.9	29.2	28.5
Illuminants	7.1	3.9	4.0	4.1	5.3
Oxygen	1.0	1.0	0.7	1.8	0.9
Hydrogen	30.2	42.9	43.5	42.0	43.8
Carbon monoxide	18.6	5.2	4.8	4.1	4.1
Paraffin hydrocarbons (C _n H _{2n+2})	19.0	9.1	10.1	9.9	10.5
Nitrogen	5.3	4.6	2.2	7.2	5.2
Heating value, B. t. u. per cubic foot: ^b					
Gross	516	343	360	351	384
Net	475	309	324	316	346
Oil recovery, per cent	80.2	?	89.0	93.3	100.1
Heating value of gas per ton of shale, net B. t. u.	2,004,500	1,884,900	1,260,360	1,068,080	1,456,660
Total heating value of gas, net B. t. u.	9,547,500	9,857,100	8,812,800	8,626,800	11,002,800

^a Throughput decreasing after higher rate. Oil produced from more shale than was weighed as throughput.
^b At 60° F. and 29.92 inches mercury.

Operation of N-T-U Retort

In all, until June 30, 1927, twenty-nine runs were made with the N-T-U retort. The total amount of shale retorted was 788.4 tons, and the total oil recovered was 13,774 gallons—an average yield of 17.47 gallons of oil per ton. The assay values of the shales retorted ranged from 11.0 to 38.4 gallons per ton, and oil recoveries ranged from 36 to 94 per cent of the assay values of the shales. These yields and recoveries do not include light naphtha and oil recoverable from the retort gases. An evident characteristic of the internally-fired retort is the production of an oil fog or mist from which the oil cannot be recovered by ordinary scrubbing. Electrostatic precipitation will probably be necessary for complete recovery of the oil in this fog, although at the experimental plant much oil precipitated in a 300-foot waste-gas line installed to carry the fog well away from the plant buildings. In the only run in which scrubber naphtha and oil fog yields were determined, recovery of these products would have increased the retort yield from 85 to 92 per cent of the assay value of the shale.

The N-T-U retort successfully handled all grades of shales except those of the coking variety. The coking shales shortly after the start of a run formed enough coke practically to stop gas circulation. Future study may determine operating methods which will permit coking mixtures to be handled. The richer non-coking shales undergo some change during

retorting that causes a great increase in resistance to gas flow through the retort, particularly when the air-gas mixture is most suitable for good oil recovery.

Note—The shales of the Green River formation contain high percentages of carbonates, chiefly calcium carbonate. These decompose to a greater or less extent during retorting and the oxides are probably hydrated in the cool upper part of the retort by the moisture in the return gas. This is a possible explanation of the building up of resistance to gas flow. Two or three hours after the start of a run the shale in the top of the retort is usually cool enough to permit such hydration.

The exhaust fan originally installed at the experimental plant did not have sufficient capacity to retort the richer non-coking shales so rapidly as was expected when air-gas ratio and volumes considered best for good recovery were used. The economical capacity of the retort has thus not yet been determined; to do this, the power necessary to retort a given shale at different rates and with good oil recoveries must be known. For the work in 1928-29 an exhaustor of much larger capacity has been installed to make possible more rapid retorting rates. Up to the present, using shales ranging in assay value from 11 to 38 gallons of oil per ton, with different volumes of combustion gases ranging in composition from straight-air to a mixture containing 54 per cent of return gas, the time required to retort a charge has been from 18¾ to 48 hours.

Crude Oil Produced June 20, 1927, Pumpherson Retort

Shale throughput rate, 7.60 tons per day	Assay value of shale, 30.0 gallons per ton
Steam rate to retort, 375 gallons per day	Recovery, 87.0 per cent
Crude made, 193.7 gallons	
Scrubber naphtha recoverable, 4.7 gallons	
Specific gravity, 0.8945	A. P. I. gravity, 26.7°
Sulfur, 0.74 per cent	Water, 0.76 per cent
Nitrogen, 1.35 per cent	Setting point, 65° F.
Saybolt Universal viscosity at 100° F., 50 seconds	

Distillation, Bureau of Mines, Hempel Method

Air distillation, 300 cc. Barometer, 620 mm. First drop, 57° C. (135° F.)		PER SUM SP. GR. ° A. P. I. VISCOSITY		MELT- CLOUD ING		TEMP.		
TEMP. ° C.	CENT CUT	PER CUT	OF CUT	AT 100° F. Seconds	° F. ° F.	° F. ° F.	° F. ° F.	
Up to 75	0.16	0.16	0.773	51.5			Up to 167	
75-100	0.30	0.46						167-212
100-125	1.16	1.62						212-257
125-150	3.28	4.90		257-302			302-347	
150-175	5.23	10.13	0.808	43.6			347-392	
175-200	5.46	15.59	0.829	39.2			392-437	
200-225	7.21	22.80	0.843	36.4			437-482	
225-250	7.71	30.51	0.863	32.5			482-527	
250-275	10.30	40.81	0.881	29.1				

Vacuum distillation at 40 mm.

Up to 200	6.72	47.53	0.899	25.9	54	Too dark	56	Up to 392
200-225	13.33	60.86	0.909	24.2	65	Too dark	58	392-437
225-250	10.91	71.77	0.9215	22.0	101	Too dark	72	437-482
250-275	12.34	84.11	0.9352	19.8	170	Too dark	88	482-527
275-300	12.17	96.28	0.9405	18.9	174 (130° F.)	Too dark	100	527-572

Carbon residue of residuum, 12.2 per cent

Crude Oil Produced June 25, 1927, Pumpherson Retort

Shale throughput rate, 8.05 tons per day	Assay value of shale, 29.05 gallons per ton
Steam rate to retort, 425 gallons per day	Recovery, 93.6 per cent
Crude made, 212.3 gallons	
Scrubber naphtha recoverable, 6.6 gallons	
Specific gravity, 0.9008	A. P. I. gravity, 25.6°
Sulfur, 0.65 per cent	Water, 0.1 per cent
Nitrogen, 1.20 per cent	Setting point, 75° F.
Saybolt Universal viscosity at 100° F., 56 seconds	

Distillation, Bureau of Mines, Hempel Method

Air distillation, 300 cc. Barometer, 623 mm. First drop, 73° C. (163° F.)		PER SUM SP. GR. ° A. P. I. VISCOSITY		MELT- CLOUD ING		TEMP.		
TEMP. ° C.	CENT CUT	PER CUT	OF CUT	AT 100° F. Seconds	° F. ° F.	° F. ° F.	° F. ° F.	
Up to 75	0.06	0.06	0.780	49.9			Up to 167	
75-100	0.89	0.95						167-212
100-125	1.15	2.10						212-257
125-150	1.54	3.64		257-302			302-347	
150-175	5.68	9.32	0.810	43.2			347-392	
175-200	5.40	14.72	0.832	38.6			392-437	
200-225	7.17	21.89	0.850	35.0			437-482	
225-250	7.83	29.72	0.869	31.3			482-527	
250-275	9.87	39.59	0.885	28.4				

Vacuum distillation at 40 mm.

Up to 200	3.24	42.83	0.899	26.0	53	Too dark	54	Up to 392
200-225	12.45	55.28	0.903	25.2	66	Too dark	57	392-437
225-250	12.45	67.73	0.924	21.6	96	Too dark	66	437-482
250-275	11.44	79.17	0.937	19.4	174	Too dark	84	482-527
275-300	13.92	93.09	0.947	18.0	184 (130° F.)	Too dark	99	527-572

Carbon residue of residuum, 11.75 per cent

The operation of the retort is quite simple; usually after conditions have been established at the beginning of the run it requires little attention, except an occasional adjustment of the valves, until the charge is ready to dump. The oil fog in the waste gas was a serious nuisance until means were provided for its proper disposition. Occasionally oil congealed in vapor lines, but the retort itself operated very smoothly. Certain air-gas mixtures, apparently those particularly suitable for rapid retorting and good oil recovery, cannot be used, except in the final stages of a run, because

for some of the low oil recoveries when the charge was dumped before all the oil had been distilled; and second, for some of the long retorting times when the charge was evidently dumped some time after all the oil had been produced. This problem will probably be solved when the operators become more familiar with the behavior of the retort.

The oils produced by the N-T-U retort are uniformly heavier and contain a smaller amount of the more volatile fractions than those produced by the Pumpherson retort, but otherwise are quite similar to them. Evidently there is less secondary decomposition in the N-T-U retort. Correlation of the properties of the N-T-U oils with varied retorting conditions has not yet been possible; this will be one of the objects of the study planned for 1928-29. The two distillation analyses given below indicate the nature of the oils produced by the N-T-U retort.

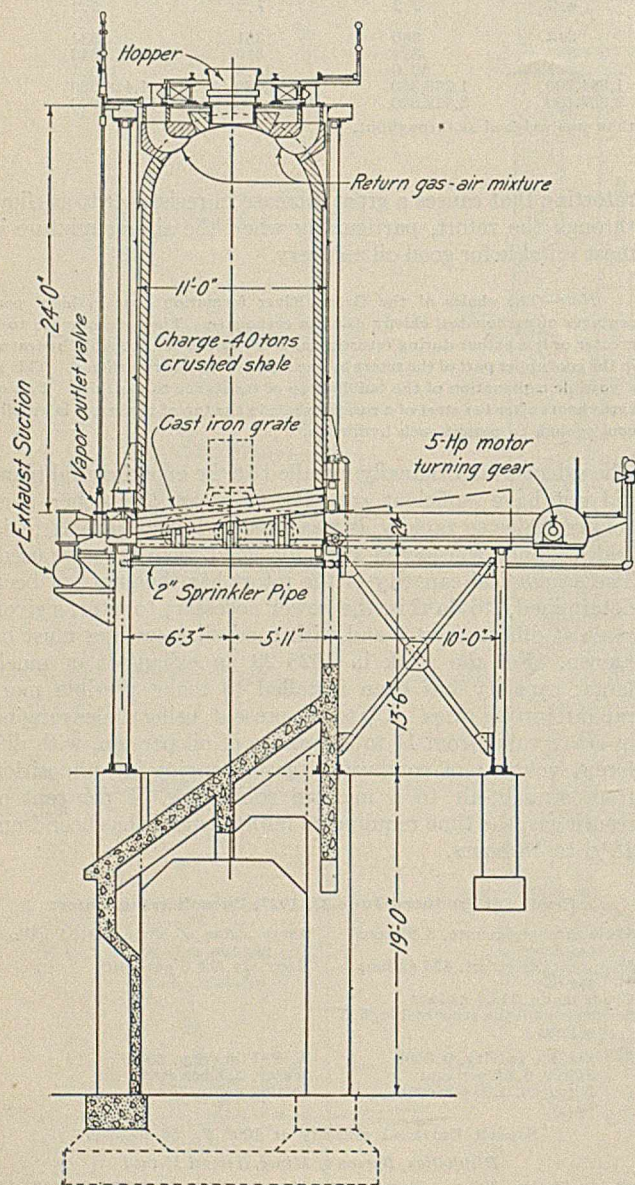


Figure 6—Vertical Section N-T-U Oil-Shale Retort

they are explosive. The explosions which did occur were never strong enough to cause damage, but naturally such mixtures were not used so long as they caused explosive puffs at the top of the retort. Data are not sufficiently complete to permit conclusions to be drawn, but evidently the rate of retorting is a direct function of both volume and percentage of air in the air-gas mixture supplied to the retort, and the percentage of oil recovered is a direct function of the richness of shale retorted and of both amount and percentage of gas in the air-gas mixture.

It was sometimes difficult to determine just when the charge was completely retorted. This fact accounts, first,

N-T-U Crude—Run 2

Specific gravity, 0.920
Sulfur, 0.85 per cent
Saybolt Universal viscosity at 100° F., 112 seconds

A. P. I. gravity, 22.3°
Water, trace
Pour point, 75° F.
Color, brownish black

Distillation, Bureau of Mines, Hempel Method

Air distillation. Barometer, 624 mm. First drop, 90° C. (194° F.)

TEMP. ° C.	PER CENT CUT	SUM OF PER CENT	SP. GR. OF CUT	° A. P. I. VISCOSITY		CLOUD ING TEST ° F.	MELT- ING POINT ° F.	TEMP. ° F.
				AT 100° F. Seconds	AT 100° F. Seconds			
Up to 50								Up to 122
50-75								122-167
75-100								167-212
100-125	0.6	0.6	0.755	55.9				212-257
125-150	0.6	1.2	0.770	52.3				257-302
150-175	2.9	4.1	0.796	46.3				302-347
175-200	4.4	8.5	0.820	41.1				347-392
200-225	4.8	13.3	0.837	37.6				392-437
225-250	6.2	19.5	0.856	33.8				437-482
250-275	8.0	27.5	0.876	30.0				482-527

Vacuum distillation at 40 mm.

Up to 200	2.6	2.6	0.892	27.1	43	Too dark	Up to 392
200-225	7.0	9.6	0.900	25.7	55	Too dark	392-437
225-250	7.0	16.6	0.921	22.1	83	Too dark	437-482
250-275	6.8	23.4	0.931	20.5	150	Too dark	482-527
275-300	11.4	34.8	0.936	19.7	280	...	95 527-572

Carbon residue of residuum, 7.1 per cent

N-T-U Crude—Run 29

Specific gravity, 0.9236
Sulfur, 0.86 per cent
Nitrogen, 1.40 per cent
Saybolt Universal viscosity at 100° F., 176 seconds.

A. P. I. gravity, 21.7°
Water, 0.36 per cent
Pour point, 90° F.
Color, brownish black

Distillation, Bureau of Mines, Hempel Method

Air distillation. Barometer, 625 mm. First drop, 67° C. (153° F.)

TEMP. ° C.	PER CENT CUT	SUM OF PER CENT	SP. GR. OF CUT	° A. P. I. VISCOSITY		CLOUD ING TEST ° F.	MELT- ING POINT ° F.	TEMP. ° F.
				AT 100° F. Seconds	AT 100° F. Seconds			
Up to 50								Up to 122
50-75	0.03	0.03						122-167
75-100	0.03	0.06						167-212
100-125	0.10	0.16						212-257
125-150	0.69	0.85	0.822	40.6				257-302
150-175	1.82	2.67						302-347
175-200	3.18	5.85						347-392
200-225	4.97	10.82	0.848	35.4				392-437
225-250	6.20	17.02	0.865	32.1				437-482
250-275	10.44	27.46	0.882	28.9				482-527

Vacuum distillation at 40 mm.

Up to 200	1.09	28.55	0.8987	26.0	67	Too dark	54 Up to 392
200-225	3.90	32.45				Too dark	392-437
225-250	9.32	41.77	0.9116	23.7	91	Too dark	63 437-482
250-275	11.51	53.28	0.9308	20.5	156	Too dark	82 482-527
275-300	13.22	66.50	0.9481	17.8	186 (130° F.)	Too dark	99 527-572

Carbon residue of residuum, 9.87 per cent

The amount and composition of waste or surplus gas produced by the N-T-U retort depend on the nature of the shale retorted and on the volumes of air and return gas supplied to the retort. In a typical run with a charge of 29 tons, the total volume of waste gas was 568,000 cubic feet. The composition of this gas is given below:

	Per cent		Per cent
Hydrogen sulfide	0.1	Hydrogen	3.5
Carbon dioxide	22.6	Carbon monoxide	3.1
Illuminants	0.1	Methane	1.5
Oxygen	3.4	Nitrogen	65.7

Note—The gas-forming reactions within the retort are those of distillation, combustion, production of carbon dioxide from the carbonates in the shale, and the production of carbon dioxide, carbon monoxide, and hydrogen from the water in the return gas and the hot carbon of the spent shale.

The calculated net heating value is 35.0 B. t. u. per cubic foot.

Possible Modification of Retorts

The relative merits of the two retorting systems at the experimental plant cannot be discussed at this early stage of their use. The work has indicated that certain design features of both retorts might advantageously be modified. Future work will not improbably lead to suggestions as to retort design and methods of operation that will be particularly suitable for American shales and economic conditions. Another year's work should establish the economic capacities of the two methods of producing shale oils, should make it possible to obtain some definite idea as to the rates of depreciation of the two retorts, and should furnish other data on which reasonably accurate estimates of the costs of producing shale oil may be based. The writer is particularly pleased that the utility of both retorts as large-scale experimental units has been satisfactorily demonstrated.

Refining Studies

Oils produced by both retorts at the experimental plant have been shipped to the experimental refinery at Boulder and to various petroleum-refining companies which have agreed to furnish the Bureau of Mines with the results of their studies of the oils. Up to the present time only a few of these companies have submitted reports.

The following conclusions may be drawn, however, from the results obtained to date:

1—The oils produced by the two retorts are essentially similar, except that the Pumpherson oil contains a greater amount of secondary decomposition products than that produced by the N-T-U retort.

2—The motor-fuel fractions from the crude oils, cut to the final boiling point required by present specifications for

motor gasoline, are not sufficiently volatile to meet present specification requirements, and contain more than 0.5 per cent sulfur. (Some of the reports show as much as 0.8 per cent sulfur in the motor-fuel fraction.)

3—By a combination of topping and cracking operations similar to those used in the petroleum industry, 64 per cent of motor fuel has been made from the Pumpherson crude and 52 per cent from the N-T-U crude. These are the reported yields of finished products with final boiling points of 437° F., but do not contain enough of the more volatile fractions to meet present specification requirements. The cracked distillates apparently are more easily refined than are the straight-run products, and contain somewhat less sulfur. The Boulder laboratory recently reported that the cracked fuels have been refined with a treating loss of 5 per cent, yielding a fuel that meets all present specification requirements except as regards sulfur. New methods of treating will probably have to be developed, if it is necessary materially to reduce the sulfur content without incurring heavy treating and polymerization losses.

4—One company reports that the motor fuels have antiknock values equivalent to straight-run Pennsylvania gasolines containing from 30 to 50 per cent benzol. The cracked fuel from the Pumpherson crude has the higher antiknock rating.

5—Little work has been done with other products. The high sulfur content of the fractions indicates that new refining methods will have to be developed before products entirely meeting present specification requirements can be made. The oils are apparently not suitable for the production of viscous lubricants.

6—Tar bases removed from the gasoline and kerosene fractions, by treatment with dilute acids, have interesting possibilities as insecticides, wood preservatives, shingle stains, etc.

The refining work in 1928-29 will be concentrated on the production of finished motor fuels and Diesel and other fuel oils. Some work will be done on wax production, and tar bases will be studied in more detail.

The Countercurrent Use of Decolorizing Carbons¹

M. T. Sanders

ATLAS POWDER COMPANY AND DARCO CORPORATION, WILMINGTON, DEL.

IT IS commonly conceded that the countercurrent method of applying decolorizing carbons is more saving of carbon than any other method. The nature of the material handled makes the true countercurrent method difficult to apply. However, the stepwise countercurrent method—that is, the use of the carbon in two or more stages—is not difficult. By this method the fresh carbon is used to treat partially decolorized liquid, and this partially spent carbon is, in turn, used to partially decolorize the fresh liquid. The magnitude of the savings possible by use of the stepwise countercurrent treatment is shown in this paper.

Certain investigators^{2,3,4,5,8} have shown that the action of a decolorizing carbon on liquids follows Freundlich's adsorption equation, and that in this equation color units based on the

extinction coefficient may be used for the concentration terms X and C . Systems of such units have been given by Meade and Harris,⁶ Sanders,^{4,5} and Peters and Phelps.⁷

Freundlich's equation is usually written as follows:

$$\frac{X}{M} = KC^{1/n} \quad (1)$$

where X = amount of solute adsorbed by M grams of adsorbent
 C = concentration of solute at equilibrium

$1/n$ and K are constants dependent on the solvent, solute, and adsorbent, and in addition for K , on the units used for X , C , and M .

X and C may be expressed in color units, or as a fraction of the original color.

M may be expressed: (1) as grams or pounds of carbon used to treat a given volume or weight of liquid; (2) as a fraction of the weight of the liquid; or (3) as a fraction of the weight of the solids in the liquid—i. e., as a fraction of the weight of solids in a sugar solution.

A plot of X/M vs. C on rectangular coordinate paper is a

¹ J. IND. ENG. CHEM., 12, 687 (1920).

² Bur. Standards, *Tech. Paper* 338.

³ Teeple and Mahler, *IND. ENG. CHEM.*, 16, 498 (1924).

¹ Presented before the Division of Sugar Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² Tadokoro, *J. Chem. Ind. Japan*, 21, 405 (1918); through *C. A.*, 13, 1947 (1919).

³ Zerban and Byall, "Adsorption Isotherms of Some Decolorizing Carbons," paper read at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

⁴ *J. IND. ENG. CHEM.*, 15, 784 (1923).

⁵ *Chem. Met. Eng.*, 28, 541 (1923).

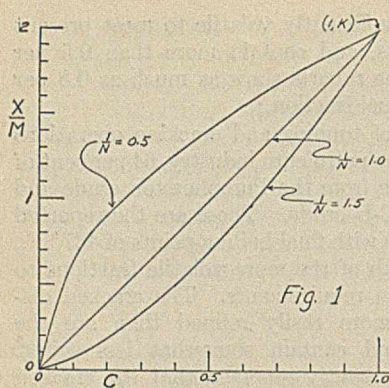


Fig. 1

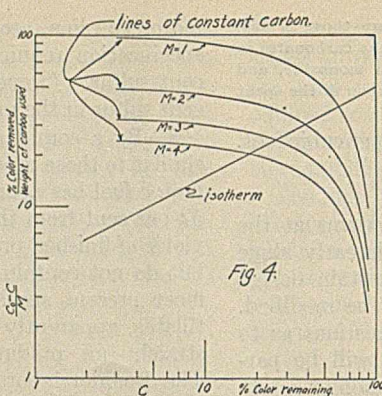


Fig. 4

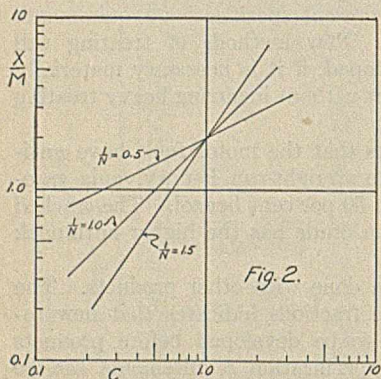


Fig. 2

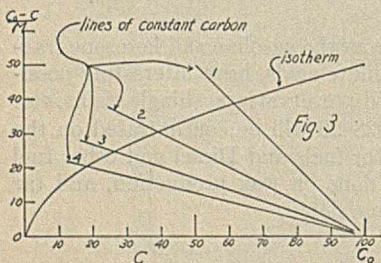


Fig. 3

parabola which goes through the origin and the point (1, K). A plot of $\log X/M$ vs. $\log C$ is a straight

line whose slope is $1/n$ and which has K for its ordinate where $C = 1$. Figure 1 represents a family of such curves on rectangular coordinate paper. In Figure 2 these curves are shown plotted in the logarithmic form.

Most writers on the subject of adsorption isotherms state that the value $1/n$ is ordinarily between 0.2 and 0.8 and never exceeds 1.0. This is inaccurate, as with certain refinery sirups the writer has found values as high as 2.0. Vegetable oils, also, give steep isotherms.

For simplicity, Freundlich's equation will be used in a slightly modified form. If we let

C_0 = original color of liquid
 C = color after decolorization

then $C_0 - C$ = amount of color removed by M weight of carbon, or the term X in equation (1)

Our equation now stands as

$$\frac{C_0 - C}{M} = KC^{1/n} \quad (2)$$

There is one property of these graphs which apparently has been overlooked. In any family of isotherms representing the action of different carbons on a given sample liquid, all points of constant carbon fall on a common line. In a plot of $(C_0 - C)/M$ vs. C on rectangular coordinate paper these lines of constant carbon are straight and go through C_0 ; on double logarithmic paper they are curved sharply and are asymptotic to C_0 . (Figures 3 and 4) These lines

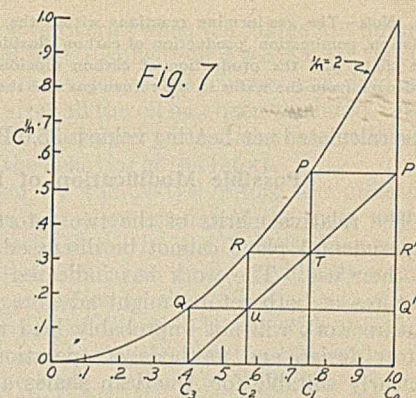


Fig. 7

of constant carbon are obtained by plotting $(C_0 - C)/M$ vs. C , keeping M constant and equal to the weight of carbon for any given line; that is, for $M = 2$, we plot $(C_0 - C)/2$ vs. C , etc.

This process can be reversed, and if one has the isotherm plotted he can readily determine to what color any given weight of carbon will decolorize the liquid. A special case in which a unit weight of carbon is considered is given by Freundlich⁹ who, in turn, credits it to Mecklenburg.¹⁰

Two-Step Countercurrent Process

Let us now derive the expression showing the relative amounts of carbon required by a two-step countercurrent treatment and a single application.

In Figure 5, let C_0 = original color of the liquid
 C_2 = final color of decolorized liquid
 C_1 = color of solution between first and second use of carbon in a two-step countercurrent treatment
 M_1 = weight of carbon needed to obtain a color of C_2 in a single use
 M_2 = weight of carbon needed to obtain a color of C_2 in the two-step current

K and $1/n$ are the constants of the adsorption isotherm and are determined by experiment.

It is assumed that the isotherm holds throughout.

For the single use we have

$$\frac{C_0 - C_2}{M_1} = KC_2^{1/n} \quad (3)$$

Since in a two-step treatment the same amount of color will be removed and the carbon will leave in equilibrium with C_1 , we have

$$\frac{C_0 - C_2}{M_2} = KC_1^{1/n} \quad (4)$$

Combining equations (3) and (4), we have

$$\frac{M_2}{M_1} = \frac{C_2^{1/n}}{C_1^{1/n}} \quad (5)$$

In the first stage of the two-step treatment we have

$$\frac{C_1 - C_2}{M_2} = KC_2^{1/n} \quad (6)$$

Combining equations (3) and (6), we have

$$\frac{M_2}{M_1} = \frac{C_1 - C_2}{C_0 - C_2} \quad (7)$$

Combining (5) and (7), we have

$$\frac{C_1 - C_2}{C_0 - C_2} = \frac{C_2^{1/n}}{C_1^{1/n}} \quad (8)$$

⁹ Hatfield's translation of Freundlich's "Kapillarchemie," p. 178.

¹⁰ Naturw. Wochenschrift., 15, 409 (1916).

Substituting the values of C_0 , C_2 , and $1/n$ in equation (8), we obtain the value of C_1 . We can now calculate the value of M_2/M_1 by either equation (5) or (7).

Equation (8) is most easily solved by graphical methods. Figure 8 shows a nomographic chart for this purpose. This chart gives the value of C_2/C_1 . To use the chart, connect the given value of $1/n$ with the desired value of C_2 . The line will intersect the curved scale at the corresponding value of C_2/C_1 . C_1 can then be calculated, or the quantity C_2/C_1 may be raised to the power $1/n$ by means of a log-log slide rule. (A log-log slide rule, one which carries scales of e^x and e^{-x} in addition to the usual scales, is almost a necessity in making decolorizing carbon calculations.)

In a previous paper⁴ a nomographic chart for solving Freundlich's equation was given.

Three-Step Countercurrent Process

Referring to Figure 6, let

C_0 = original color of liquid

C_3 = final color of liquid

C_1 = color after third step

C_2 = color after second step

M_1 = weight of carbon required to obtain the color C_3 in a single use

M_3 = weight of carbon required to obtain the color C_3 in a three-step use

By inspection, we can write

$$C_0 - C_3 = M_1 K C_3^{1/n} \quad (9)$$

$$C_0 - C_3 = M_3 K C_1^{1/n} \quad (10)$$

$$C_1 - C_3 = M_3 K C_2^{1/n} \quad (11)$$

$$C_2 - C_3 = M_3 K C_3^{1/n} \quad (12)$$

Combining equations (9) and (12), we have

$$\frac{M_2}{M_1} = \frac{C_2 - C_3}{C_0 - C_3} \quad (13)$$

or from (9) and (10) we have

$$\frac{M_3}{M_1} = \frac{C_3^{1/n}}{C_1^{1/n}} \quad (14)$$

Combining (13) and (14), we have

$$\frac{C_2 - C_3}{C_0 - C_3} = \frac{C_3^{1/n}}{C_1^{1/n}} \quad (15)$$

Combining (11) and (12), we have

$$\frac{C_1 - C_3}{C_2 - C_3} = \frac{C_2^{1/n}}{C_3^{1/n}} \quad (16)$$

If one prefers, he can solve these equations, the easiest way being to assume arbitrary values of C_2 in equations (15) and (16), calculate the corresponding values of C_1 , and then plot the values of C_1 vs. C_2 . The values of C_1 and C_2 at the intersection of the curves are the ones which satisfy equations (15) and (16). The ratio M_3/M_1 can then be calculated from either equation (13) or (14).

An easier way to determine the values of C_1 and C_2 is as follows: From equations (10), (11), and (12), we can write

$$\frac{C_0 - C_3}{C_1^{1/n}} = \frac{C_1 - C_3}{C_2^{1/n}} = \frac{C_2 - C_3}{C_3^{1/n}} \quad (17)$$

According to elementary algebra,

$$\frac{A \pm B}{C \pm D} = \frac{A}{C} = \frac{B}{D} \quad (18)$$

Using this relation, we have from equation (17):

$$\frac{C_0 - C_1}{C_1^{1/n} - C_2^{1/n}} = \frac{C_0 - C_2}{C_1^{1/n} - C_3^{1/n}} = \frac{C_0 - C_3}{C_1^{1/n}} \quad (19)$$

Geometrically this means that if, as in Figure 7, we draw the curve $C^{1/n}$ vs. C on rectangular coordinate paper, the line C_3P' will cut the line QQ' at the color C_2 , and the line RR' at the color C_1 . This is obvious, for in the similar triangles $P'R'T$, $P'Q'U$, and $P'C_0C_3$ we have

$$P'R' = C_1^{1/n} - C_2^{1/n} \quad (20)$$

$$P'Q' = C_1^{1/n} - C_3^{1/n} \quad (21)$$

$$P'C_0 = C_1^{1/n} \quad (22)$$

$$R'T = C_0 - C_1 \quad (23)$$

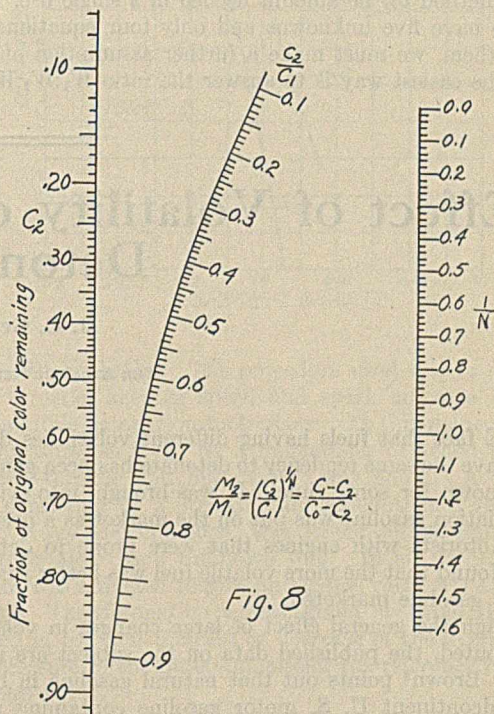
$$Q'U = C_0 - C_2 \quad (24)$$

$$\frac{R'T}{P'R'} = \frac{Q'U}{P'Q'} = \frac{C_0 - C_3}{P'C_0} \quad (25)$$

which is the same as equation (19).

The same method may be used in the case of the two-step or a four-step process.

A plot on rectangular coordinate paper of $C^{1/n}$ vs. C and a few trials thus enable one to determine quickly the values of C_1 and C_2 . M_3/M_1 can readily be calculated by either (13) or (14).



The values of $C_1^{1/n}$, when the color is expressed as a fraction¹ of the original color, represents the work the carbon has done in terms of the theoretical maximum that it would do in an ideal countercurrent treatment.

Re-use of Partially Spent Carbon on Fresh Liquid

From time to time, in hopes of saving carbon, operators propose the re-use of carbon on fresh, undecolorized liquid. Let us assume

W_1 = quantity of liquid treated the first time by M_1 weight of carbon

W_2 = quantity of liquid treated the second time by M_1 weight of carbon

W_3 = quantity of liquid treated the third time by M_1 weight of carbon

the same batch of carbon being used for each treatment and becoming spent to a greater degree each time

C_3 = color of first batch after decolorization

C_2 = color of second batch after decolorization

C_1 = color of third batch after decolorization

W_4 = quantity of liquid which M_1 weight of carbon could have decolorized in one application

Let us further assume that C_2 is the color desired after decolorization and, therefore, that it is the color of the mass of liquid obtained by mixing W_1 , W_2 , and W_3 .

We can write the following equations:

$$W_1(C_0 - C_3) = M_1 K C_3^{1/n} \quad (26)$$

$$W_1(C_0 - C_3) + W_2(C_0 - C_2) = M_1 K C_2^{1/n} \quad (27)$$

$$W_1(C_0 - C_3) + W_2(C_0 - C_2) + W_3(C_0 - C_1) = M_1 K C_1^{1/n} \quad (28)$$

$$\frac{W_1 C_3 + W_2 C_2 + W_3 C_1}{W_1 + W_2 + W_3} = C_2 \quad (29)$$

Combining (28) and (29), we have

$$(W_1 + W_2 + W_3)(C_0 - C_2) = M_4 K C_1^{1/n} \quad (30)$$

By definition,

$$W_4(C_0 - C_2) = M_4 K C_2^{1/n} \quad (31)$$

Therefore

$$\frac{W_4}{W_1 + W_2 + W_3} = \frac{C_2^{1/n}}{C_1^{1/n}} \quad (32)$$

which is the ratio we are trying to calculate.

It represents the ratio of the amount of carbon required by this method to the amount needed in a single use.

As we have five unknowns and only four equations connecting them, we must make a further assumption of some sort. The easiest way is to answer the ratio $W_1:W_2:W_3$.

We have carried out these calculations with the ratio $W_1 = W_2 = W_3$ and with $W_1 = 2W_2 = 4W_3$.

We assumed $1/n = 0.33$, $C_2 = 0.10$, $C_0 = 1.00$.

Compared with the carbon required for a single use, the savings were: two-step countercurrent, 45; $W_1 = W_2 = W_3$, 20; and $W_1 = 2W_2 = 4W_3$, 28 per cent. We may therefore dismiss this last method when considering the re-use of carbons, as the saving in carbon is less than in a two-step countercurrent treatment.

In deciding whether or not to use a two- or three-step countercurrent treatment, one must know the cost of filtering the liquid in question. There is no point in using a process which requires an extra filtration if the saving in carbon is eaten up by the additional filtration expense. The greater degree of decolorization desired and the greater the value of $1/n$, the greater the saving by using the stepwise countercurrent method.

Effect of Volatility of Petroleum Fractions on Detonation Value¹

J. C. Geniesse and H. F. Huf

THE ATLANTIC REFINING COMPANY, PHILADELPHIA, PA.

THE fact that fuels having different volatilities do not have the same tendency to detonate has been generally known for some time. It was brought into evidence when aviation gasoline was put on the market as a premium fuel. Motorists with engines that were prone to detonate quickly found that the more volatile fuel was better than the ordinary gasoline marketed.

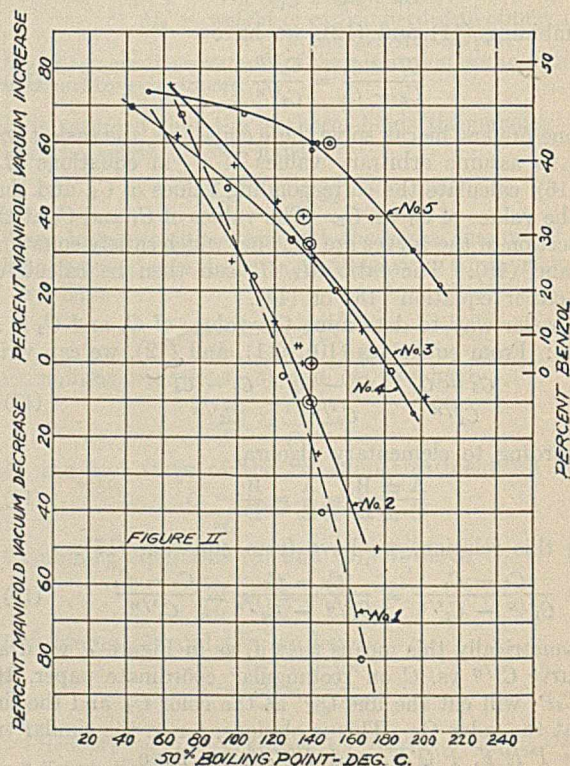
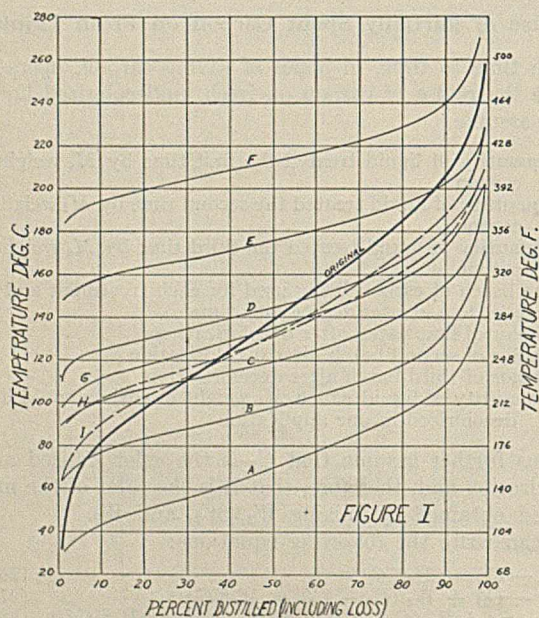
Although the general effect of large changes in volatility is undisputed, the published data on the subject are inconclusive. Brown² points out that natural gasoline in blends with midcontinent U. S. motor gasoline containing up to

50 per cent of the former is about one-half to one-third as effective as benzene. As would be expected, the beneficial effect depends upon the volatility of the natural gasoline and the detonation characteristic of the fuel with which it blended. Marley, Stevens, and Gruse³ show that it is possible to obtain gasolines of different end point but of the same detonation value as well as gasolines of the same end point but different detonation values. Their data furnish some evidence that the detonating tendency of a fuel is related to the

³ *J. Soc. Automotive Eng.*, 20, 214 (1927).

¹ Presented before the Division of Petroleum Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² *Natl. Petroleum News*, 18, 28 (1926).



volatility as a whole rather than to any specific point on the distillation curve. Egloff and Morrell⁴ present data showing that the distillation end point may be varied from 390° to 430° F. with but very little change in the detonation value. This is not surprising, as it takes but a very small quantity of heavy material to effect the end point because of the relatively good fractionating efficiency of the A. S. T. M. distillation apparatus as the dry point is approached.

In commercial work it is often necessary to predict what detonation improvement may be accomplished by changing the A. S. T. M. distillation of a naphtha from a given source. With the view of detecting any relation existing between the volatility and the detonation value of fractions taken from the same source, the experiments outlined below were undertaken.

Experimental

Five petroleum naphthas of known source were used: (1) a straight-run Pennsylvania naphtha; (2) a straight-run midcontinent naphtha; (3) a straight-run California naphtha; (4) a liquid-phase cracked distillate made from midcontinent gas oil; (5) a liquid-phase cracked distillate made from a selected gas oil. These naphthas were cut into six fractions by simple distillation. Close fractionation was purposely avoided in order not to accumulate non-detonating hydrocarbons in certain fractions. The A. S. T. M. distillation data and gravities of the originals, the fractions, and some blends of the fractions are given in Table I. The distillation data for fuel naphtha No. 2 are shown graphically in Figure I. Only the values are given for the other set of fuels, as they were all made in a similar manner.

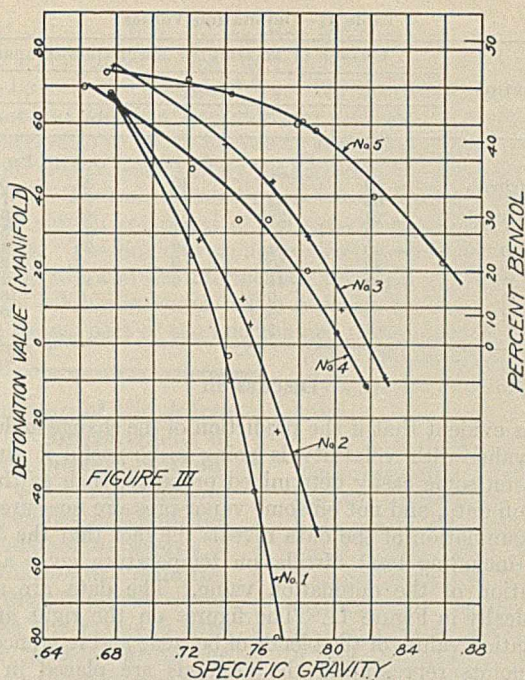
The detonation tests were made in the single-cylinder Lockwood-Ash motor as described by Cummings.⁵ The only modification was the substitution of a dynamometer

⁴ Oil Gas J., 25, 146 (1926).

⁵ J. Soc. Automotive Eng., 22, 448 (1928).

Table I—Distillation and Specific Gravity

FUEL (NAPHTHA)	FRAC-TION	SPECIFIC GRAVITY	DISTILLATION TEMPERATURE				
			Over point	20%	50%	80%	Dry point
			° C.	° C.	° C.	° C.	° C.
1	Original	0.742	60	104	140	184	177
	A	0.679	49	47	71	102	170
	B	0.722	63	90	107	135	199
	C	0.743	88	110	125	154	213
	D	0.756	108	128	146	174	228
	E	0.778	129	150	167	193	237
2	F	0.781	157	181	192	214	244
	Original	0.756	48	97	139	185	248
	A	0.685	33	50	68	95	151
	B	0.726	64	84	98	118	170
	C	0.758	91	107	120	142	194
	D	0.769	115	130	144	167	210
3	E	0.791	143	163	174	193	228
	F	0.817	184	199	213	229	267
	Blend G	0.757	99	117	134	158	202
	H	0.754	86	110	131	162	209
	I	0.753	62	103	132	170	227
	Original	0.764	39	100	138	178	220
4	A	0.679	17	40	64	96	164
	B	0.739	56	83	99	105	170
	C	0.767	90	108	121	142	184
	D	0.784	112	127	142	161	199
	E	0.804	138	165	168	185	213
	F	0.826	172	188	200	236	238
5	Original	0.748	26	78	138	176	200
	A	0.663	19	28	44	73	160
	B	0.723	53	77	95	125	176
	C	0.764	94	124	130	145	190
	D	0.785	121	140	154	171	198
	E	0.802	153	164	174	185	209
6	F	0.817	170	186	194	199	220
	Original	0.792	36	84	151	194	216
	A	0.675	17	33	53	88	170
	B	0.743	50	81	103	125	190
	C	0.790	94	121	140	167	204
	D	0.821	134	160	173	193	214
7	E	0.844	152	182	196	205	223
	F	0.859	188	203	210	217	232
	Blend G	0.783	66	117	140	174	206
	H	0.780	36	88	143	184	209



for the Prony brake. The procedure used was to gradually open throttle, keeping speed and spark advance constant, until audible detonation took place. At this point the absolute pressure, as given by a manometer attached to intake between throttle and inlet valve, was noted. A reference fuel, consisting of a straight-run midcontinent gasoline of U. S. Navy specifications, was tested either immediately before or after each unknown fuel. In all cases the carburetor was adjusted to give an air-fuel ratio of 12.5 to 1 by weight. The detonation values, given in Table II, are expressed in per cent increase or decrease of the average absolute pressure in the intake manifold, the reference fuel being the zero point.

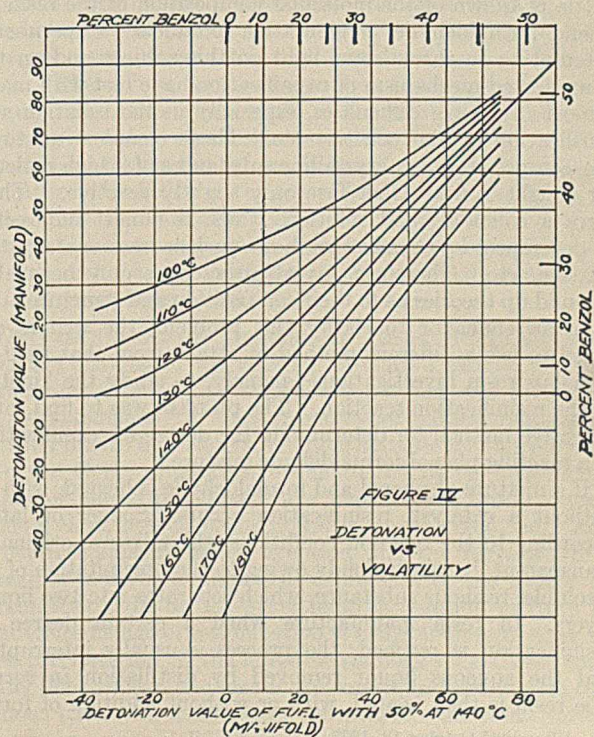


Table II—Detonation Values

FRACTION	CHANGE IN MANOMETER ABSOLUTE PRESSURE				
	NAPHTHA				
	No. 1	No. 2	No. 3	No. 4	No. 5
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Original	- 10	0	40	34	60
A	68	62	75	70	74
B	24	28	54	48	68
C	- 3	12	44	34	58
D	- 40	-24	29	20	40
E	- 80	-50	9	3	31
F	-108	-44	- 9	-11	22
G		0			60
H		5			60
I		5			

Discussion

It is evident that if the prediction of the change in detonation value with volatility is going to be useful it must be based on some easily determined property, such as the distillation data, and not on some vapor-pressure measurement. An examination of the data reveals the fact that the 50 per cent (including loss) distillation temperature gives a good indication of the detonation value. The data are shown graphically in Figure II. The figures on the right are the detonation values of the blends of benzene and reference fuel. The points representing the originals are placed in large circles. They are in general slightly better than the corresponding narrow fractions. It was found that if some lower temperature was used, such as the 35 per cent boiling point,

the blends agreed slightly better with the narrow fractions, but that the relation then involved a distillation point which is not included in a fuel specification and, therefore, was not so useful.

On examination of the data, another interesting but less useful relationship became apparent. It is shown graphically in Figure III. In this case the blends fall on both sides of the curves, showing a slightly better agreement than with the 50 per cent boiling points. However, this relationship is not so useful as the one previously given, because it involves the use of specific gravities which have no value per se.

In order to make the data more useful the chart in Figure IV has been constructed from the curves in Figure II. The detonation values on the vertical axes are those for fuels having the 50 per cent boiling points shown on the curves. The values on the horizontal axes are those for fuels having 50 per cent off at 140° C. Any prediction as to the effect of volatility on detonation on a naphtha from a given crude may be made by the use of this graph.

Conclusion

There is a definite relationship between the specific gravity of a fraction from a given crude and its detonation value, and also between the 50 per cent (including loss) distillation temperature of a fraction from a given crude and its detonation value. A graph constructed from these data makes it possible to predict what effect changing the volatility will have on the detonation value.

Phenol-Formaldehyde Resinification—I¹

Jan Novák and Vojtěch Čech

CZECH TECHNICAL HIGH SCHOOL, BRNO, CZECHOSLOVAKIA

THE increasing application of the phenol-formaldehyde resins in industry and daily life gives constantly greater importance to their composition and chemical properties. Little is known of the molecular composition of the resinous phenol-formaldehyde condensation products. Experiments attempting to throw some light on this subject and on the complicated mechanism of resinification have met with many almost invincible difficulties, especially in the isolation and purification of the constituents. These complex mixtures are composed of non-crystalline substances of a high molecular weight and are therefore only slightly reactive. They form a colloidal solid solution, which is almost impossible to decompose by chemical methods, such as fractional crystallization, etc. Therefore, investigators have only been able to build up theories as to their composition and structure.

In an endeavor to clarify this problem, the writers decided to use a different method of attack from that used in previous resin investigations—namely, to study the kinetics of the resinification reaction. The problem was to find some objective method for determining the degree of resinification of a reacting phenol-formaldehyde mixture.

If a mixture of phenol and formaldehyde is heated, with or without a catalyst, resinification occurs. Sooner or later, according to the reaction conditions, the mixture, originally transparent, becomes cloudy owing to the precipitation of an insoluble, resinous substance, which separates into two liquid layers. In resin manufacture when a certain degree of resinification is reached, the process is usually interrupted and the aqueous liquor removed by distillation *in vacuo*. The resin is then heated, with or without addition of form-

aldehyde or catalysts, until it is completely transformed into a jelly-like substance or a solid, more or less insoluble and infusible mass. During resinification this mass increases in viscosity and becomes less soluble. It was believed, therefore, that this fact might be useful in devising a method which would throw some light on the resinification problem and make it possible subsequently to work out an analytical procedure for testing the final resinous products as they are found in the trade.

From the beginning it was realized that it would be impossible to determine the degree of resinification by absolute physical constants, but that only relative figures could be obtained. On this basis one chemical and two physical methods were worked out. The physical methods involved the testing of refractive properties and viscosity. The chemical method was based on the behavior of the reaction mixtures toward an acid bromine solution, and the results were called "bromine value." The other properties—e. g., boiling point, density, electric properties, etc.—make no characteristic change during resinification and so many difficulties are encountered in their determination that they are not suitable for a kinetic study of resinification.

Historical

The first to note the increasing viscosity of the reaction mixture of phenol and formaldehyde was Jablonower,² and he was followed some time later by van Voorhout.³ Drummond⁴ gives the first figures in this connection, but he refers only to the

² *J. Am. Chem. Soc.*, **35**, 811 (1913).

³ *Kunststoffe*, **11**, 59 (1921).

⁴ *J. Soc. Chem. Ind.*, **18**, 323T (1899); *Kunststoffe*, **15**, 3 (1925).

¹ Received October 12, 1927.

absolute viscosity of the resinous, solid, sirupy, and final condensation products in trying to find out the relation between the viscosity and the temperature. Critical miscibility proportions of resin and solvent, measured as "solvent powers," were determined by Mardles,⁵ and were judged by the volume of gasoline necessary to effect precipitation from 20 per cent solutions of the resins.

Steinitzer⁶ showed that phenol-formaldehyde resins produce phenol on heating with solutions of sodium hydroxide or fusing with solid sodium hydroxide, and that the phenol could be determined by color reactions. This reaction, which is scarcely sufficient for the identification of synthetic resins of the phenol-formaldehyde type, was improved by Herzog.⁷ Redman, Weith, and Brock⁸ worked out some methods for the determination of phenol in mixtures with formaldehyde and hexamethylene-tetramine, but they point out that these methods are of no value when saligenin-like resinous bodies are present, which is of course the case when degree of resinification is being determined. Morgan and Meighan⁹ determined the free phenol of phenol-formaldehyde resinification products by volumetric measurement of the hydrogen evolved on adding metallic sodium to solutions of the resins either in gasoline or in a known amount of additional phenol. This method, however, is not suitable for aqueous resinification mixtures.

Ormandy and Craven¹⁰ made great progress in analyzing these resinification mixtures as follows: The formaldehyde was determined by the method of Heywood and Smith,¹¹ phenol, according to the authors' statement, having no influence on the oxidizing reaction. The phenol was determined either by extraction with benzene and subsequent evaporation of the solvent or by iodometric titration (Kebler's method as triiodophenol) generally after elimination of the formaldehyde by means of hydrogen peroxide. A less exact method for phenol suggested by the authors is its separation by addition of sodium sulfate.

Resinification without catalyst, or with ammonia or phosphoric acid as catalyst, was studied by determining free formaldehyde in samples taken at different stages of resinification until the separation into two layers took place. Since this represents only a small part of the total resinification process, the investigations were incomplete.

Finally, Petrov¹² analyzed the final hard, insoluble phenol-formaldehyde condensation product, determining a "bromine value" after dissolving the material in chloroform and treating it in a manner similar to that used in determining the iodine value of fats and oils. This method, however, seems to have justification only for the author's condensation product.

Refractive Index Measurement

Owing to the success with refractive index determinations achieved in various branches of industry by means of the precision refractometers of Zeiss and Goerz, the possibilities of its application to the determination of the degree of resinification were studied. After much experimentation the method was found suitable for this purpose.

When phenol and formaldehyde are boiled together, with

or without a catalyst, the reaction mixture very quickly acquires a high luster so that its refractive power is increased, as can be seen with the naked eye. Refractive index measurements with the Zeiss refractometer (Abbé type) confirmed this observation. With increasing resinification the mixture becomes cloudy, solid or oily insoluble substances being precipitated. The reaction mixture therefore represents a heterogeneous system composed of the aqueous liquid and a resinous layer. The liquid is an aqueous solution of free phenol, formaldehyde, and the intermediate products of resinification that are soluble in water. The resinous layer is composed of the resins, part of the uncombined phenol, and formaldehyde. Water is also generally adsorbed in small quantities.

An attempt was first made, therefore, to separate the two components of this heterogeneous system in order to determine the refractive index of each. A quantitative separation proved difficult, however, so it was decided to determine the refractive indices of both parts of the mixture directly, without separation. Preliminary experiments were made by thoroughly mixing different substances either totally immiscible or of limited mutual solubility and determining their refractive indices. The following systems were tested: aniline-water, benzene-water, phenol-water, and finally resin-water, as formed in the usual phenol-formaldehyde resinification.

In these experiments a separation was observed in the thin film between the prisms of the apparatus and two border lines appeared between the dark and light parts of the eyepiece. These lines correspond to two refractive indices, belonging to the two components of the mixture. These two parts are in mutual equilibrium; that is, the final state, after separation between the prisms, is one of equilibrium between the saturated solution of the component A in B, and also B in A. It is therefore clear that under constant conditions of temperature and composition of mixture reproducible results are obtained. Such mixtures may thus be characterized by two refractive index numbers.

DETERMINATION OF DEGREE OF RESINIFICATION—After intensive shaking of the reactive mixture a sample is withdrawn and a few drops are placed between the prisms of the refractometer. A Zeiss (Abbé type) refractometer with jacketed prisms has been found more suitable for this purpose than the Goerz apparatus, owing to the better achromatization of the border line where high indices are involved. When a clear, homogeneous liquid is to be tested, only one border line appears in the eyepiece, and the corresponding refractive index is a numerical expression of the degree of resinification. If, on the other hand, a reaction mixture in an advanced stage of resinification is being analyzed—that is, after precipitation of the insoluble resinous substances—two border lines appear, one for the aqueous liquid and one for the resinous part. By keeping the temperature constant during these measurements (20° C. being the most favorable), repro-

Three methods for the determination of the degree of resinification are described: (1) Measurement of the refractive indices of the reaction mixture, without separation of the resinous part from the aqueous liquid; (2) determination of the viscosity of a solution of the reaction mixture in ethyl alcohol by means of Ostwald's viscometer; (3) determination of "bromine value" of the reaction mixture by dissolving the tested sample in acetic acid, precipitating the resinous substances by the addition of water, and titrating the filtered liquids, free from insoluble resinous compounds according to Koppeschaar's method.

The results so obtained are plotted to illustrate the course of resinification. The mechanism of resinification is described on the basis of the data obtained. Condensation is found to occur almost during the whole period of resinification, while polymerization, according to the reaction conditions, sets in after precipitation of the insoluble resinous substances.

Different agents are found to have different catalyzing power. They are therefore divided into condensation catalysts (acid bodies) and polymerization catalysts (alkaline bodies).

New applications of these methods are suggested.

⁵ *J. Chem. Soc. (London)*, **127**, 2940 (1925).

⁶ *Kunststoffe*, **5**, 109 (1915).

⁷ *Z. angew. Chem.*, **34**, Aufsatzteil 97 (1921).

⁸ *J. IND. ENG. CHEM.*, **6**, 205 (1914).

⁹ *Ibid.*, **17**, 626 (1925).

¹⁰ *J. Soc. Chem. Ind.*, **42**, 18T (1923).

¹¹ *J. Am. Chem. Soc.*, **27**, 1183 (1905).

¹² *Kunststoffe*, **16**, 81, 107, 124 (1926).

ducible results may be obtained, even when the resinification is very high, making separation of the components difficult. Even the slight change in the refractive index of the resinous part caused by occlusion of the aqueous liquid by the resins is always the same, and since only relative values are desired this can be ignored. The degree of resinification can thus be determined by these figures, because a definite refractive index belongs to each stage.

When refractive indices of very highly resinified mixtures are to be determined, sometimes the second border line, belonging to the aqueous liquid, cannot be found. Turning the prisms away from the light usually removes this difficulty. The resin border line may be made more distinct by a slight loosening and subsequent tightening of the prism screw. Compared with homogeneous mixtures the border lines are not so sharp, sometimes widening to a narrow band. The eye soon becomes accustomed to this, however.

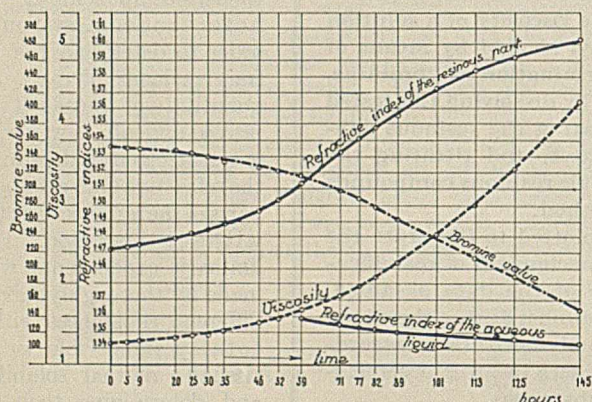


Figure 1—Resinification without Catalyst

Viscosity

The increasing viscosity of the reaction mixture during resinification is used in phenol-formaldehyde resin manufacture as an approximate indication of the condition of the reacting masses. Since this test is only approximate, an attempt was made to work out a precise method for determining the viscosity of such mixtures in order to obtain numerical values which would indicate the course of resinification as was done by following the refractive indices.

Inasmuch as quantitative separation of the aqueous liquid from the resin had been found impossible, the viscosity of the mixture was measured directly by dissolving a sample and determining the viscosity of the solution. Ethyl alcohol was selected as the solvent because it dissolves nearly all phenol-formaldehyde resinification products except the hard resistant form. Denatured spirit is unsuitable because of its varying composition. One part of the resinous mixture to two parts of alcohol by weight proved to be the most practical proportion. The determinations were carried out in an Ostwald viscometer, which not only gives precise results but permits, by changing the dimensions of the tube, regulation of the sensitivity of the instrument.

In carrying out these tests it was observed that the alcohol solutions, especially those from products of acid resinification, tend to precipitate small particles, probably some form of the polymerized formaldehyde, which retard the flow of liquid in the capillary tube, and therefore affect the viscosity determination. These particles settle after 4 hours' standing, and it is then possible, without agitation of the liquid, to withdraw the volume of solution required for the viscometer free from them. This is better than filtration to remove the particles, which introduces new errors due to evaporation and adsorption by the filtering material.

RESINIFICATION TEST—A sample of the reaction mixture is placed in a flask provided with a ground-glass stopper and weighed on an analytical balance. A sample weighing about 10 grams is sufficient. Twice the weight of alcohol is then added from a buret and the flask is shaken until solution is complete. After standing 4 hours the viscosity of the liquid is determined, using a 5-cc. sample.

The viscosity of the alcohol must first be determined in the same apparatus and under the same conditions as the resinous solutions and is fixed as 1, since only relative numbers are wanted. The viscometer must be thoroughly cleaned by washing with alcohol and then with ether and carefully dried. Five cubic centimeters of the alcohol solution are then put in the apparatus and the viscosity tested in the usual manner. The optimum temperature is 20° C., and is maintained by means of a small glass thermostat electrically heated with an electrical temperature-control apparatus. In order to obtain reproducible results the viscometer must be fixed vertically in the water bath.

The average of at least three determinations is used for calculating the relative viscosity of the reactive mixture according to the following formula:

$$n = n_0 \frac{st}{s_0 t_0}$$

where t_0 = time of flow of alcohol used for the dissolving (in seconds)

s_0 = density of alcohol used for the dissolving

n_0 = viscosity of alcohol used for the dissolving (= 1)

t = time of flow of resinous solution

s = density of resinous solution

n = viscosity of resinous solution

s/s_0 is very nearly equal to 1, because the densities of the resinous solutions do not differ much from the densities of the alcohol and, furthermore, the differences in densities of the alcohol solutions prepared from mixtures at the beginning and end of the resinification are so small that they can be ignored. Therefore, since n_0 is also equal to 1, the relative viscosity formula becomes $n = t/t_0$ —that is, it is equal to the relation of the times of flow of the resinous solution and the alcohol solvent. This relative number is a measure of the degree of resinification.

Bromine Value

In determining the degree of resinification by chemical means it was also necessary to resort to relative values—similar to the determination of iodine values of fats. The method of Ormandy and Craven,¹⁰ determining the free formaldehyde or phenol in the mixture, cannot be applied after the insoluble substances have been precipitated. Furthermore, it is doubtful if formaldehyde could be estimated in the presence of a large quantity of phenol, and the method does not take into consideration the presence of unstable phenol-formaldehyde compounds, whose behavior has not yet been studied. The presence of intermediate products will also influence results by Heywood and Smith's method for formaldehyde. The authors themselves state that they used this method for studying resinification only to the point where the two layers separated, thus only a short time.

Finally a thorough study was made of the application of Koppeschaar's¹³ method for phenol to the determination of resinification. These experiments showed that formaldehyde has no influence on the results, but that the insoluble resinous intermediate products do not react so smoothly with bromine as phenol and cause the results to vary. An attempt was made to eliminate these resinous substances by dissolving the tested sample in methanol and adding water to precipitate the resin. However, after filtering, an emulsion of the resin

¹³ *Z. anal. Chem.*, **15**, 233 (1876).

in water remained, which reacted with bromine in the same way as if insoluble substances had been present. In the meantime it was found that those intermediate resinification products that are soluble in water react with bromine quite smoothly. This suggested seeking for some solvent which readily dissolves even highly resinified mixtures and on addition of water precipitates the resinous products, not in the form of an emulsion, but as filtrable flakes. Such a solvent was found in glacial acetic acid. Sometimes emulsions are also formed, but they can be eliminated by intensive shaking and repeated filtration.

The filtrate contains the following substances in the water solution—unreacted phenol, possibly some phenol formed by action of the acetic acid (although the solution seems to have more of a physical character), and water-soluble intermediate products of resinification. This aqueous liquid can be easily brominated according to Koppeschaar's method. The figures thus obtained do not represent the free, unreacted phenol alone, because the water-soluble intermediate products also take part in the bromination. A relative value is obtained, however, which is characteristic for every stage of the reaction between phenol and formaldehyde, and is therefore indicative of the degree of resinification. Any possible chemical changes in the phenol-formaldehyde compounds caused by the glacial acetic acid are of no importance because only relative values are desired. However, these figures agreed so closely with approximate results using methanol that it is unlikely that any chemical changes did take place in the resin.

DETERMINATION OF BROMINE VALUE—About 5 grams of the mixture are placed in a 100-cc. volumetric flask and weighed exactly on an analytical balance; the flask is then filled to the mark with glacial acetic acid which is free from oxidizable substances. Twenty cubic centimeters of this solution are pipetted into a 1000-cc. volumetric flask which has previously been filled three-fourths full with distilled water. The pipetting must be done drop by drop while the water-filled flask is being agitated by a slow, circular movement. The resin precipitates in flakes. The flask is then filled to the mark with distilled water and, after thorough agitation, the contents are repeatedly filtered until the filtrate is clear, for only perfectly clear liquids can be used for bromination. The first filtrate is rejected in order to prevent errors due to adsorption by the filter paper.

Twenty-five cubic centimeters of this filtrate are pipetted into a 250-cc. bottle provided with a ground-glass stopper and 25 cc. of 0.1 *N* solution of potassium bromide and bromate are added. (This solution is prepared by dissolving 2.7836 grams of potassium bromate and about 10 grams of potassium bromide in 1000 cc. of distilled water.) Water is then added until the bottle is half filled, followed by 3 cc. of concentrated hydrochloric acid. After 20 minutes 10 cc. of a 1:10 solution of potassium iodide are added and after 2 minutes more the contents of the bottle are titrated with 0.1 *N* sodium thiosulfate solution, starch being used as indicator. At the same time a blank experiment is carried out by pipetting 25 cc. of the bromate-bromide solution, adding 0.5 cc. of glacial acetic acid, and titrating in the same manner. This gives the value for the bromate-bromide solution. In order that constant results may be obtained, all conditions, such as size of sample, dilution, etc., must be carefully observed.

From the titration results the bromine value is calculated. The bromine value of the resinification mixture is a number corresponding to the number of cubic centimeters of an exactly 0.1 *N* bromate-bromide solution that are needed for the bromination of precisely 1.000 gram of the resinification mixture. It is calculated as follows:

Weight of the sample: 4.6987 grams dissolved in 100 cc. of acetic acid, 20 cc. of this solution pipetted into 1000 cc., 25 cc. then used for the titration.

0.1 *N* sodium thiosulfate solution for titration (average of at least two measurements)..... 14.70 cc.
 Blank experiment..... 21.77 cc.
 For the bromination of 25 cc. of the filtrate are needed 7.07 cc.
 For the bromination of 1000 cc. are needed 7.07×40 , and for the 100 cc. of the acetic acid solution:
 $7.07 \times 40 \times 5 = 1415$ cc.
 $4.6987:1415 = 1.0000:x$
 $x = 301 = \text{bromine value}$

Typical Phenol-Formaldehyde Resinifications

The application of various methods for determining degree of resinification having been studied, typical resinifications were investigated, first without a catalyst, then with alkaline and acid catalysts. Nine experiments were conducted by each method of resinification—three in which the degree of resinification was determined by the refractive index method, three by the viscosity method, and three in which bromine values were determined. The results are shown in the accompanying graphs.

The resinifications were conducted in Jena glass bulbs, and glass reflux condensers having tightly fitting ground-glass stoppers at their lower ends were used. Cork connections, which would be easily attacked by the hot fumes, were avoided. Heating was done over an electric stove provided with a sand bath.

The purest obtainable phenol was used and was distilled three times *in vacuo* shortly before the resinification. Analysis showed it to contain 99.42 per cent of C_6H_5OH . The formaldehyde was also of the highest purity, containing 39.20 per cent of CH_2O . It was free from insoluble polymers and precipitated no insoluble substances after standing in the dark for several months. The same proportions of phenol

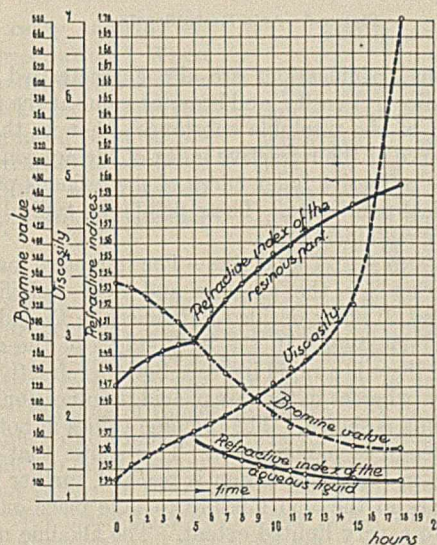


Figure 2—Alkaline Resinification

and formaldehyde were used in all experiments—approximately equimolecular quantities or 200 grams of phenol to 160 grams of formaldehyde. The phenol and formaldehyde were mixed and the catalyst, dissolved in the smallest possible quantity of water, was added. For the alkaline resinification 0.2 gram of sodium hydroxide, or 0.1 per cent of the weight of the phenol, was added, and for the acid resinification 9 mg. of hydrochloric acid, or 0.0045 per cent of the weight of phenol. Samples were withdrawn by means of glass tubes, usually at 1-hour intervals, until the resinification mixture became so viscous and had separated into layers to the extent that an average sample could not be taken. They were kept in small glass bottles provided with ground-glass stoppers.

Results

NO CATALYST—The curves (Figure 1) show decided differences between the results without catalyst and with alkaline and acid catalysts. Where no catalyst was added the chief difference was the relatively slow decrease in bromine value, especially at the beginning of the resinification, indicating that here the reaction between phenol and formaldehyde is incomplete and that unstable substances are formed which react with bromine in a manner similar to phenol. On distillation *in vacuo* these substances are decomposed, and a resin is formed the bromine value of which does not differ much from the bromine values for the products of alkaline and acid resinifications. This indicates either that part of the resinous mass is volatile or that decomposition in free phenol, which subsequently distils, takes place. The curves have no maxima or minima.

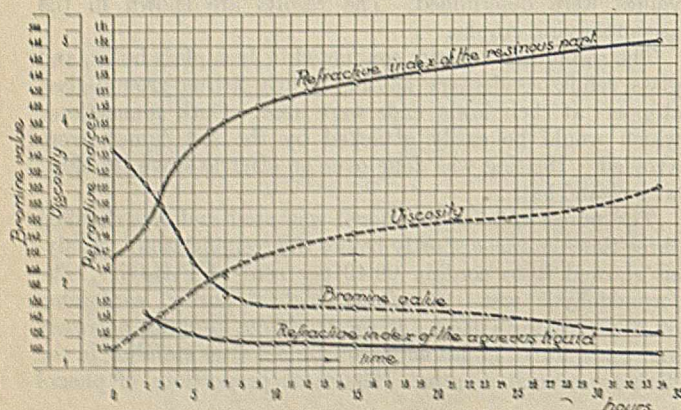


Figure 3—Acid Resinification

The various resinifications are also characterized by the refractive indices, viscosity, and bromine value at the point of precipitation of the insoluble substance—that is, the point where the curve of the refractive index of the aqueous liquid begins. The refractive index curve of the resinous part also shows a critical point here. These points are typical for the three types of resinification.

ALKALINE AND ACID CATALYSTS—The refractive index and viscosity curves for the alkaline and acid resinifications (Figures 2 and 3) show decided differences in the advanced stages of resinification. In the later stages of the alkaline resinification there is a rapid increase both in refractive index and viscosity, whereas in the case of acid resinification a tendency to maxima is shown. The bromine values in both cases have a tendency to a minimum. This shows that after a certain stage in the resinification is reached, further heating causes changes in the acid mixture to take place only very slowly and to a very limited extent. The alkaline mixture, on the other hand, shows a permanent increase in refractive index and viscosity curves, with no tendency to reach a state of equilibrium.

The values for precipitation of insoluble substances from the reaction mixture are as follows:

RESINIFICATION	REFRACTIVE INDEX		VISCOSITY	BROMINE VALUE
	Resinous part	Aqueous liquid		
No catalyst	1.5120	1.3580	1.64	318
Alkaline	1.4980	1.3690	1.86	274
Acid	1.4870	1.3650	1.54	309

Discussion of Results

These results give definite data to prove facts that have hitherto only been assumed and throw new light on the obscure phenomena of resinification. Thus, numerical values are given to show that the products of resinification are quite

different according to whether no catalyst or acid or alkaline catalyst is used—that is, the values at the point of precipitation of insoluble substances are typical for each kind of resinification.

Several conclusions as to the mechanism of the resinification can therefore be made. In general, the reaction consists of condensation and polymerization. As to whether the two processes are simultaneous or successive is still only a matter of conjecture. Jablonow² believes that condensation takes place first, and that polymerization follows. This theory, however, can be proved only to a limited extent.

On the basis of the three methods for the determination of degree of resinification described herein, condensation is shown chiefly by the decrease in bromine values and refractive indices of the aqueous liquid, and polymerization by the increase in refractive indices of the resinous part and partly by the increase in viscosity. It is therefore evident that no polymerization occurs before the resinous substances are precipitated, and the reaction is simply a condensation of phenol and formaldehyde. But from this point on, not only does polymerization of the product take place, but also a further condensation of the unreacted phenol and formaldehyde, as may be seen from the curves of the refractive indices of the aqueous layer and of the bromine values. If polymerization only occurred in this part of the resinification, there would be no noticeable change in the aqueous liquid. But such a change does take place, and the only possibility is a further reaction of free phenol or formaldehyde or of the intermediate resinous products with phenol or formaldehyde—that is, by condensation processes. On the other hand, it is impossible that the whole process is one of condensation. The relatively small decrease in the refractive indices of the aqueous layer corresponds to a relatively high increase in refractive index of the resinous part and of the viscosity of the mixture, and these great changes cannot be caused by condensation only, as the amount of free phenol and formaldehyde is very small at these stages of the resinification. They must therefore be due to intramolecular reactions, or polymerization. Furthermore, the fact that condensation reactions will change the bromine values to a large extent and polymerization only slightly is another indication that in the latter stages of resinification we have polymerization accompanied by condensation.

On the basis of these facts the reaction mechanism of the different resinifications—that is, in aqueous mixtures—can be explained. The behavior of the resinous substances after distilling off the water and further heating and addition of catalysts is quite different and will be discussed in a subsequent paper. In the case of resinification without catalyst the refractive index of the resinous part and the viscosity increase slowly until the resin precipitates. This is the condensation reaction, when a small quantity of intermediate product is formed, which reacts toward bromine in a manner similar to phenol. On further reaction this product is precipitated and undergoes polymerization, as indicated by the increasing refractive index of the resinous part and the increasing viscosity. At the same time condensation continues as the refractive index of the aqueous liquid decreases. The polymerization predominates, however; the aqueous liquid contains unreacted phenol and formaldehyde even in the later stages of resinification. Since there is no catalyst, heat alone brings about both the condensation and polymerization.

With acid resinification the refractive index curves of the resinous part and the viscosity increase rapidly, whereas there is a rapid decrease in the bromine values and refractive indices of the aqueous liquid. All curves show a tendency to minima or maxima, but no state of equilibrium is reached. Condensation occurs during the first part of the reaction and

predominates also after the precipitation of the resins. By comparing the curves for the refractive indices of the resinous part with the corresponding curves where no catalyst was used, it can be seen that the presence of acid does not accelerate the polymerization. This fact shows that any changes in the products formed by the first intensive reaction between phenol and formaldehyde are due chiefly to heat, and not to the presence of catalyst.

In the alkaline resinification there is no tendency to maxima or minima except in the bromine value and aqueous liquid refractive index curves. The formation of an initial condensation product is accelerated, as in the acid resinification. Condensation continues after precipitation, but at the same time very intensive polymerization occurs. The bromine values change only slightly near the end of the reaction, as shown by a change into a rubbery, highly viscous product, the condensation being suppressed by polymerization. This rapid polymerization is influenced by the catalyst and not due to the action of heat alone.

Catalysts

Catalysts may be divided into two classes—condensation catalysts and polymerization catalysts. In general, acid cata-

lysts are condensing agents, and alkaline catalysts, polymerizing agents. Polymerization catalysts also have some condensation catalyzing action. Polymerization must be preceded by condensation. In the presence of an alkaline catalyst there is an intensive reacting of the two components before the resinous substances precipitate, but the polymerizing action of this catalyst is much more typical than the condensing one. Products of acid resinification, especially in the presence of water, have a very limited tendency to polymerization, whereas resinification mixtures with alkaline catalysts polymerize very readily. The frequent failure of batches of resin manufactured with an alkaline catalyst can only be explained by the polymerization influence of the catalyst. Products of acid resinification do not have this difficulty.

Bakeland's and Lebach's classification of the resinous products acquires a more rational basis from the numbers obtained by these methods. Thus, Bakelite A is characterized as a polymerizable resin, while acid resinification products, Novolaks, are only polymerizable to a limited extent.

This discussion is the first of a series of studies of hitherto little understood resinification phenomena, for the purpose of attaining more rational control in manufacture. A similar study is now being made of hardened resins.

Introfiers, or Impregnation Accelerators¹

Marc Darrin

MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PA.

IT IS well known that many liquid mixtures have a greater fluidity than the weighted average of their component parts. A familiar instance is the thinning of heavy crankcase oils by small amounts of motor fuels. Resins are softened by very small amounts of oils.

Glues are rapidly thinned by water. There are many liquid mixtures, such as those used in the nitrocellulose industry, which have greater solvent powers than their component parts. There are others which have greater wetting and penetrating powers. In the following section of this paper are cited examples of substances which, when added in small amounts to melted sulfur, greatly increase the penetrating properties of the sulfur; i. e., these substances accelerate the rate of sulfur penetration into porous or fibrous substances, such as wood, paper, pulp, fiberboard, asbestos, concrete, and the like. Such substances have been termed "sulfur introfiers." Whether or not introfaction is a general property cannot be definitely stated at present; but there are indications that it applies to liquids having in equilibria units of different molecular association, differing from the sulfur introfaction examples given below chiefly in degrees and direction of introfaction. Sometimes introfaction may be in a negative direction. Different classes of substances require different types of introfiers, just as different catalysts are required for different reactions. The fundamental characteristic of introfiers is the possession of certain structural groupings specific for each substance being introfied. For instance, a sulfur introfier must have a molecular structure containing at least two rings of the general benzene type.

An introfier (Latin *introfero*, to carry or bring in) is a substance that accelerates impregnation. When an introfier is added to an impregnating material, it changes its fluidity and specific wetting properties towards the substance being impregnated so as to increase the facility with which penetration is affected. The mechanism of introfaction cannot be explained as a mere thinning action, as the amount of introfier required is often very small.

Sulfur Introfiers

As mentioned, impregnation with sulfur can be greatly accelerated by suitable introfiers. In the course of the author's research the sulfur-introfying properties of a large number of compounds were tested. It was found

that all substances having certain structural groupings were sulfur introfiers, and that no substances were sulfur introfiers which did not have these groupings. Although the degree of introfaction varied, it was not in a way inconsistent with structural relations of various introfiers. No exceptions were found unless due to one or more of the following causes: (1) insolubility in melted sulfur, (2) volatility at the temperature of melted sulfur, or (3) chemical reactivity towards melted sulfur. Not many substances were found which answered these requirements and which did not possess the molecular groupings characteristic of sulfur introfiers, indicating a relationship between solubility and introfaction. This solubility is a frequent indication of introfaction, but it is not a measure of introfying properties. For example, triphenylguanidine is only very slightly soluble in melted sulfur, but is a good introfier. On the other hand, the condensation product of phenol and sulfur chloride is soluble in melted sulfur in all proportions, but is not an introfier.

The molecular structure required by sulfur introfiers is a plurality of cyclic nuclei,² such as naphthalene or anthracene. It is not necessary that the benzene rings be of the naphthalene type joined on the sides, for diphenyl, wherein the benzene rings are joined on the ends, is a strong introfier. The rings may be joined through inorganic radicals, as in

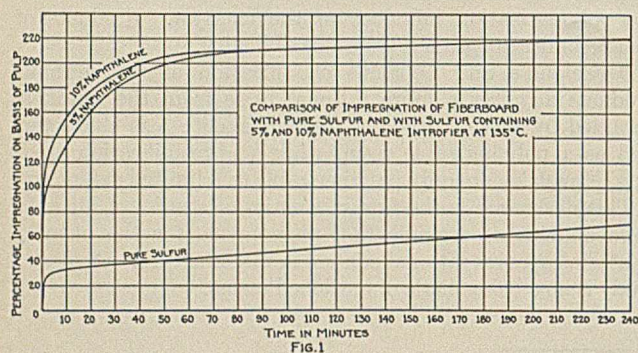
¹ Received March 6, 1928.

² Darrin, U. S. Patent 1,644,711 (October 11, 1927).

the case of triphenyl phosphate. The introduction of alkyl groupings rapidly decreases the degree of introfaction unless the alkyl groups are introduced between the points of union of two phenyl groups. For instance, tricresyl phosphate is a poorer introfrier than triphenyl phosphate. But when the union of the phenyl groups is through alkyl groups, the introfrying properties are not greatly reduced. In some cases this alteration actually improves an introfrier because of the consequent reduction in volatility. To illustrate, dibenzyl is superior to diphenyl. Likewise benzyl ether is superior to phenyl ether. Dibenzyl ketone is also satisfactory.

the case of triphenyl phosphate. Such substances are less soluble than diphenyl compounds or more closely united triphenyl compounds, but they have the advantage of non-volatility.

The following substances have been found to be sulfur introfriers. Their related molecular structures are also given.



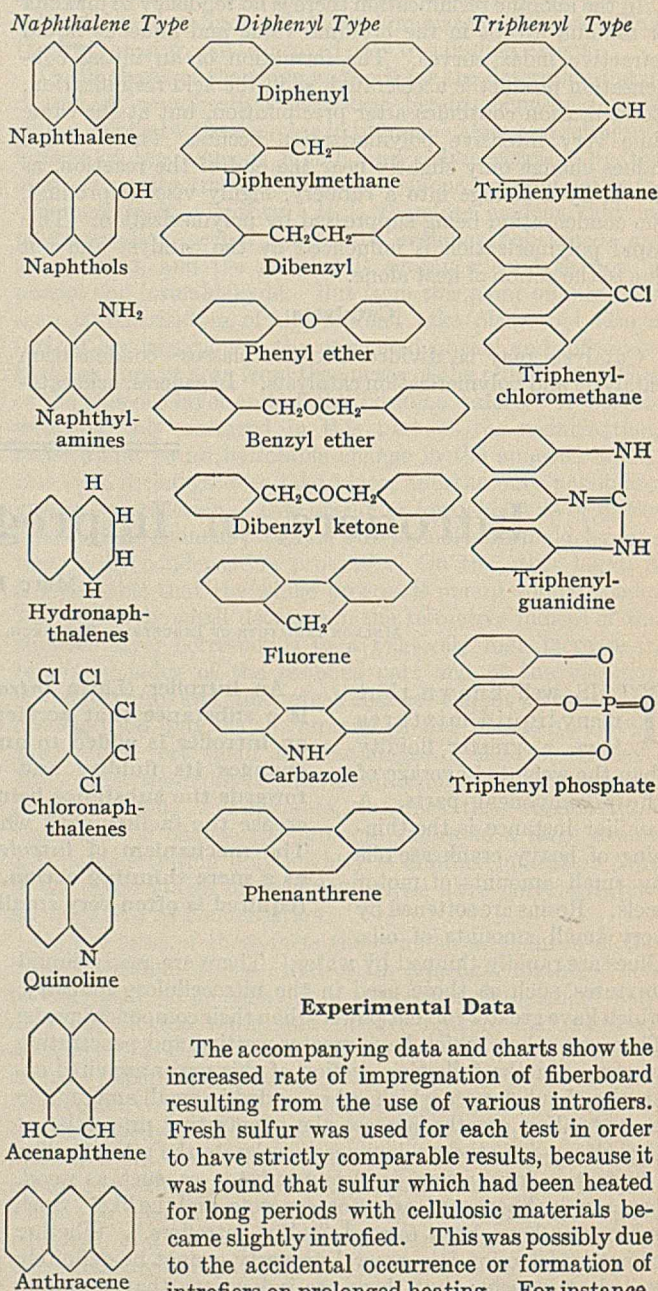
Hydrogenation and chlorination may improve introfrier properties, chlorination also having the advantage of reducing flammability. Tetrahydronaphthalene and all chloronaphthalenes from mono to hexa are good introfriers. The introduction of phenolic groups such as β -naphthol is not harmful. Likewise amine groups can be substituted, as in the case of α -naphthylamine. Nitrogen can be directly substituted in the ring, as in the case of quinoline.

In general, two-ring compounds are more soluble in melted sulfur than three-ring compounds. On the basis of the amounts dissolved, however, the three-ring compounds are often quite powerful introfriers. Examples are anthracene and phenanthrene. The latter, which is of the diphenyl type, is the more soluble. Diphenyl types are usually more soluble than naphthalene types. Two six-membered rings joined by a five-membered ring also produce good introfriers, the same general rules applying. These introfriers are desirable because of comparative non-volatility. Acenaphthene is an example of the naphthalene type; and fluorene and carbazole are illustrations of the diphenyl type. Carbazole colors sulfur deep red. When naphthols and naphthylamines are employed as introfriers, the sulfur is able to take up various coloring substances—as, for example, indigotin, which produces a deep green. Deep yellows, oranges, browns, and blacks can be produced in a similar manner.

No four-ring compounds were found which were soluble in melted sulfur, but there is no evidence that, if such a compound were found, it would not be an introfrier. Single-ring compounds, such as benzene, are not introfriers, although some of the higher homologs of the order of mesitylene are quite appreciably soluble in melted sulfur. One of the difficulties with such highly alkylated substances is a tendency to react with melted sulfur to produce small amounts of sulfurized substances which are held in viscous colloidal dispersion. Such alkyl radicals might be termed "negative introfriers," since the phenomenon of introfaction is probably of a colloidal nature.

Three phenyl groups joined through a carbon atom produce good introfriers, two examples being triphenylmethane and triphenylchloromethane. Three phenyl groups may also be joined through three nitrogen atoms or three oxygen atoms, in turn joined by a carbon atom, as in the case of triphenylguanidine, or even by an inorganic radical, as in

Sulfur Introfriers



Experimental Data

The accompanying data and charts show the increased rate of impregnation of fiberboard resulting from the use of various introfriers. Fresh sulfur was used for each test in order to have strictly comparable results, because it was found that sulfur which had been heated for long periods with cellulosic materials became slightly introfied. This was possibly due to the accidental occurrence or formation of introfriers on prolonged heating. For instance, lignin might serve as the starting point for a mild introfrier. Lignin is of a highly complicated and uncertain molecular constitution, but is generally accepted to contain at least two phenyl-like groupings. Tannins might also behave in a similar manner.

Method—1500 to 1700 grams of sulfur were heated in a beaker on an electric hot plate until melted. The desired introfrier was introduced and the temperature kept constant. The thermometer was immersed to 2.5 cm. (1 inch) from the bottom. The outside of the beaker was thoroughly insulated. Blocks of Cornell fiberboard measuring $5.1 \times 7.6 \times 0.43$ cm. ($2 \times 3 \times 0.17$ inches) were used. These were always immersed to the same depth and drained in the same manner. The blocks

Table I—Impregnation of Fiberboard with Sulfur Using Various Introfiers after Different Immersion Periods

INTROFIER ^a	1 MIN.	5 MIN.	15 MIN.	30 MIN.	45 MIN.	60 MIN.	90 MIN.	2 HOURS	4 HOURS	6 HOURS	8 HOURS
	%	%	%	%	%	%	%	%	%	%	%
Pure sulfur	28	31	35	37	..	41	..	48	70	..	123
5% Naphthalene	84	108	148	191	195	210	212	214	..	226	..
10% Naphthalene	111	130	173	190	195	205	251	..
1% Trichloronaphthalene	..	26	40	46	..	60	..	134
5% Trichloronaphthalene	63	99	132	150	181	202	..	212	..	257	..
10% Trichloronaphthalene	111	149	189	199	..	205	262
0.2% Triphenyl phosphate	26	37	44	45	93	..	142
0.4% Triphenyl phosphate	32	42	48	52	61	81	..	137	190
5% Anthracene, 150° C.	64	94	121	171	188	201	..	208	237
5% Diphenyl	..	129	200
5% Carbazole, 200° C.	..	66	95	110
5% Carbazole residue, 150° C.	..	95	160	177
2.5% Phenanthrene	..	67	74	94
5% Acenaphthene	..	96	137	171
5% Tetrahydronaphthalene	..	81	144	165
2.5% Monochloronaphthalene	..	45	84	104	..	126
1% Diphenylmethane	..	25	37	53	..	61

^a All impregnations at 135° C., unless otherwise noted.

were weighed before and after immersion, and the dry weights were determined by oven drying. All figures are given on basis of bone-dry pulp. Unless otherwise stated, the bath was kept at a uniform temperature of 135° C.

Table I presents the percentage impregnation of fiberboard with pure sulfur and with variously introfied sulfur after different periods of immersion. Some irregularities will be noted in these data and also in the accompanying curves, probably due to variations in porosity of the fiberboard samples. But all figures point clearly in one direction, indicating a marked increase in rate of impregnation when using introfiers. In Table II is given the percentage increase in total sulfur impregnation, due to introduction of various introfiers after different periods of immersion.

Table II—Increase in Sulfur Impregnation Due to Introduction of Introfiers after Various Periods of Immersion, as Compared with Pure Sulfur for Same Period

INTROFIER	1 MIN.	5 MIN.	15 MIN.	30 MIN.	60 MIN.
	%	%	%	%	%
5% Naphthalene	129	248	323	415	330
10% Naphthalene	296	319	394	415	330
5% Trichloronaphthalene	125	219	277	306	321
10% Trichloronaphthalene	296	281	441	437	327
5% Diphenyl	..	315	471

Table III—Rate of Absorption of Pure Sulfur Compared with Introfied Sulfur at Different Times during Immersion (Grams sulfur per 100 grams pulp per minute)

	1ST MIN.	5TH MIN.	15TH MIN.	30TH MIN.	60TH MIN.
	Pure sulfur	28	0.8	0.4	0.3
5% Naphthalene	84	6.0	4.0	2.9	0.6
10% Naphthalene	111	4.6	4.3	2.1	0.5

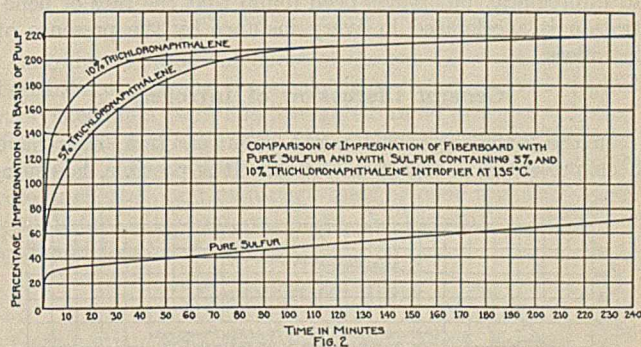
Table IV—Rate Increase of Sulfur Absorption Due to Presence of Introfiers at Different Times during Immersion (Calculated from Table III)

	1ST MIN.	5TH MIN.	15TH MIN.	30TH MIN.	60TH MIN.
	%	%	%	%	%
5% Naphthalene	129	650	900	870	200
10% Naphthalene	296	475	980	600	150

In all sulfur impregnation tests, whether using pure sulfur or introfied sulfur, it was noted that the rate of sulfur absorption during the first minute was very much higher than later. This appeared to be due to a superficial or surface clinging of the sulfur, particularly in the case of pure sulfur. If the rate of absorption of sulfur during various intervals of immersion is considered, instead of the total sulfur absorption at the end of different periods of immersion, this will in a measure correct for the initial or superficial impregnation and show that the actual rate of sulfur impregnation after the first minute is even greater for introfied sulfur than indicated by Tables I and II. This fact is demonstrated in Table III, which gives the rate of absorption of pure sulfur as compared with naphthalene-introfied sulfur at different times during immersion, as grams sulfur per 100 grams pulp per minute. Table IV expresses the same thing as percentage increase in rate of sulfur absorption due to the presence of naphthalene introfiers at different times during the immer-

sion. It will be noted that the rate of absorption of introfied sulfur compared with pure sulfur attains a maximum difference between the fifth and fifteenth minute, being about ten times (900 per cent) faster during this period than pure sulfur.

Figure 1 presents a comparison of impregnation of fiberboard with pure sulfur and with sulfur containing 5 and 10 per cent naphthalene introfier. It is clear therefrom that the rate of sulfur impregnation of pure sulfur was very slow after the first minute, but that introfied sulfur continued to impregnate rapidly for at least 15 minutes. There was not a very great difference in rate of impregnation whether 5 or 10 per cent naphthalene introfier was used, the mere presence of the introfier being of more importance than its amount. Figure 2 shows a similar comparison for trichloronaphthalene introfiers. Figure 3 illustrates the behavior of very small amounts of triphenyl phosphate introfiers. In this case the introfying properties were counteracted by difficult solubility. Figure 4 shows the behavior of anthracene introfiers at 150° C. Ordinarily, at this temperature sulfur starts to become viscous. This thickening of sulfur between 150° and 200° C. can be prevented by introfiers, as shown in the findings given in Table I, where a carbazole introfier was used at 200° C.

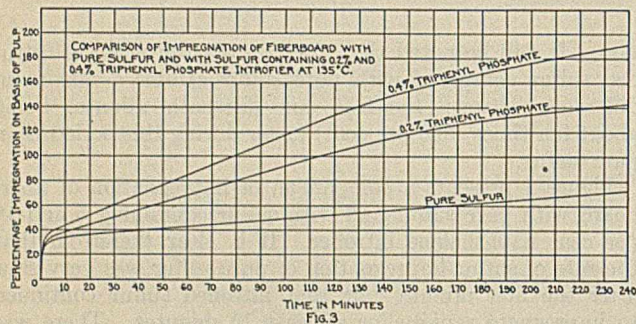


Commercial Applications of Sulfur Introfiers

The data presented are chiefly for naphthalene introfiers, as most complete figures were available for this substance. The brief data given for other introfiers are sufficient, however, to indicate their general behavior. Naphthalene has the advantage of commercial availability and low cost. It has technical disadvantages due to its volatility and odor, which make its use undesirable in the impregnation of articles for household use. It is satisfactory, however, for sulfur impregnation of wood,³ such as is used for railroad ties, cross-arms, piling, posts, poles, planks, and many other purposes where hardness or resistance to decay is desired. Sulfur-

³ Kobbé, *Chem. Met. Eng.*, **33**, 354 (1926); U. S. Patents 1,599,135 and 1,599,136 (September 7, 1926). These patents are by the old method without use of introfiers.

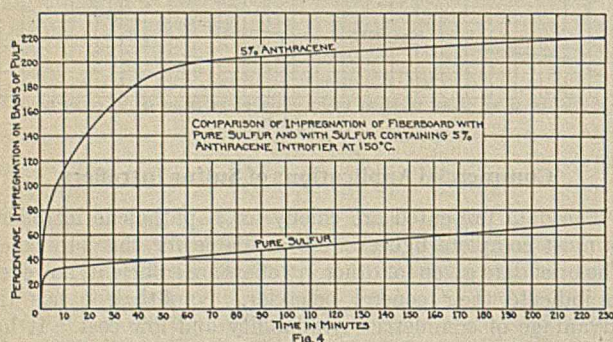
impregnated wood, although much harder and heavier than ordinary wood, can be sawed and cut by wood-working tools, and takes a very high natural polish, retaining the grain of the wood. Art effects can be produced by suitably coloring the wood or sulfur. Special introfiers can be used where special properties are required. For instance, chlorinated introfiers, such as the chloronaphthalenes, can be used for fireproofing.⁴ Where odorless materials are required, such introfiers as triphenyl phosphate, triphenylguanidine, anthracene, carbazole, phenanthrene, etc., can be used. Impregnated asbestos panels and molded shapes are particularly resistant to electrical arcing. They are good electrical insu-



lators and do not break down, as do certain artificial resins or other carbonaceous materials, under the temperature produced by electric arcing to form a conducting carbon path. Sulfur-impregnated asbestos or pulp can be hot-pressed. When hot it can be cut somewhat like cheese. When cold it can be sawed or machined, taking a fine natural polish. It is hard, rigid, and chemically inert. Only small amounts of introfiers are required for rapid impregnation of such porous materials as molded pulp, asbestos, and concrete.⁵ Pressed fiberboards are somewhat denser and slower to impregnate than blown pulp, but require no pressure or vacuum for complete penetration. More dense fibrous materials, such as various species of wood, are still slower to impregnate, but it has been found that the rate of penetration is accelerated in every instance by the presence of introfiers.

General Discussion of Introfiers

In the foregoing consideration of introfaction, data have been presented in regard to sulfur. It is possible, however,



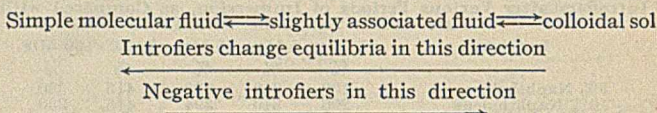
that introfaction may be a general property of all substances which have a tendency to form more or less viscous colloidal dispersions when in the liquid state, such as sodium silicates, certain sugars, starches, glycols, blown or partly polymerized

⁴ Marx, U. S. Patent 1,619,357 (March 1, 1927).

⁵ Bacon and Kobbé, U. S. Patents 1,561,767 (November 17, 1925) and 1,594,417 (August 3, 1926). These patents are by the old method without use of introfiers.

or oxidized drying oils, rosin oils, tars, resin and gum solutions, cellulose compounds, rubber dispersions, glues, gelatin compounds, tannins, certain dyestuffs, etc. Different classes of materials require different types of introfiers. For example, glue and gelatin are rendered most fluid and penetrating by water. The molecular groupings found most favorable to solution and fluidity of gelatin and gelatin compounds were the hydroxy, acid hydrogen, chloro, and organic sulfate. These might be termed "gelatin introfier" groupings. As in the case of sulfur introfiers, other molecular groupings were observed to exert a strong reverse effect, as, for instance, alkyl, ketone, ether, and ester groups. These might be termed "negative gelatin introfier" groupings. In the case of resins and oils, introfiers are of a character almost the reverse of gelatin. Halogenation of many introfiers has a peculiar effect. No example was found where it changed the direction of introfaction, but it sometimes intensified its effect. For instance, a chlorinated alcohol was found to be a much better solvent for gelatin than the unchlorinated alcohol; and chlorination of hydrocarbons often increased their solvent powers towards partly polymerized drying oils, notwithstanding the fact that in all other respects introfiers for oils and for gelatin are almost reversed.

In conclusion, the author wishes to point out that introfaction is closely related to solubility, but it is not identical, since it also takes into consideration fluidity and wetting properties which, in turn, are related to colloidal conditions. Introfaction may be closely related to changes in the equilibria between associated and unassociated molecules in the liquid phase, as follows:



Much to his regret, the author will be unable to devote further study to the subject of this paper, because he has entered upon another field of investigation. He realizes that the value of the present contribution would be enhanced by the addition of experimental data on viscosity, surface tension, etc., and will be glad to be of advisory assistance to anyone who is sufficiently interested to undertake the completion of the research.

Nutrition. BY WALTER H. EDDY. 237 pages. Williams and Wilkins Company, Baltimore, 1928. Price, \$2.50.

The purpose of this book is stated as "to try to present in simple language some of the fundamental principles which nutrition experts have found necessary to follow in selecting proper food for man." Presumably this is being done for the lay person, since it is stated that the job of selection is one which few can have done for them. Such a purpose is laudable in that such information in simple, readable form is very much needed at the present time, when there is so much incorrect and incomplete information being written about food, for a gullible audience.

This book covers the field fairly completely and the facts are, in the main, technically correct, as would be expected from Doctor Eddy. The treatment is sketchy, the relative emphasis badly balanced, and insufficient practical application made of the points. More frequent summaries in form of application would have helped. In view of the need for this information for lay groups, it seems unfortunate that the information is not "stepped down" and the book made more readable. The expressions are too technical, the illustrations are not well chosen, and too much mathematical detail is included. The statement in the preface, "We shall try to outline some of the modern problems in nutrition and the manner in which they are being studied," scarcely justifies the detail of method included, particularly in vitamin tests. One concludes the book a bit confused. The material is too sketchy for the specialist and too technical for the layman. Perhaps in future editions this can be remedied and the book better adapted to the need for which it was intended.—LOUISE STANLEY

Ethylene Oxide as a Fumigant¹

R. T. Cotton and R. C. Roark

BUREAU OF ENTOMOLOGY AND BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.

DURING the course of an investigation of several aliphatic compounds to determine their value as fumigants, it was discovered that the vapors of ethylene oxide are highly toxic to insects. In so far as the writers are aware, there are no previous references to the use of this material as an insecticide.

Properties of Ethylene Oxide

Ethylene oxide is made from ethylene chlorohydrin ($\text{CH}_2\text{OHCH}_2\text{Cl}$) and potassium hydroxide solution. At ordinary temperatures it is a colorless gas; at low temperatures it is a mobile colorless liquid, boiling at 10.5°C . The specific gravity of liquid ethylene oxide is 0.887 at $7^\circ/4^\circ\text{C}$. The empirical formula is $\text{C}_2\text{H}_4\text{O}$, and the structural formula is CH_2 . The molecular weight is 44.031. It is miscible with



water in all proportions and is soluble in the usual organic solvents. On heating it unites with water to form ethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OH}$). Ethylene oxide is very reactive and combines with all compounds having a labile hydrogen atom, such as water, alcohol, ammonia, and acids.

The concentrated vapors of ethylene oxide are inflammable, but concentrations lethal to insects can be used with safety.

Ethylene oxide is not highly toxic to man, but when inhaled for a long time it produces a cyanosis, which, however, is counteracted by the use of carbon dioxide gas.

Availability and Cost

Owing to lack of knowledge regarding the usefulness of ethylene oxide, there has been no demand for it, and consequently it is quoted at a rather high figure. The writers were able to purchase it in small quantities at a cost of \$2.00 per pound. It is now commercially available and could undoubtedly be made to sell for from 50 cents to 75 cents per pound.

Experimental

Preliminary tests in half-liter Erlenmeyer flasks containing 200 grams of wheat indicated that about 20 mg. per liter constituted the minimum lethal dose for specimens of the rice weevil under those conditions.

Tests on a larger scale were conducted in a 500-cubic foot fumigation vault. Insects in cotton-stoppered glass vials were placed in the vault. The fumigant was applied by pouring it into a shallow trough near the top of the vault or by allowing it to escape into the vault from a small cylinder containing the fumigant in liquid form under pressure.

A dosage of 1 pound per 1000 cubic feet of space for 20 hours proved to be 100 per cent lethal to specimens of the clothes moth, *Tineola biselliella*; the carpet beetles, *Attagenus piceus* and *Anthrenus vorax*; the rice weevil, *Sitophilus oryza*; the Indian meal moth, *Plodia interpunctella*; the saw-toothed grain beetle, *Oryzaephilus surinamensis*; the red-legged ham beetle, *Necrobia rufipes*; and the flour beetle, *Tribolium confusum*.

For commercial fumigation work it is recommended that

the fumigant be used at the rate of 2 pounds per 1000 cubic feet of space.

For comparative purposes tests were made in the same vault with the vapors of carbon disulfide and carbon tetrachloride. The results of these tests are given in Table I.

Table I—Relative Toxicity of the Vapors of Ethylene Oxide, Carbon Disulfide, and Carbon Tetrachloride to Various Insects Infesting Stored Goods

FUMIGANT	EXPOSURE Hours	TEMPERATURE ° F.	MINIMUM LETHAL DOSE Lbs./1000 cu. ft.
Ethylene oxide	24	70	1
Carbon disulfide	24	70	1 1/2
Carbon tetrachloride	24	85	30

The data in Table I indicate that the vapors of ethylene oxide are somewhat more toxic to stored-product insects than are those of carbon disulfide and about thirty times as toxic as those of carbon tetrachloride.

Effective at Low Temperatures

Owing to its low boiling point ethylene oxide is effective at comparatively low temperatures. The experiments above reported were conducted in a vault without artificial heat, the temperature during the experiment ranging from 60° to 75°F .

Penetration

Tests in the 500-cubic foot vault indicate that this fumigant has excellent powers of penetration. Insects buried in overstuffed furniture, sealed in packages of cereals, and buried in jars of rice were killed with ease.

Effect upon Commodities

In order to study the effect of the gas upon commodities, foodstuffs of various types, clothing, furniture, and metals were placed in a vault and fumigated for 24 hours at a dosage of 2 pounds per 1000 cubic feet. No deleterious effect was noticeable. Foodstuffs, such as nut meats and dried fruits, were unaffected, and no foreign taste or odor was discernible immediately after removal from the fumigation chamber. No liquid foods were treated.

Germination Tests

Germination tests with fumigated wheat indicate that seeds for planting purposes should not be fumigated with ethylene oxide since the vapors seriously affect the germination.

Vacuum Fumigation

Preliminary tests in a vacuum fumigation tank indicate that it can be successfully used for this type of fumigation.

Japanese Synthetic Fertilizer Factory—A new synthetic fertilizer factory which will be operated by the Haber-Bosch method is to be erected in Japan. It is reported that the output of the factory will be approximately 30,000 tons of pure nitrogen per year. This development may have a far reaching effect, since Japanese fertilizers would naturally be at a great advantage in Asia, from the standpoint of transportation costs, over those from more distant countries.

¹ Presented as part of the Symposium on Insecticides and Fungicides before the Division of Agricultural and Food Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

Studies in the Drying Oils¹

VIII—Adsorption of Liquids by Oil Gels

J. S. Long, E. K. Zimmermann,² and S. G. Nevins³

LEHIGH UNIVERSITY, BETHLEHEM, PA.

WHEN drying oils are converted into thick, semisolid or solid products by heat-bodying, the unsaturation decreases and the molecular weight increases greatly. The reactions vary according to the conditions, but involve couplings of various kinds at the ethylene linkages.

If one tries to visualize in space the building up of the simple molecules by various couplings leading to molecules of considerable complexity, he finds an interlacing network of carbon chains. The spaces within this network are of molecular dimensions, but the length of the molecules is so great compared to their cross section as to make these spaces relatively large. Further, the carbon chains which make up this network contain many ethylene linkages.

Langmuir,⁴ who has determined the dimensions and shape of some of these molecules, has put forward the premise that cohesion, adsorption, and other physical processes may be explained on the basis of chemical forces of primary and secondary valence. He also makes the premise that "the configurations of the adsorbed molecules are of great influence in determining the number of molecules that can be adsorbed per unit area."

It seemed logical to the writers that if the structure postulated is correct the products should be gels, at least in the sense of the word that they should exhibit the phenomenon of adsorption for liquids of such nature that they would be attracted by these interlacing carbon chains sufficiently to "wet" them.

From previous work it seemed that, in the ordinary process of solidification of films of oil, paint, and varnish at room temperatures, these same types of reactions might be considered to occur that take place more rapidly and in different sequence and to different relative extents at high temperatures. This suggested that the solidification of oil films at ordinary room temperatures might then involve, as a major factor, reactions leading to the building up of the molecules into a gel structure similar to that postulated for the heat-bodying process.

The present investigation was undertaken to determine (1) whether further experimental evidence could be secured on the premise that the semisolid bodies obtained by heat-body-

The quantitative percentage adsorption of various liquids by several extracted oil gels has been measured. Linseed oil films formed by exposure to air, when extracted with acetone, yield a gel-like product which also exhibits the ability to adsorb liquids. The adsorption of various liquids by extracted heat-bodied oil gels and by extracted linseed oil films produces similar changes in physical characteristics. Both extracted heat-bodied oil gels and extracted linseed oil films show selective adsorption of fatty acids from solution.

The heat of combustion of linseed oil and linseed gels was determined. The rate of change of heat of combustion of linseed oil films with and without drier was determined. Comparison of the heat of combustion of extracted and unextracted films and of the extracted oil offers further support to the premise that the liquid phase in a film is adsorbed rather than mechanically entrained.

The bomb calorimeter has been shown to be a convenient and helpful means of studying the progress of various reactions in the solidification of drying oils.

ing of drying oils are gels; and (2) whether films made by the ordinary drying process have in part a gel structure similar to that obtained by heat-bodying. The phenomenon of adsorption was used as a criterion for these two premises and, within the limitations of the work done, both questions are answered in the affirmative. Determination of the heat of combustion of films and gels confirms the conclusions based on adsorption measurements.

Adsorption Measurements

MATERIALS—The oils used to make the gels had the following constants:

CONSTANT	REFRIGERATED LINSEED	RAW LINSEED	CHINA WOOD	PERILLA
Specific gravity at 15.5°/15.5° C.	0.9355	0.9394	0.9405	0.9358
Refractive index at 25° C.	1.4776	1.4778	1.5160	1.4808
Iodine number, Wijs (30 min.)	187.6	185.5	163.0	205.0
Hexabromide number	37.6	43.2		47.8
Acid value	1.91	1.91		3.08
Molecular weight	760.0	785.0		765.0
Browne heat test			9.5	

In all cases the materials with which the gels were treated to measure adsorption were the highest quality c. p. chemicals. The mineral oil was a thick, viscous oil, the kind commonly used in laboratory vacuum pumps.

PREPARATION OF GELS AND FILMS—In all cases except in gel No. 6 (Table I) the process of jellying was carried out in the usual manner; that is, the oil was heated in an open agate kettle at 293° C. and mechanically stirred at 200 r. p. m. until solid. About 500 grams of the oil were taken in each case. In No. 6 the temperature was held at 200° C. in order to prolong the boiling. This gave a China wood gel of different structure from that of run No. 2. After the gel was formed it was removed from the kettle and 200 grams were placed in a 2-liter Pyrex flask. This flask was half filled with acetone and refluxed on a steam bath. After each 12 hours of refluxing the acetone solution was poured off and fresh acetone added and refluxing continued as before. When the oil obtained from the acetone poured off on four successive times was 0.1 gram or less in each case, the refluxing was stopped. This required about 4 weeks. The extracted gels were preserved under acetone to prevent oxidation.

A film was made by carefully brushing 5 cc. of oil containing 0.15 per cent manganese over a clean glass surface of 310 sq. cm. After the film had dried for 72 hours, a second coating was put on and allowed to dry. This gave a film of a suitable thickness which was uniformly dried throughout. Forty-eight films were made. They were allowed to dry on the glass for varying lengths of time and were then scraped

¹ Presented before the Division of Paint and Varnish Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² Pfister & Vogel Leather Company Research Fellow at Lehigh University.

³ Archer-Daniels-Midland Company and William O. Goodrich Company Research Fellow at Lehigh University.

⁴ *J. Am. Chem. Soc.*, **39**, 1848 (1917).

off with a razor blade. They were then extracted in a Soxhlet extractor using acetone continuously for one week. After extraction, the films and oils obtained were kept under carbon dioxide to prevent oxidation.

METHOD OF DETERMINING ADSORPTION—For the adsorption measurements the films and gels were thoroughly evacuated in a flask immersed in hot water. The flask plus gel plus fittings was then weighed and the weight of gel obtained. The liquids to be adsorbed were admitted to the evacuated flask and gel from a dropping funnel projecting through the stopper. After standing 24 hours the liquid and gel were poured through a filter paper. The gel was washed to remove liquid on the surface and then weighed. The difference is the weight of liquid adsorbed. Alcohol was used to wash the gel in cases where fatty acids were adsorbed. Ether was used in the case of mineral oil and water in the case of glycerol.

Table I—Gels

GEL No.	OIL	DRIER Grams/liter	TEMPERATURE	TIME TO
			° C.	GEL Hours
2	China wood	None	293	9 min.
3	Refrigerated linseed	PbO 20	293	4
4	Raw linseed	None	293	7.5
5	Raw linseed	PbO 20	293	5.25
		Fe linoleate 6		
		Mn linoleate 50		
6	China wood	None	200	2.20
7	Perilla	None	293	4

Heat of Combustion

As shown by Table III, the percentage of acetone-soluble fluid oil in the films decreased as the age of the films increased. To gain insight into the mechanism of the action it seemed desirable to determine to what extent these changes were related to oxidation. It was believed that any progressive oxidation of the fluid part of the mass could be followed very accurately and conveniently by determining the rate of change in the heat of combustion of the extracted oil and of the insoluble gel material.

The bomb calorimeter has not been much used to follow reactions occurring in drying oils. The writers found, however, that the technic widely used in determining the heat of combustion of coal or various hydrocarbons could be applied to drying oils and the films and gels derived from them, and that a high degree of accuracy is possible. The determination is simple and easily carried out. It can be completed and the result calculated in 70 minutes. One man can run six determinations in one day.

Preliminary measurements showed that the heat of combustion decreased from 9367 calories for raw linseed oil to about 7000 calories for dry linseed oil films. This decrease is sufficiently large to permit study of reactions occurring under different conditions, as follows:

The heat of combustion of linseed oil films, with and without drier, was determined at various stages throughout the drying period for the purpose of observing the changes in this factor and at what points change in heating value of the films is most apparent.

METHOD OF DETERMINATION—The heat of combustion was determined with an Emerson fuel calorimeter of the bomb

type. A standardized Beckmann thermometer was used to record the change in temperature.

The samples of films, whether in the liquid or solid condition, were weighed directly into the fuel sample pan of the calorimeter. The use of capsules was avoided, since the oil is not appreciably volatile at room temperatures. The weight of sample varied from 0.7 to 0.8 gram. Iron fuse wire was used to ignite the sample. In all cases the washings from the bomb after ignition were titrated with a standard solution of ammonium hydroxide and the combined fuse wire weighed and corrections applied for the weight of wire burned and the oxidation of nitrogen in nitric acid. The calorimeter was standardized against Bureau of Standards naphthalene of known heat of combustion.

FILMS MADE WITH RAW LINSEED OIL CONTAINING COBALT LINOLEATE DRIER—Raw linseed oil containing 4.0 cc. of a 40 per cent solution of cobalt linoleate drier (equivalent to 0.14 per cent cobalt) per 100 cc. of oil was prepared. Films were prepared on glass plates 23 by 30 cm. by pouring 3 grams of oil on each plate and spreading evenly over the plates to an average thickness 0.04 mm. These films were placed in a drying cabinet on racks arranged in a horizontal position. The cabinet was kept in a dark room excluding all light. Air at a definite humidity of 62.6 per cent was passed through the cabinet, entering at the bottom and escaping through a hole at the top. The rate of the entering air was fixed at 5.66 liters per minute. The temperature of the cabinet varied from 20° to 22° C. The humidity of the entering air was kept constant by bubbling it through a train of gas-washing bottles containing sulfuric acid (sp. gr. 1.280) at 20° C. This was adjusted daily. At various stages throughout the drying period, samples were scraped from the glass plates by means of a razor blade and the heat of combustion was determined. The character of the films was noted at the same time.

Table III—Adsorption Tests on Linseed Oil Films

TIME AFTER SETTING UP	EXTRACTED OIL	GEL IN FILM	OLEIC ACID ABSORBED	
			Per cent	Per cent
Weeks	Per cent	Per cent	Per cent	
0	70.0	30.0	52.6	
1	60.4	39.6	41.1	
2	50.4	49.6	50.9	
3	44.5	55.5	52.7	
4	42.6	57.4	51.8	
6	30.4	69.6	53.5	
8	30.6	69.4	54.3	
Film dried at 65.5° C. (Fe, Pb, and Mn driers)				
52	0.5	99.5	27.4	
Film dried at 65° C. (3 hours)				
	47.0	53.0	70.6	

FILMS MADE WITH RAW LINSEED OIL (NO DRIER)—These films were prepared in the same manner as those containing cobalt drier. The plates were then set in a horizontal position in a section of the laboratory exposed to indirect light and room temperature. No attempt was made to keep the humidity or temperature constant. Samples were taken at various intervals during the drying process and the heat of combustion was determined.

Table IV shows the decrease in heat of combustion with increasing time of exposure and also the condition of the

Table II—Adsorption of Liquids by Drying-Oil Gels

GEL No.	OIL	DRIERS Grams/liter	BUTYRIC ACID %	OLEIC ACID %	LINOLEIC ACID %	MIXED FATTY ACIDS (85%) %	STEARIC ACID %	RAW LIN- SEED OIL %	MINERAL OIL %	MINERAL OIL + 10% FREE FATTY ACIDS %	WATER %	GLYC- EROL %	AMYL ACETATE %
2	China wood	None	21.5	19.7	22.4	17.7	62.6	15.9	15.9	35.8	0.0	16.4	37.4
3	Refrigerated linseed	PbO 20	104.8	78.3	82.9	110.5	119.9	19.7	10.6	39.2	0.0	17.5	21.5
4	Raw linseed	None	267.4	115.9	157.5	165.9	163.6	53.1	14.9	28.4	0.0	42.1	144.3
5	Raw linseed	PbO 20	311.8	151.9	167.5	160.8	150.5	44.6	9.4	27.3	0.0	5.0	67.2
		Mn linoleate 6.0											
		Fe linoleate 50											
6	China wood	None	97.6	21.5	19.8	35.8	69.1	14.0	3.9	6.9	0.0	3.7	46.6
7	Perilla	None	270.3	98.0	92.1	121.9	200.0	75.4	16.3	8.5	0.0	5.8	93.9

film at the various stages, both for films made from oil containing drier and from oils without drier.

Table IV—Heat of Combustion of 0.04-mm. Raw Linseed Oil Films

TIME EXPOSED Hours	HEAT OF COMBUSTION Gram cal./gram film	REMARKS
COBALT LINOLEATE DRIER ADDED		
0	9347	
24	9370	No change observed
50	8091	Gummy, not quite dry to touch
74.5	7204	Hard, dry, elastic
149	7112	Hard, dry, elastic
171.5	7003	Hard, dry, elastic
267	6893	Hard, dry, elastic
335	6846	Hard, dry, elastic
1823	6945	Hard, dry, elastic
NO DRIER		
0	9367	Sample as taken from drum
24	9388	Unchanged
48	9328	Wet, no change in drying observed
72	9243	Wet, no change in drying observed
94	8920	Starting to gum
101	8205	Drying on edges
144	8002	Dry to touch
193	7492	Hard, dry, elastic
259	7453	Hard, dry, elastic
333	7204	Hard, dry, elastic
481	7147	Hard, dry, elastic
721	7018	Hard, dry, elastic

Table V—Heats of Combustion on Unextracted and Extracted Films, 0.12 to 0.17 mm. Thick

TIME AFTER SETTING UP Weeks	EXTRACTED FILM		UNEXTRACTED FILM		
	EXTRACTED FILM	EXTRACTED OIL	Detd.	Calcd.	Diff.
0	7192		7960		
1	7325	7843	7407	7637	230
2	7320	7825	7447	7574	127
3	7105	7695	7164	7367	203
4	7197	7635	7359	7383	24
6	7089	7556	7111	7231	120
8	7089	7201	7134	7123	-11
Film dried at 65.5° C. for 3 hours					
	7261	7603	7627	7422	-205

Table VI—Ultimate Analyses

CONSTITUENT	C %	H %	O %
Raw linseed oil	78.96	10.69	10.35
Extracted linseed oil film, 0.15% Mn:			
14 days old	63.82	8.67	27.51
56 days old	64.02	8.63	27.35
Linseed oil film, no driers, 63 days old, unextracted:			
61.5% film	63.40	8.71	27.89
38.5% oil			
Extracted oil from 63-day film	65.35	8.75	25.90
Linseed oil film, 0.14% Co, 114 days old, unextracted	63.36	8.63	28.01

Discussion of Results

ADSORPTION DATA—When liquids were adsorbed by the drying-oil gels, changes in the physical properties of the gels were noted in some cases. For example, after adsorption of mineral oil and in some cases glycerol, the gels changed from a dry material which could be readily crumbled to a hard, rubber-like substance having considerable compressive strength. This phenomenon was most noticeable in the linseed gel having no drier present and was more pronounced with mineral oil than glycerol. All the gels showed some hardening with the mineral oil and the mineral oil containing 10 per cent of free fatty acids.

The hardening was retarded by the presence of the 10 per cent of fatty acids. The presence of driers in the gels seems to have an effect on this phenomenon, as in each case the hardening was not so noticeable in the gels containing them. With glycerol no hardening was evident in the gels containing driers. Butyric acid, however, seemed to have a softening effect on the gels and the compressive strength was greatly reduced. Here, as before, it was most noticeable in gels that did not contain driers.

Not only did the extracted linseed films show the same property of adsorption towards many liquids as did the gels made by heat-bodding, but also the changes in the physical

characteristics of the extracted films were identical with those in the gels made by heat-bodding. Fatty acids softened the films and also the gels. Mineral oil and glycerol adsorbed by the heat-bodded gels produced tough, rubbery products. Exactly the same effect was observed in the case of the films.

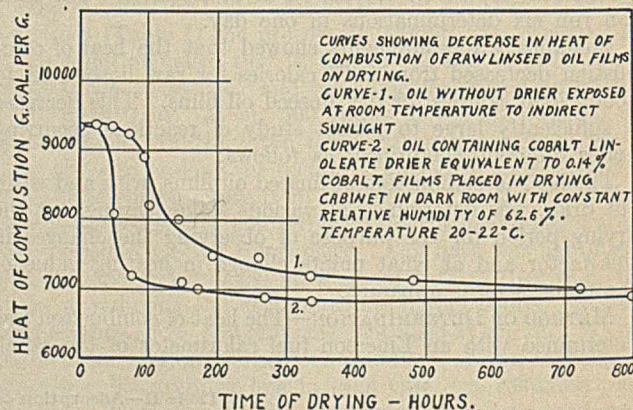
It is logical to inquire to what extent adsorptions measured are related to "wetting." This rather ambitious question is not here answered in full, but the results of some work done may be mentioned.

Acetic, butyric, oleic, and other fatty acids were strongly adsorbed by both gels and films when the extracted gels were flooded with them or with solutions of them in solvents that wetted the gel. When, however, extracted gel was flooded with an aqueous solution of acetic acid, no adsorption of acetic acid, within the accuracy of the measurements, took place in 48 hours.

Benzene and acetone, of course, wet the gel. Benzene swells the gels greatly. The benzene or acetone thus taken up escapes on exposure or evacuation.

Extracted linseed oil films adsorbed oleic acid, butyric acid, mineral oil, and glycerol, and did not adsorb a quantity of water measurable within the limits of accuracy of the method. The percentage of oleic acid adsorbed by films is approximately half as large as that adsorbed by linseed gel No. 4. As shown by Table III, the number of grams of oleic acid adsorbed per gram of film remained sensibly constant from week to week, although the percentage of extractable liquid decreased and the percentage of solid phase increased correspondingly. Although the network of the solid phase became more intricate from week to week, the number of grams of oleic acid adsorbed per gram of this solid gel structure remained constant. If liquid taken up was held mechanically entrained, the percentage of it taken up by the gel structure would decrease as the solid network increased from week to week. If the adsorption was dependent on intricacy of texture of the gel, it should increase as time went on.

The most logical general theory is that the adsorbed liquid is definitely oriented in the solid gel phase. Langmuir⁴ has previously developed this picture of adsorption as related to the chemical constitution of the substances concerned. This concept seems to explain the constancy of the percentage adsorption of oleic acid in the extracted films and also permits the wide difference in percentage adsorptions of widely different substances by the same gel.



HEATS OF COMBUSTION—The accompanying graph shows that the heats of combustion follow different paths, but even under the rather widely different conditions chosen the curves converge and approach the same value. It would not be expected that films in which the mechanism of solidification, as shown by the curves, is quite different, would approach the same values. This rather lends support to the idea developed by the adsorption studies, that only after the liquid

has changed by the several possible types of reactions, perhaps in different sequence, to a product of definite molecular complexity, does it change to solid. From this viewpoint the mechanism of solidification of drying oils, after the initial surface set, involves chemical change of the adsorbed, oriented liquid phase into molecules of the definite complexity characteristic of the solid. The solid then undergoes relatively little change except in so far as destructive agencies promote reactions of different nature and in general, opposite type. This view receives further confirmation from the fact, as shown in Table V, that the heat of combustion of the solid phase after extraction is sensibly constant. There is, of course, some variation in the films due to differences in spreading, drying, and thickness, but there is no real drift of the values in any direction.

The heat of combustion of the extracted oil, on the other hand, decreases steadily from the much higher value characteristic of slightly oxidized oil.

The heat of combustion of gel No. 4 was determined to be 8985 calories. This value, by comparison with the average value of 7205 given by the extracted films, indicates that in forming the gel structure by heat-bodying relatively little oxidation in the narrow sense of the term occurred. The ethylene linkages were used up mostly in couplings, whereas in the settling of films there is a stage, as shown by the heat of combustion curves, where the decrease in unsaturation runs coincident with a decrease in heat of combustion and an increase in the percentage of oxygen in the product. The changes at this stage involve oxidation to a large extent.

The heat of combustion of the film calculated from the percentages of solid and liquid phases and their heats of combustion is in nearly every case higher than the determined value. This indicates that the adsorption of the liquid phase by the solid gel structure in the process of solidification of the oil is exothermic and confirms the promise of adsorption involving definite structure and orientation as against the idea of simple mechanical entanglement of liquid in the film.

ULTIMATE ANALYSIS—Corresponding to the change in heat of combustion, the ultimate analysis of linseed oil films (Table VI) shows a much greater percentage of oxygen than that present in the raw oil. Extracted films 14, 56, and 114 days old with driers, complete unextracted film 63 days old, and the oil extracted from it—all have very nearly the same composition. Their rather remarkable agreement suggests afresh the premise that the solid phase being formed in the solidification of the oil films is one of very definite composition and complexity, and that variations in the compositions of films as a whole are due to liquid phase which has not yet been sufficiently changed by the various reactions to produce this solid substance. As the films age the composition of the liquid phase approaches that of the solid.

Acknowledgment

Acknowledgment is due and cheerfully given to the Pfister and Vogel Leather Company and to the Archer-Daniels-Midland Company and the William O. Goodrich Company for grants under which this work was carried out. The writers wish also to acknowledge the help given by J. G. Smull.

Studies in the Drying Oils^{1,2}

IX—Action of Cold-Blowing on Linseed Oil

J. S. Long and W. S. Egge

LEHIGH UNIVERSITY, BETHLEHEM, PA.

THE curves for the rate of oxidation of linseed oil rise slowly for some time, but after the initial induction period the slope increases rapidly. The complete curves are similar to those obtained in autocatalytic reactions.

Study of the oxidation of drying oils by changes in films on relatively non-porous surfaces is difficult. The penetration of oxygen in the stationary oil is slow, and the depth to which oxygen penetrates is not great unless the oil is in motion. The film is therefore often not uniform throughout. In studying the nature of the reactions which occur, it seems logical to use conditions which permit (1) steady progress of the reactions, and (2) uniform samples for examination. The blowing process fulfils these conditions to some extent and has been studied

Linseed oil has been blown at 30° C. in the presence of various substances. In the presence of a positive catalyst, reactions occur which cause decrease in the unsaturation. Negative catalysts prevent this.

Combination processes—e. g., heating and blowing—permit accentuation of various types of reactions and enable the operator to get a greater variety of products or to make a desired product more readily.

Thioglycolic acid is suggested as a means for the precipitation of lead, manganese, cobalt, iron, and other metals of groups I, II, and III as usually classified in qualitative analysis, from drying oils, bodied oils, varnishes, and like products—(a) for purposes of quantitative estimation, (b) as a means of study of the course of various types of reactions. This throws light on the function of driers in oils, paints, and varnishes.

from certain points of view.³ The writers had previously blown linseed oil at temperatures of 120° to 140° C., corresponding to some blowing practice, but they felt that even at these temperatures the effects of oxidation were too greatly masked by other reactions which took place at these temperatures. The present investigation was undertaken to eliminate this masking and get some information as to the nature and course of the oxidation reactions at 30° C.

Since the reactions are suspected of being autocatalytic to some extent, various substances were tried to retard or accelerate the oxidation.

Materials

Linseed Oil. Refrigerated linseed oil derived from Northwest seed was treated to remove the break, chilled to 6.6° C. to separate part of the saturated glycerides, and filtered cold. Alkali-refined linseed oil was also used. These oils had the following characteristics:

¹ Presented before the Division of Paint and Varnish Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² This work was carried out under the New Jersey Zinc Company Fellowship at Lehigh University.

³ Chatterji and Finch, *J. Soc. Chem. Ind.*, 45, 333T (1926).

	REFRIGERATED LINSEED OIL	ALKALI-REFINED LINSEED OIL
Specific gravity at 15.5°/15.5° C.	0.9355	0.9364
Refractive index at 25° C.	1.4776	1.4782
Iodine number, Wijs (1 hour)	187.6	180.0
Hexabromide number	39.6	36.9
Acid value	1.91	0.8

Thioglycolic acid, c. p., made by the Eastman Kodak Company. *Free fatty acids* from linseed oil; titration shows about 100 per cent acids.

Method

In each of the runs given in Table I, 300 grams of linseed oil were blown with a stream of dry air at the rate of 6.2 liters per minute. The oil was in a glass tower 37 cm. high and 4 cm. in diameter. This tower was contained in a thermostat at 30° C. The air was admitted at the bottom of the column through a single orifice 1.5 mm. in diameter. The incoming air was conditioned by passing it through a solution of potassium hydroxide (1:1), then through concentrated sulfuric acid and glass wool. It then passed through a coil immersed in the thermostat, so that it was at the same temperature as the oil by the time it reached the tower.

Table I—Effect of Cold-Blowing on Linseed Oil

AFTER BLOWING Hours	SPECIFIC GRAVITY (15.5° C.)	REFRACTIVE INDEX (25° C.)	ACID VALUE	IODINE NUMBER (Wijs, 1 Hour)	HEXABROMIDE NUMBER
SET 1—REFRIGERATED OIL, WITH 0.1 PER CENT MANGANESE COMBINED AT 150° C.					
0	0.9355	1.4776	1.91	187.6	39.6
8	0.9422	1.4782	2.3	179.8	33.4
16	0.9468	1.4796	2.7	170.1	24.1
24	0.9580	1.4824	4.4	162.3	17.9
32	0.9662	1.4848	6.8	155.4	11.8
40	0.9820	1.4880	9.3	141.2	4.3
(Color of samples, dark amber)					
SET 2—ALKALI-REFINED OIL, WITH 0.10 PER CENT MANGANESE COMBINED AT 30° C					
0	0.9364	1.4782	0.8	180.0	36.9
8	0.9420	1.4780	1.5	177.6	30.8
16	0.9465	1.4792	1.6	175.4	22.0
24	0.9572	1.4820	3.5	163.8	16.6
32	0.9660	1.4842	4.2	152.6	9.5
45	0.9818	1.4878	6.1	136.3	3.8
(Color of samples, extremely pale, almost water white)					
SET 3—REFRIGERATED OIL, WITH 0.5 PER CENT α -NAPHTHOL COMBINED AT 30° C.					
0	0.9355	1.4776	1.91	187.6	39.6
8	0.9410	1.4780	1.9	186.8	41.6
16	0.9412	1.4782	2.0	186.7	41.1
24	0.9416	1.4782	2.4	186.8	40.9
32	0.9416	1.4784	2.4	186.6	40.0
50	0.9418	1.4788	2.4	186.2	41.1
100	0.9418	1.4792	2.4	185.5	42.0
SET 4—REFRIGERATED OIL, WITH 0.1 PER CENT MANGANESE AND 0.6 PER CENT α -NAPHTHOL COMBINED AT 30° C.					
0	0.9355	1.4776	1.91	187.6	39.6
8	0.9414	1.4782	1.9	187.0	41.0
16	0.9414	1.4784	1.8	186.7	40.6
24	0.9442	1.4788	1.9	186.8	40.9
32	0.9468	1.4794	1.9	187.0	41.1
50	0.9500	1.4802	1.8	186.9	40.4
100	0.9522	1.4816	1.8	187.0	40.3
SET 5—REFRIGERATED OIL, WITH 1 PER CENT SODIUM OLEATE AND 0.1 PER CENT MANGANESE					
6	0.9426	1.4784	4.2	175.3	35.8
12	0.9602	1.4830	9.6	152.0	18.3
18	0.9822	1.4878	12.0	130.1	2.1
SET 6—REFRIGERATED OIL, WITH 1 PER CENT CALCIUM OLEATE AND 0.1 PER CENT MANGANESE					
6	0.9424	1.4782	3.8	177.2	36.9
12	0.9600	1.4828	5.4	159.9	20.1
18	0.9818	1.4876	7.9	144.6	4.3
SET 7—FREE FATTY ACIDS OF LINSEED OIL, WITH 0.1 PER CENT COBALT COMBINED AT 30° C.					
8	0.9038	1.4690	189.3	189.5	39.8
16	0.9204	1.4724	181.6	176.4	26.5
24	0.9438	1.4766	173.2	162.1	18.0
32	0.9648	1.4810	164.0	144.7	8.3
40	0.9804	1.4852	156.4	125.3	0.0

In each of the runs given in Table II, 100-gram samples of linseed oil were heated in an atmosphere of carbon dioxide at the specified temperatures for a period of 8 hours. The oil samples were then blown. The time required to reach a given body (refractive index 1.4880) is shown in this table.

Table III gives preliminary data on the separation of driers from oils by means of thioglycolic acid. Samples of c. p. driers were put into solution by warming with benzene,

and filtered. In each case 1 cc. of this solution was ignited and weighed. This was used as a blank test. One cubic centimeter of the same solution was added to 30 cc. of linseed oil and the mixture warmed until solution was complete. Five or six drops of thioglycolic acid (calculated to be an excess) were added and the samples set aside for 1 hour with occasional shaking. The precipitate was separated by means of quantitative filter paper, washed with V. M. P. naphtha, dried, ignited, and weighed.

Table II—Effect of Previous Heat Treatment on Blowing.
Set 8—Refrigerated Linseed Oil

AFTER HEATING IN INERT ATMOSPHERE Hours	TEMPERATURE ° C.	HEXABROMIDE NUMBER	IODINE NUMBER (Wijs, 1 Hour)	SPECIFIC GRAVITY (15.5° C.)	BLOWING NECESSARY TO ACQUIRE GIVEN BODY (n _D ²⁰ 1.4880) Hours
8	100	39.2	182.6	0.9408	42
8	150	28.3	179.5	0.9418	38
8	200	15.7	177.2	0.9432	37
8	225	8.6	175.6	0.9435	28
8	250	3.8	173.1	0.9462	24
8	265	1.9	169.0	0.9496	18
8	280	0.0	160.4	0.9502	11

Table III—Separation of Driers by Means of Thioglycolic Acid.
Set 9—Refrigerated Linseed Oil

DRIER	WEIGHT OF RESIDUE AFTER IGNITING 1 CC. SOLN.	WT. ON ADDING THIOLYCOLIC ACID BEFORE IGNITING Gram
Cobalt resinate	0.0234	0.0230
Cobalt linoleate	0.0295	0.0294
Manganese resinate	0.0239	0.0236
Manganese linoleate	0.0292	0.0290
Lead resinate	0.0318	0.0318
Lead linoleate	0.0340	0.0338
Iron linoleate	0.0262	0.0259
Mixture of lead, cobalt, and manganese resinates	0.0256	0.0255

Bailey's modification of the Steele and Washburn method for the hexabromide number was used. In determining acid values a mixture of alcohol and benzene (1:1) was employed as the solvent.

Discussion of Results

The decrease in iodine number and hexabromide number in Set 1 (positive catalyst present) indicates that oxyglycerides are formed at the points of unsaturation in the glyceride molecules. The total decrease in hexabromide number corresponds to $0.353 \times 0.367 = 0.1295$ gram of that linolenic acid which forms the solid hexabromide. If two ethylene linkages in each molecule had become saturated the decrease in iodine absorption would be $\frac{4 \times 126.93}{278.24} \times 0.1295 = 0.236$ gram of iodine per gram of oil. The actual decrease observed amounts to 0.464 gram of iodine per gram of oil, which is approximately twice as great. This shows that the decrease in unsaturation cannot be ascribed merely to that linolenic glyceride which forms the insoluble hexabromide.

In Set 2 the same general trend is noticed. The color of the samples is very pale. The acid value does not increase so rapidly as in Set 1.

Morrell⁴ has studied the effect of α -naphthol as a retarder or negative catalyst in the oxidation. In Set 3, 0.5 per cent of α -naphthol was added to the oil before blowing. The hexabromide number increased at once from 39.6 to 41.6, and then remained sensibly constant throughout the run. This may be explained by assuming that the negative catalyst breaks down some linolenic oxyglycerides that had previously formed in the raw oil used. There was no bodying action in this run.

Set 4 shows that a negative catalyst in combination with a positive catalyst inhibits the reaction almost as much as

⁴ J. Oil Colour Chem. Assoc., 10, 278 (1927).

a negative catalyst alone. This set shows a slight bodying action.

Sets 5 and 6 show the effect of sodium and calcium oleate on the rate of bodying. The time to acquire a given body is about one-half of that required in Set 1. The oleates of sodium and calcium lower the surface tension and thus permit the immediate formation of a thick, stable foam. The interface between the oil and the air is increased greatly, permitting more rapid absorption of oxygen.

Set 7 shows the variation of the constants, when free fatty acids of linseed oil are bodied by blowing. The acid value is reduced, showing that the carboxyl group is affected in the course of the reaction.

In Set 8 samples of linseed oil were heated in an inert atmosphere (CO_2) for 8 hours at various temperatures. The hexabromide number falls off steadily and reaches zero in less than 8 hours at 280°C . These samples were then blown to a given body (refractive index 1.4880).

On the premise that one ethylene linkage in each molecule of linolenic acid has been saturated by heating, the decrease in hexabromide number is quite comparable to the decrease in unsaturation as measured by the decrease in iodine number. The oil has also bodied somewhat. It would seem, therefore, that the shorter time required to oxidize the previously heated oils is due to previous coupling reactions. The coupling reactions have produced molecules which cause the oil to have different characteristics—e. g., surface tension—from that of the original oil.

The results and the products obtained in this run are not without significance in indicating that purposed combinations of treatments, each of which accentuates a certain type of reaction, will enable us to get a greater variety of products desired for various industrial processes and will also enable us often to get a certain desired product more surely and more easily than when we use one treatment—e. g., blowing, heating, or raying, alone.

Meyers⁵ has prepared various metallic salts of thioglycolic acid and has indicated some of their properties.

The present writers found that thioglycolic acid (0.5 per

cent) added to the oil retards the bodying as does α -naphthol. They also made the interesting discovery that the addition of this acid precipitates the metals of metallic driers present in the oil. The precipitation is practically quantitative, as shown by the results in Table III.

The precipitated lead, manganese, cobalt, and iron derivatives of thioglycolic acid are insoluble in petroleum ether or in naphtha. The precipitate can therefore be washed free from oil and weighed. Thick oils made by heat-bodying or blowing can be diluted with naphtha before adding the thioglycolic acid. The metals are then completely precipitated from the diluted heavy-bodied oils in which they had been previously incorporated by heating. A few preliminary tests were made with resin varnishes. The metals were precipitated by the thioglycolic acid as in the case of raw or bodied oils.

For scientific purposes the use of thioglycolic acid enables an investigator to study whether the function of a given drier lies in starting a reaction and building up bodies that then react on each other in later stages of the process (blowing, cooking, etc.), or whether the metal drier is needed constantly during the entire process to stimulate a certain reaction or type of reaction. The drier can be removed at any time during the process and comparison thus obtained of its effect (1) when present all through the process, and (2) when present for only part of the process.

It now becomes possible to use certain driers to promote desired reactions during the heating or blowing process and then to remove part or all of these driers from the processed oil and introduce the type and quantity of driers desired for the subsequent use of the product. This avoids the compromise necessary when the drier is used to promote reactions in processing, and then remains in the product and influences the oxidation of the product in paints, varnishes, and other protective coatings.

The act that free fatty acids can be oxidized at 30°C . to a heavy body is of interest as indicative of reactions in the early part of the drying process leading to the formation of molecules of sufficient complexity to be a factor in the adsorption process, which seems to play an important role in the latter part of the process of solidification of drying oils.

⁵ *J. Lab. Clin. Med.*, 6, 359 (1921).

Dialysis of Putrescible Liquids¹

O. M. Urbain

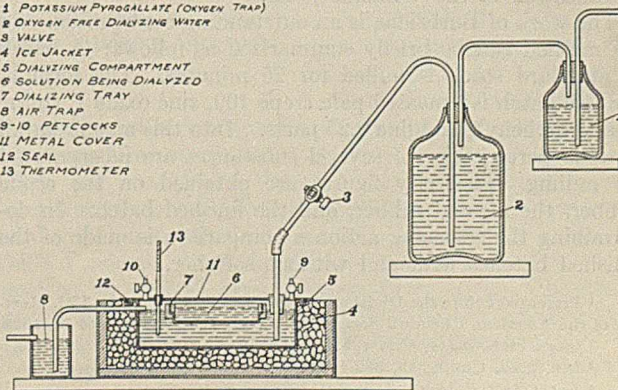
URBAIN & HUNT, 209 SOUTH HIGH ST., COLUMBUS, OHIO

THE dialyses of putrescible liquids, such as domestic sewage and the waste solutions from tanneries, creameries, canneries, etc., present some unique problems. If the results of the dialyses are to be reasonably accurate, the bacterial decomposition and the oxidation of the putrescible material in such solutions during dialysis must be eliminated.

A dialyzer constructed as shown in the accompanying drawing has been used for a number of years with excellent results. The dialyzing water consisted of distilled water, the dissolved oxygen of which had been expelled by boiling. A 25-gallon, bottle-shaped, tinned-copper vessel was used for this purpose. After boiling, oxygen traps were attached to prevent the entry of oxygen during the cooling period. The metal cover was then sealed in place over the dialyzing compartment. The air was removed from the compartment by aspirating nitrogen through the area by means of the petcocks in the metal cover. Dialyzing trays made of S &

S parchment paper were used and found to be very satisfactory. Several samples may be dialyzed at one time. The dialyzing area was maintained at a temperature near 0°C . by means of the ice jacket.

- 1 POTASSIUM PYROGALLATE (OXYGEN TRAP)
- 2 OXYGEN FREE DIALYZING WATER
- 3 VALVE
- 4 ICE JACKET
- 5 DIALYZING COMPARTMENT
- 6 SOLUTION BEING DIALYZED
- 7 DIALYZING TRAY
- 8 AIR TRAP
- 9-10 PETCOCKS
- 11 METAL COVER
- 12 SEAL
- 13 THERMOMETER



¹ Received May 14, 1928.

Softeners and Antisofteners¹

Erle C. Zimmerman and Leslie V. Cooper

THE FIRESTONE TIRE AND RUBBER COMPANY, AKRON, OHIO

MANY materials used in the compounding of rubber exert an influence on the plasticity. Usually a material is specifically added to increase the plasticity and is called a softener, but in some cases the effect on plasticity is purely incidental to some more important function, such as acceleration or protection against deterioration on aging. The effect of this class of materials may be towards either a more or a less plastic mix; in the latter case it is correct to class the material as an antisoftener.

Softeners or fluxes may be divided into two classes according to their action—true softeners and lubricants. The work described in this paper is confined to the evaluation of those materials which definitely affect plasticity of the rubber. In other words, no consideration is given to materials which affect the workability of raw-rubber mixtures chiefly through a lubrication or dispersing action on the pigments—i. e., substances which act through their influence on the interfacial tension, or affect the wettability of the pigment.

No attempt has been made to study shrinkage, which, although an important item in the processing of a rubber mixture, may be eliminated by correctly using materials which produce the proper plasticity. If true softening is obtained the shrinkage is reduced, but if the reverse action, antisoftening, occurs, shrinkage may become pronounced. Shrinkage also results when set-up or premature vulcanization takes place and is always caused by the generation of too much heat in processing stiff stock.

Determination of Softening Effects of Various Materials

Much has been written on various rubber softeners, but there is little available which gives a numerical evaluation. Two instruments have been developed for the measurement of crude rubber plasticity—the Marzetti extrusion apparatus² and the Williams press.³ Both types have been modified by several investigators and Burbridge⁴ in his work used a modification of the Williams press.

The work of Burbridge is an outstanding contribution and his method can be briefly summarized as follows: A batch of standard stock is milled for 25 minutes. The formula for this batch is: massed pale crepe 100, zinc oxide 1, sulfur 5, and diphenylguanidine 0.25 parts. Into this master batch various percentages of several substances are incorporated by milling. Plasticity figures are obtained on the crude rubber, the massed rubber, and the finished batch. In determining the softening action a comparison is made of the finished batches with and without softener.

Several objections may be raised to this method:

1—The test as outlined requires a break-down of the master batch and no check is made on the amount of work actually done on it before the softener is added. This is a serious fault, for in breakdown the change in plasticity is very rapid.

2—A master batch containing curing ingredients is used as a standard and is subject to change in storage and during the actual test.

3—The master batch contains diphenylguanidine, which is a softener itself—a fact which this investigator did not observe.

4—The addition of an acid softener to a stock containing zinc oxide gives the effect of the zinc salt, not the actual softener.

The method described in this paper has been in use by the writers for several years and has none of these objectionable features.

As it is necessary to have a standard grade of rubber for use in all experiments, each batch is made up of pieces of rubber cut from various sheets from different bales. It should be noted that the blend is not massed. No single piece should exceed 100 grams in weight. Six hundred grams of rubber will process easily on a 30-cm. (12-inch) mill with 15-cm. (6-inch) rolls and as a 30-gram sample is

In the manufacture of rubber goods various materials are incorporated with the rubber in order to produce a mixture that will process more easily. Such materials are usually called fluxes or softeners.

A simple method of determining the relative effects of such materials is described. This consists in mixing the material in rubber under standardized conditions and determining the plasticity of the product by the Williams method.

Some materials show stiffening instead of softening action and both types are shown in the results reported in this paper. Benzidine and *p*-amidophenol are examples of materials which stiffen rubber.

removed for crude rubber plasticity during the test, the initial amount of rubber used is 630 grams.

Of equal importance is the initial temperature of the mill rolls. By experiment 60° C. has been found to be the most satisfactory, as a higher temperature gives too hot a batch to work with and a lower temperature makes the test unnecessarily long. This initial temperature should always be obtained by heating a cool mill up to temperature by milling rubber. The temperature of 60° C. can be measured by the use of a thermocouple pad and potentiometer but may also be gaged by feel after the operator has become proficient. After this initial temperature is obtained, it is made certain that both steam and water are shut off so that the temperature of the mill may rise as it will.

The third necessary standard is the method of milling. In this work a mill with 10:9 ratio and front roll speed of 30 revolutions is used and the time periods given in Table I may not hold true for all mills, but the procedure may be adapted to any mill with a little allowance for the new speed.

Table I—Milling Cycle

TIME ELAPSE FROM START		
Minutes	Seconds	
0	0	Crepe rubber through once
0	15	Open mill to 3 mm. (1/8 inch) and start massing
3	30	Cut rubber back and forth four times
5	0	Remove sample A
5	10	Start adding material to be tested
7	40	Cut mix back and forth four times
9	0	Remove from the mill

The first creping operation insures the rubber massing continuously and not lodging in a ball on top of the rolls. The time of knitting together should be between 2 minutes 45 seconds and 3 minutes and is a definite check on all varia-

¹ Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² *Giorn. chim. ind. applicata*, 5, 342 (1923).

³ *IND. ENG. CHEM.*, 16, 362 (1924).

⁴ *Trans. Inst. Rubber Ind.*, 1, 429 (1926).

bles up to this point. Sample *A* is obtained by removing a strip, weighing out 30 grams, and returning the excess to the mill immediately. Five per cent of softener is about the maximum amount used commercially so this percentage was adopted as the standard. Sample *B* is cut from the finished batch and may be any convenient size.

As these batches contain neither sulfur nor accelerator, it is permissible to obtain a plasticity figure as though the batch were crude rubber. The machine used is the one designed by Williams,³ and *Y* value after 5 minutes in the press is obtained on samples *A* and *B*. The ratio of difference of the *Y* values of *A* and *B* to the *Y* value of *A* is the total softening percentage and is due to two causes—(1) the effect of the additional 4 minutes of milling, and (2) the effect of the ingredient added to the rubber. The total softening effect, minus the percentage drop due to milling as obtained by a control run in which no softener is used, is the effective softening action of the ingredients added.

For example, the *Y* value of *A* of the control is 296, and of *B* is 256. Thus the percentage drop due to milling is 40 divided by 296 or 13.5 per cent. The *Y* value of the *A* sample before addition of hardwood pitch is 295 and of the *B* sample is 239, a drop of 56 points, or 19 per cent, which gives an effective softening action due to hardwood pitch of 19 minus 13.5, or 5.5 per cent.

Table II—Softening Action Expressed in Percentage Change in Plasticity

	Per cent		Per cent
Stearic acid	22	Perilla oil	11
Pine tar	16.5	Vaseline	9
Liquid asphalt	16.5	Mineral rubber	8
Pine oil	16	Straw paraffin oil	8
Degras	16	Cottonseed oil	8
Rosin oil	13	Hardwood pitch	5.5
Stearin pitch	11	Carnauba wax	5

Softeners

In Table II are listed a few of the better known softeners. It may be noted that pine oil and pine tar are similar in

softening action, which probably explains why various viscosities of pine tar are about alike in their effect on plasticity. Also stearic acid by its superior power justifies a premium in price due to this property alone.

Burbridge⁴ stated that carnauba wax is a stiffener and that it is hard to incorporate, but it has been found to be a softener similar to hardwood pitch. Perhaps the previous investigator did not consider the fact that in raising the initial temperature of the mill he greatly reduced the amount of breakdown.

Antisofteners

When the total percentage drop of any batch is less than the percentage drop of the control, it is evident that the substance added is a stiffener.

It is a well-known fact that some antioxidants exert softening action to such an extent that tubed articles lose their shape due to their weight alone. Several ways are open to overcome this and one of them is to use an antisoftener in the compound.

Benzidine, an antioxidant, accelerator-activator, and a fair stiffener of cured stock, is a stiffener of uncured stock of high degree, as evidenced by Table III.

Table III—Antisoftening Action of Benzidine

BENZIDINE TO RUBBER	ACTUAL STIFFENING	TRUE STIFFENING
Per cent	Per cent	Per cent
0.0625	21.9	35.4
0.125	31.9	45.4
0.25	26.7	40.2
0.5	22.7	36.2
1.0	2.5	16
2.0	2.5	16

Another material which behaves in a manner similar to benzidine is *p*-amidophenol, which gives its optimum stiffening action (43 per cent) when 0.5 per cent on the rubber is used. Other stiffeners which have been noted are β -phenylenediamine, β -naphthylamine, α -naphthylamine, tolidine, quinone, and dianisidine.

A Study of Auto-Ignition Temperatures¹

II—Pure Compounds

Henry James Masson and William F. Hamilton²

LABORATORY OF CHEMICAL ENGINEERING, DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY, NEW YORK, N. Y.

A NUMBER of observers^{1 to 5,*} have pointed out the importance of auto-ignition temperatures in arriving at a better understanding of the molecular structure of organic compounds, and the mechanism of their combustion, and in determining the suitability of certain mixtures of them as fuels for use in the internal-combustion engine. Although the auto-ignition temperatures of several pure substances have been reported by the authors,⁶ it was considered desirable to determine these temperatures for additional pure substances of widely different properties and structure before studying the various mixtures as represented by typical commercial fuels. Previous determinations showed that the

The auto-ignition temperatures of an additional number of pure organic compounds have been determined in air at ordinary pressures. The compounds selected cover a wide range of properties and structures in order to provide data for use in studying various combustion reactions. A study has also been made of the catalytic effect of various surfaces on auto-ignition temperatures.

range of auto-ignition temperatures was far wider than was anticipated. The range of the pyrometer was therefore extended to make possible the study of a larger number of compounds. The well-known catalytic activity of platinum has indicated the

desirability of determining auto-ignition temperatures on various surfaces other than this metal.

The previous paper⁶ describes the apparatus used, the experimental method followed, and the results obtained for a number of pure organic compounds. The results given in Table I include for comparison determinations previously reported as well as those subsequently made. The compounds have been arranged according to the conventional organic groupings in order to facilitate comparisons.

A comparison of these results with those of other investigators shows a fair general agreement. Owing, however, to

¹ Received April 25, 1928.

² Research fellow, Atlantic Refining Company Fellowship.

* Numbers refer to bibliography at the end of the article.

the different forms of apparatus, technic, and catalytic activity of the surface, it was not expected that agreement would be close.

Table I—Auto-Ignition Temperatures of Pure Compounds at Normal Pressure on Platinum

SUBSTANCE	° F. ° C.		SUBSTANCE	° F. ° C.	
	° F.	° C.		° F.	° C.
Hydrocarbons:					
<i>n</i> -Pentane (tech.)	1074	579	Ethyl esters:		
<i>n</i> -Hexane	968	520	Formate	1070	577
<i>n</i> -Heptane	844	451	Acetate	1130	610
<i>n</i> -Octane	856	458	Propionate	1116	602
<i>n</i> -Decane	797	425	<i>n</i> -Butyrate	1134	612
Isobutane	1041	561	<i>n</i> -Valeriate	1095	590
Isododecane	993	534	<i>n</i> -Caproate	1079	582
Benzene	1212	656	<i>n</i> -Caprylate	1059	571
Toluene	1172	633	Pelargonate	975	524
<i>p</i> -Xylene	1145	618	Caprate	919	493
Ethyl benzene	1027	553	Palmitate	731	388
Mesitylene	1149	621	Malonate	1005	541
<i>p</i> -Cymene	871	486	Benzoate	1192	644
α - <i>n</i> -Heptylene	630 ^a	332 ^a	Oleate	667	353
Alcohols:					
Methyl	1065	574	Acetates:		
Ethyl:			Methyl	1210	654
(95%)	1054	568	Ethyl	1130	610
Absolute	1034	557	<i>n</i> -Propyl	1223	662
<i>n</i> -Propyl	1004	540	Amyl (tech.)	1045	563
<i>n</i> -Butyl	938	503	Benzyl	1091	588
Isopropyl	1148	620	Ethylene glycol diacetate	1175	635
Isobutyl	1007	542	Ethers:		
Isoamyl	965	518	Diethyl:		
Benzyl	935	502	(10% alcohol)		
Ethylene glycol	971	522	Absolute	908	487
Glycerol	974	523	Benzylethyl	915	491
Aldehydes:					
Paraldehyde	1005	541	Isoamyl	924	496
Propionaldehyde	787	419		803	428
<i>n</i> -Butaldehyde	767	408	Miscellaneous:		
Ketones:					
Acetone	1340 ^a	727 ^a	Aniline	1148	620
Diethylketone	1127	608	Ethylaniline	895	479
Ethylpropyl	1067	575	<i>o</i> -Toluidine	999	537
Methylhexyl	1062	572	<i>m</i> -Toluidine	1075	580
Methylcyclohexanone	1109	598	Nitrobenzene	1033	556
Methylheptenone	983	534	<i>o</i> -Cresol	1110	599
Cyclohexanone	1034	557	<i>m</i> -Cresol	1158	626
Acids:					
Formic	940	504	Chloroform	Above	1800
Acetic (glacial)	1110	599	Carbon tetrachloride	Above	1800
<i>n</i> -Propionic	1105	596			
<i>n</i> -Butyric	1026	552	Carbon disulfide	300 ^a	149 ^a
<i>n</i> -Heptanoic	974	523	Menthone	942	506
			Pulegon	798	426
			Ethyl bromide	1109	588
			<i>n</i> -Butyl bromide	901	483
			Benzyl chloride	1161	627
			Bromobenzene	1270 ^a	688 ^a

^a Temperature above or below millivoltmeter scale. Error is within 10° F., or 5.5° C.

Effect of Composition of Liquid

An extended study of compounds covering a wide range of properties and structures discloses large differences in auto-ignition temperatures. The auto-ignition temperature is affected more by the composition of the substance than any other factor. It is this variation of auto-ignition temperature with composition that constitutes the primary purpose of this investigation. A study of the compounds listed in Table I brings out several interesting facts. For instance, substances of widely different structures and compositions will have almost identical auto-ignition temperatures, while substances having closely related structures and compositions will have widely different temperatures.

Several observers^{7,8,9} have shown that as molecular weight or complexity increases the auto-ignition temperature decreases. The results presented in Table I show that this conclusion is not entirely warranted. If for a given series of compounds auto-ignition temperatures are plotted against molecular weight or the number of carbon atoms in the molecule, it will be found that auto-ignition temperatures do not decrease progressively. Curves showing these relationships for *n*-hydrocarbons, alcohols, acids, and esters are shown in Figure 1.

Effect of Surface Temperature, Sensitivity, and Heat Capacity

By making that part of the surface upon which the drop falls essentially the hot junction of a thermocouple, an accurate measurement of the surface temperature just prior to contact with the drop is obtained. Since the drop is at room temperature when introduced into the furnace, and

probably undergoes only a comparatively small increase in temperature through absorption of heat from the hot gases inside the furnace, the plate must supply the bulk of the heat required to raise the liquid to the boiling point, supply the latent heat of vaporization and, together with heat from the coils, raise the vapor-air mixture to the auto-ignition temperature. If the plate is of low heat capacity, or a poor conductor, a considerable drop in temperature will take place when the liquid comes in contact with the surface. The loss of heat from the plate to the drop may be so great as not to give any flash or only after a long (5 or 6 seconds) time interval. If the heat capacity for a given material is increased by making the plate very thick, a loss of sensitivity will take place, although this will depend somewhat on the location of the thermocouple. It has been found, however, that this may be overcome with apparently no loss of accuracy by making the plate quite heavy and placing several thermocouples in series around the point of contact of the drop with the surface and just above the plate. A number of determinations made in this manner gave consistent results as well as greater sensitivity due to the use of multiple couples.

When the surface is below the auto-ignition temperature, an immediate lowering of the temperature of the plate is observed due to the cooling effect of contact with the liquid. This is followed by a rise in temperature due to combustion. The drop in temperature is probably of no importance, but the rise in temperature at or near the auto-ignition temperature due to the very rapid combustion taking place seems to be of some significance. This rise has been studied for a number of pure substances and gasolines of different "knock" ratings. Very interesting results have been obtained, but as yet the relationship of this rise to other characteristics of the substance have not been sufficiently investigated to make a report.

It is found that results are reproducible only when the plate is at equilibrium with the air inside the furnace, and that if the temperature of the furnace is raised or lowered too rapidly, deviations occur due to the time required for heat transfer to and from the plate. If the rate of change of plate temperature does not exceed 1° C. per minute, the results are found to be duplicable. In the procedure previously described,⁶ the auto-ignition temperature was approximated by varying the furnace temperature. After lowering the furnace temperature about 5° C., the plate was heated by alternating current by means of its own resistance to the auto-ignition temperature of the substance. This procedure was found not to be necessary, as the auto-ignition temperature was satisfactorily reached by means of the furnace heating wires.

The time required for the flash to take place after the drop strikes the plate will be a complex function of several factors, such as vapor pressure, heat capacity, and transfer of the plate, rate of diffusion, etc. With substances like ether the flash occurs almost instantly after the liquid makes contact with the plate. The auto-ignition temperature will be very sharp; as, for instance, in the case of ether there will be no flash at 490° C., but a sharp flash will occur at 491° C., as soon as the drop makes contact with the surface. So far as can be observed, in no case does the flash occur before the drop makes contact with the plate. On the other hand, glycerol does not flash at 522° C. At 523° C. there will be a flash within 6 seconds. If the rate of change of temperature of the system does not exceed 1° C. per minute, the direction of approach to the auto-ignition temperature is immaterial.

Effect of Composition of Surface

Next to composition of the liquid, composition of the surface is the most important factor affecting the deter-

mination of auto-ignition temperatures. Results obtained on one type of surface may differ considerably from those obtained on another, owing to differences in catalytic activity of the surfaces. Unless this factor is taken into consideration deductions are liable to be misleading.

The peculiar behavior of, and the inability to obtain duplicable results on, a pure, clean platinum surface suggested a study of the catalytic activity of various surfaces, especially as to their effect upon auto-ignition temperatures and deductions relating thereto. Also, in view of the many investigations which are being carried out in an effort to explain the mechanism of combustion and "knock" in the internal-combustion engine, it seemed desirable to indicate the importance of catalysis and its effect on results and deductions. No attempt has been made to study comprehensively the complex conditions which may result through catalysis, but to add emphasis to what has been so well expressed by others as to the importance of catalysis in the study of combustion.

It will be apparent that in the study of auto-ignition temperatures we are dealing with combustions of two types: (1) combustion in the gaseous phase (indicated by the flash), and (2) surface combustion (flameless combustion on the surface of the plate). When a drop of liquid is allowed to fall upon a surface of low catalytic activity, at or above the ignition temperature, practically all the combustion will take place in the gaseous phase, a minimum amount taking place on the surface. If the surface is entirely devoid of catalytic activity, it may be assumed that the combustion will take place entirely in the gaseous phase. On the other hand, if the surface is very active catalytically, or large in size, it would be impossible to obtain a flash because little or no combustion would take place in the gaseous phase, all the reactions taking place on the surface. Therefore, assuming extreme cases, no flash would be possible in the case of a catalyst of infinite activity, the combustion being confined wholly to the surface, and in the case of a surface of zero catalytic activity the combustion would be confined wholly to the gaseous phase. However, since all known surfaces lie between these extremes, it is impossible to confine the combustion exclusively to the surface in the case of an active catalyst, or to the gaseous phase in the case of a surface of low activity.

It is obvious, therefore, that in general two surfaces of different catalytic activity will not give the same auto-ignition temperature. If, at a given temperature, the surface of low catalytic activity gives a flash, no flash will be obtained on the surface of higher catalytic activity, it being necessary to raise the temperature of the latter surface in order to cause sufficient combustion to take place in the gaseous phase to produce a flash. Therefore, all other factors being constant, the auto-ignition temperature will increase with the increase in catalytic activity of the surface. However, the catalytic activity of a given surface and material is a function of the temperature, in general approaching a maximum for each case. At high (incandescent) temperatures all distinction disappears and one surface is as good a catalyst as another. As the range of auto-ignition temperatures is below the temperature of maximum catalytic activity for most substances, differences in auto-ignition temperatures are to be expected. In addition, since the action of many catalysts is specific, differing somewhat with various substances, the auto-ignition temperature will be affected accordingly. These factors may be practically eliminated by choosing a surface of very small catalytic activity and of small temperature coefficient of activity. A surface of nil catalytic activity and zero temperature coefficient of activity should give a value of auto-ignition temperatures which

approaches the ignition temperature of a gaseous mixture. In accordance with the above it is apparent that in determining the ignition temperature of a gaseous mixture the containing vessel and the igniting source should have a minimum catalytic effect.

Catalytic Effect of Various Surfaces

In order to determine which surface would be best to choose as a standard, several different materials were studied. For present purposes the results may be considered under the following divisions: (1) Change in auto-ignition temperature using same surface and liquid; (2) change in auto-ignition temperature using same surface and different liquids, and using different surfaces and the same liquid.

CHANGES USING SAME SURFACE AND LIQUID—That there may be a change in the catalytic activity of a given material when used in a given system is well known. The study considering this point was limited to benzene on platinum. Because of the long time interval required and the desire not to interfere with the use of the platinum surface for other purposes, the change in auto-ignition temperature with time was not carried to completion. Benzene was chosen as a standard or reference substance.

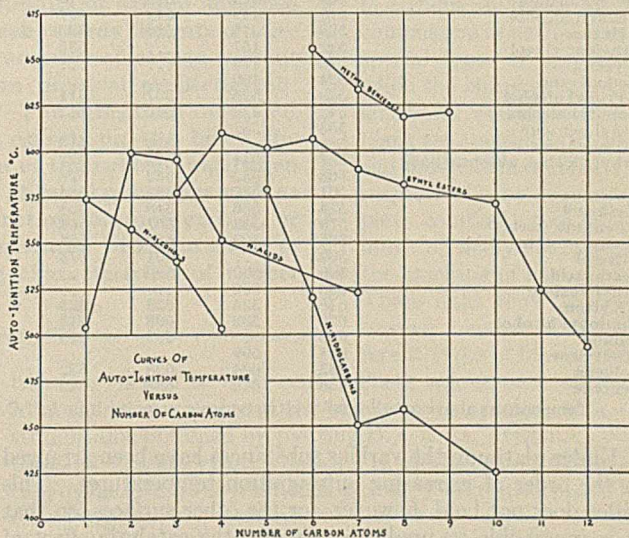


Figure 1

In determining the temperatures listed in Table I, the apparatus was checked from time to time against benzene. During the early life of the plate checks were readily obtained, but in time it was noticed that the auto-ignition temperature increased steadily. This rise was studied until the auto-ignition temperature of the benzene had risen from 656° C. to 732° C., at which point the test was discontinued. The rise of approximately 76° C. in the auto-ignition temperature after an interval of about 6 weeks indicated a change in the catalytic activity of the surface. Since the auto-ignition temperature had increased, it indicated, in accordance with the ideas previously outlined, that the surface had become activated. Such changes as the above are not unusual, similar changes in the catalytic activity of surfaces having been reported by many observers. Photomicrographic investigations of platinum and silver gauze indicate that there is a gradual increase in catalytic activity associated with the formation of minute craters or pits, the fringe of each crater being tinged with "black" metal. No photomicrographic studies were made of the platinum plate, but it has probably been affected in the same manner. Upon heating the plate to a higher temperature by means of an oxy-acetylene torch, the

original condition was not restored, making it impossible to use the plate. In determining auto-ignition temperatures therefore—for example, using platinum—the temperature must be checked from time to time against some standard reference material. Also, it is necessary that the liquid under test be free from any material which might affect the surface adversely. In studying gasolines containing lead tetraethyl this became a serious matter, making necessary frequent replacements of the platinum surface. This procedure was followed in determining the values in Table I whenever checks could not be obtained.

CHANGES WITH DIFFERENT SURFACES OR DIFFERENT LIQUIDS—The change of auto-ignition temperature with composition of the surface and liquid was, however, somewhat more fully investigated. The surfaces selected were platinum, gold, silver, and glass (Pyrex). The results are given in Table II.

Table II—Change of Auto-Ignition Temperature with Composition of Surface and Liquid

SUBSTANCE	PLATINUM	GLASS	GOLD	SILVER
	° C.	° C.	° C.	° C.
α -n-Heptylene	332 ^a	338 ^a
n-Heptane	451	477	474	476
n-Octane	458	435	482	476
p-Cymene	466	508
Diethyl ether (10% alcohol)	487	...	479	474
Benzyl alcohol	502	443	519	510
Isoamyl alcohol	518	449	513	492
n-Hexane	520	515	538	536
Ethylene glycol	522	457	...	535
Glycerol	523	429
Isododecane	534	499
n-Propyl alcohol	540	526	537	511
Isobutyl alcohol	542	522	540	512
Ethyl benzene	553	557
Nitrobenzene	556	...	526	513
Ethyl alcohol, absolute 95%	557	544	523	522
	568	552	532	528
Isooctane	561	537	583	584
Methanol	574	536	548	558
n-Pentane (tech.)	579	543	557	564
Benzyl acetate	588	503	588	556
o-Cresol	599	...	601	573
Acetic acid	599	562	599	...
Ethyl acetate	610	569
p-Xylene	618	595	623	623
Isopropyl alcohol	620	532	608	619
Aniline	620	...	592	620
Mesitylene	621	599
Toluene	633	604	638	632
Benzene	656	618	656	649

^a Temperature above or below millivoltmeter scale, error is within 5.5° C.

Under platinum the various substances have been arranged in the order of increasing auto-ignition temperatures. This order does not hold, however, for the other surfaces, so that it is impossible to predict accurately the catalytic effect of the surface. In the case of auto-ignition temperatures, as in other catalytic phenomena, the effect on substances of different composition and structure is not of the same order. The auto-ignition temperature of some substances was considerably affected by the change in surface, whereas other substances were hardly affected. Not only must the effect of composition and structure be taken into account in esti-

ating catalytic effect, but the change in catalytic activity with temperature previously mentioned. Because of the very nature of the measurement it was impossible to keep the temperature of the surface constant and so eliminate this factor.

A comparison of auto-ignition temperatures on platinum, a catalytically active metal, and on glass, a substance of much less catalytic activity, is interesting. In accordance with the theory previously evolved, it would be expected that a substance of marked catalytic activity would raise the auto-ignition temperature. With the exception of n-heptane, α -n-heptylene, and p-cymene, all the substances have higher auto-ignition temperatures on platinum than on glass. The recent work of Coward and Guest¹⁰ on natural gas-air mixtures is of interest in this connection. They found that "in parallel experiments the metals of greater catalytic effect must be hotter to cause ignition than metals or other substances of smaller catalytic effect." As one set of experiments was carried on initially in the gaseous state and the other in the liquid, the results are not entirely comparable. The formation of a film of silver oxide on the silver caused difficulties. The presence of such a film affects the auto-ignition temperatures in an anomalous manner. The difficulty of obtaining oxidized surfaces which would produce constant and duplicable results has limited observations to this or other oxidized surfaces. It is appreciated that this phase of the subject has been studied only in a preliminary fashion, but sufficient has been presented to show the importance of catalysis in the determination of auto-ignition temperatures.

Experimental work is now in progress on the auto-ignition temperatures of binary mixtures of pure substances, gasolines of known "knock" rating, and other mixtures of interest.

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Department of Commerce to Make Survey of Industrial Equipment

The Department of Commerce is about to undertake a requested study of industrial equipment. One of the objectives of this study, which will be conducted by the Domestic Commerce Division, under the immediate direction of H. C. Dunn, is to determine the amount of obsolete equipment and its importance as a factor in the inability of firms manufacturing similar products to compete on an equally profitable basis.

Replacement of machinery, which in point of service may have many years of usefulness but which in point of satisfying the latest fancies of the consumer market is obsolete, is an important matter for the manufacturer and one which is behind the request for the survey.

Obsolescence merits a definite understanding, especially that it may not be confused with depreciation. The obsolescence of factory equipment is effected largely by style changes or by the

new product of inventive genius, and not by wear and tear which are factors in depreciation.

The practical value of this study would probably be a truer accounting for obsolescence as a hazard rather than an arbitrary compromise with depreciation as at present. Wear and tear, or depreciation, is a scientific measurement and can be determined accurately in cost accountings. Obsolescence is analogous to fire as a risk. It cannot be determined any more than the date a building will burn can be determined. An arbitrary basis of accounting for the two factors does justice to neither, and fails inadequately providing a fund for replacing machinery when its value has been destroyed by its being worn out or rendered obsolete.

If obsolescence is defined as representing the dead line beyond which a machine can compete profitably with another machine, none of the machine's value is destroyed until the dead line is reached, then the value is destroyed all at once. Depreciation approaches its dead line by gradual and constantly diminishing value. Therefore, the two cannot accurately be confused.

Effect of Various Types of Carbon Black on Certain Physical Properties of Rubber Compounds¹

D. J. Beaver and T. P. Keller

COMBUSTION UTILITIES CORPORATION, LONG ISLAND CITY, N. Y.

IT IS well known to rubber technologists that different shipments of carbon black vary in their reinforcing value and in their effect on rate of cure. The cause of this variation has not been determined precisely as yet, although several investigators have offered tentative theories. Johnson² recently showed that the variation in color value could be correlated with reinforcing value in rubber if the samples of blacks came from the same plant, while no relationship was observed between these two properties if the blacks were produced at different plants. On the other hand, Twiss and Murphy³ thought that the differences in the rate of cure of various types of carbon black were due to the adsorption of more or less of the natural accelerator from the rubber (an unaccelerated stock was used). However, Spear and Moore⁴ have shown that there is no general relationship between stiffening effect in rubber and adsorption of acid or basic dyes from either water or benzene, and have shown further that there is no relation between adsorption and rate of cure. Another possible cause of the retarding effect of carbon black on the rate of cure of rubber compounds would be the presence of acidic intermediate decomposition products from the natural gas. However, no results reported in the literature substantiate this conclusion and, as will be shown later, no measurable differences in the acidity of water extracts of blacks could be noticed.

In view of the importance of the effect of carbon black on the aging of rubber compounds, it is surprising that no study of the comparative aging effect of various types of carbon black has been published. Ruby and Depew⁵ showed that a stock containing carbon black aged more rapidly than one containing zinc oxide and thought that this difference was due to the oxygen adsorbed on the carbon black being activated by the carbon black itself sufficiently to oxidize the rubber. The results obtained by Tener, Smith, and Holt⁶ on the comparative aging of stock containing whiting and carbon black are inconclusive because several other factors such as amount of sulfur, accelerator, and softener were changed at the same time. In view of these uncertainties it was decided to investigate this question more completely.

Relation between Physical Properties of Blacks

In an exhaustive study of carbon blacks from various sources, Neal and Perrott⁷ found that the ultimate compo-

sition of these blacks was approximately the same except for the oxygen content. The data presented by these authors show that the per cent oxygen combined with or adsorbed on the black varies inversely with the calorific value within an average deviation of ± 100 B. t. u., or 0.7 per cent.

Table I gives a summary of certain physical properties of different types of carbon blacks which were used in the present tests. The ink black is a standard product made by the complete combustion of natural gas in the channel or disk

process; the M black is a standard channel black for use in rubber; the B black is made by a slightly modified channel process; the D and G carbons are made by the combustion of natural gas in special types of apparatus; while the lampblack, acetylene black, and thermatomic black are standard commercial products manufactured, respectively, by the incomplete combustion of oil residues or acetylene and by the cracking of natural gas. These data show that the oxygen content of the different types of blacks varies

between 1.2 and 10.7 per cent. These values were obtained from the heating value of the blacks by comparison with the straight line obtained by plotting B. t. u. vs. oxygen content (from Neal and Perrott's data). It will be seen that the per cent oxygen shows no relationship to the iodine adsorption, the oil adsorption, the acetone extract, or the specific gravity. The only property which varies regularly with the oxygen content is the ease of oxidation. This determination was made by heating an acidified 0.02 M solution of potassium permanganate to 70° C. with 1 gram of black for 15 minutes and titrating the excess permanganate with sodium oxalate. It is probable that part of the oxygen is combined with carbon to form partially oxidized compounds and these compounds are more easily oxidized than pure carbon itself. The data given in this table bear out this conclusion in a qualitative manner. Another interesting fact brought out is the difference in the ratio of iodine adsorbed to the linseed oil adsorbed. For example, this ratio is 0.07 for lampblack and 0.54 for ink black. This eightfold difference emphasizes in a very striking manner the specificity of adsorption phenomena.

The effect of various types of carbon black on the rate of cure, tensile properties, aging, and abrasion loss of rubber has been determined. It has been found that the presence of different amounts of oxygen adsorbed on or combined with the black retards the rate of cure in direct proportion to the amount of oxygen present and decreases the maximum physical properties obtainable from a given stock. The aging data show that the higher the amount of oxygen on the black the more rapid the deterioration of the rubber stock when aged at 70° C. in air. Other physical properties such as oil adsorption, iodine adsorption, acetone extract, or color value could not be correlated with the effect of these blacks on the curing characteristics of rubber compounds.

Table I—Physical Properties of Carbon Blacks Studied

BLACK	IODINE ADSORPTION Mg./g.	OIL ADSORPTION Cc./100 g.	CALORIFIC VALUE B. t. u.	ACETONE EXTRACT %	OXIDIZED BY 0.02M KMnO ₄ %	OXY-GEN %	Sp. Gr.
Ink	79.1	146	12,810	0.36	70.6	10.7	1.88
B	8.0	150	13,480	0.30	...	7.1	1.76
M	57.4	140	13,825	0.30	43.5	5.3	1.73
Lampblack	9.2	130	13,820	0.84	28.5	5.3	1.73
Acetylene	42.7	325	14,310	0.36	26.8	2.6	1.84
D	3.1	100	14,540	0.3	...	1.3	1.82
G	22.2	100	14,550	0.5	9.9	1.2	1.82
Thermatomic	6.1	46	14,550	0.5	7.7	1.2	1.84

¹ Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² *India Rubber World*, **78**, 65 (1928).

³ *J. Soc. Chem. Ind.*, **45**, 121 (1926).

⁴ *IND. ENG. CHEM.*, **18**, 418 (1926).

⁵ *Ibid.*, **12**, 1155 (1920).

⁶ Bur. of Standards, *Tech. Paper* **342** (1927).

⁷ *Bur. Mines, Bull.* **192** (1922).

Study of Properties of Rubber Compounded with Various Blacks

Since it was found that the various physical properties of the different types of blacks did not vary in the same manner, it was decided to determine if possible what property or properties could be used as a criterion to judge the suitability of a certain black for use in rubber. In the first series of tests the following compound was used: 100 parts pale crepe, 5 zinc oxide, 3 sulfur, 1 stearic acid, 25 of black, and varying amounts of Grasserator 808, to give as near as possible the same time of cure. All samples were cured in a paraffin bath regulated at $140^{\circ} \pm 0.50^{\circ}$ C. and tested in accordance with the recommendations of the physical testing committee of the Rubber Division of the AMERICAN CHEMICAL SOCIETY except for the constant temperature and humidity control of testing room. It was found that the ink black required 2 per cent of accelerator, the M black and lampblack 1.5 per cent, and G black, thermatomic and acetylene blacks 0.5 per cent. The data for modulus at 500 per cent elongation, tensile at break before and after aging 4 days in a hot-air oven at 70° C. are given in Table II.

Table II—Effect of Blacks on Properties of Rubber Compounds Containing Them

BLACK	MODULUS AT 500% ELONGATION			TENSILE AT BREAK			EFFECT OF AGING 4 DAYS AT 70° C.	
	Minutes' Cure						% of original tensile (50-min. cure)	% of original abrasion (40-min. cure)
	40	50	60	40	50	60		
	<i>Kg. per sq. cm.</i>			<i>Kg. per sq. cm.</i>				
Ink	118	140	183 ^a	185	211	240 ^a	41 ^a	68 ^a
M	197	205	201	310	303	284	57	70
G	181	183	187	254	243	241	72	76
Lampblack	183	185	192	233	222	218	66	78
Acetylene	184	185	188	250	233	235	92	90
Thermatomic	177	184	180	220	206	196	100	92

^a 80-minute cures.

It will be seen that all the blacks except the ink-making black reach their maximum physical properties in 50 minutes while this black required 80 minutes to reach its maximum properties. It is evident, therefore, that the presence of large amounts of oxygen on the carbon retards the rate of vulcanization of the rubber. The acetylene black is the only one that is at all out of line, since according to its oxygen content it should give a slower curing compound than either G black or thermatomic, while it is found to give exactly the same curing time. The aging data show that as more oxygen is carried into the rubber compound with the black the stock ages much more rapidly. Again this relationship holds true for all the blacks except acetylene, which gives better aging stocks than blacks containing less oxygen. This difference might be due to the presence of intermediate decomposition products, although the acetone extract is only 0.36 per cent.

In order to test this point, the acetylene black was extracted with acetone and this extract was added to an equal weight of M black. These two treated blacks were milled in rubber and aging tests were made on these stocks. It was found that this treatment had not improved the aging characteristics of the M black nor decreased those of the acetylene black. At present no satisfactory explanation for the superior aging of acetylene stocks can be offered.

The abrasion resistance of these compounds as determined by means of the Grasselli abrader⁸ before and after aging shows that the deterioration as measured by this test has not been so great as decrease in tensile at break. This difference is due to the fact that the abrasion tests were run for 10 minutes whereas if they had been run for only

2 minutes the loss would have been considerably higher, since the deterioration of the surface of the blocks is greater than at the center owing to the action of oxygen on this surface layer. (For a more complete discussion of the abrasion loss of aged stock, see paper by Plummer and Beaver.⁹)

Effect of Oxygen Content of Black

In order to determine more precisely the effect of the amount of oxygen in the black on the physical properties of the rubber compound, a series of mixtures of ink black and M black was made using the following formula: 100 parts pale crepe, 5 zinc oxide, 4 sulfur, 1 stearic acid, 25 black, 0.75 diphenylguanidine. The data are given in Table III and show that the tensiles at break of the 140-minute cure of these stocks fall on a straight line. Since the amount of oxygen carried into the rubber mixes by the blacks varies in a continuous manner, it is evident that the physical properties as measured by the tensile at break vary inversely as the per cent oxygen on the blacks. Plotting the modulus at 500 per cent elongation brings out this same relationship, showing that the rate of vulcanization is also proportional to the amount of oxygen on the black. The aging data on this series of compounds are not given, since the stocks containing high percentages of the ink black are so uncured that they show no indication of the actual aging characteristics of the black.

Table III—Relation between Oxygen Content of Mixtures of Ink Black and M Black on Properties of Rubber Compounds

(140-minute cure at 140° C.)				
BLACK	MODULUS AT 500% ELONGATION	TENSILE AT BREAK	OXYGEN ON BLACK	
Ink M	<i>Kg. per sq. cm.</i>	<i>Kg. per sq. cm.</i>	%	%
100 0	50	94	10.7	
75 25	77.5	115	9.4	
50 50	114	158	8.0	
25 75	148	184	6.6	
0 100	169	207	5.2	

Another possible explanation of the data presented here is that the differences in the tensile or modulus figures are due to the difference in the reinforcing properties of the black and not to the retarding effect of the oxygen on the rate of cure. However, the data in Table II show that with sufficient accelerator present the ink black will give a stock with as high a modulus and tensile as that of the M black. That the adsorptive characteristics of the blacks are not responsible for the differences in the rate of cure can be seen from Table I. For example, lampblack adsorbs only 21.5 per cent as much iodine and 40 per cent as much linseed oil as acetylene black, but requires about three times as much accelerator to give the same rate of cure. On the other hand, the ink black adsorbs 38 per cent more iodine than the M black and requires somewhat more than 33 per cent accelerator to give it the same time of cure. However, its oil adsorption is only 4 per cent greater than the M black. It seems reasonable to conclude that adsorption of iodine or linseed oil does not indicate the curing characteristics of the black. Therefore, it can be concluded that the differences noted above are due to the presence of the oxygen in the black.

Further confirmation of this conclusion is given in Table IV. These data were obtained with the same test formula used for the ink black-M black mixtures, and show that the properties of compounds containing mixtures of G and M blacks also vary in a continuous manner. Since the difference in the amount of oxygen on these two blacks is not so large as it was with the previous mixtures, the slope of the modulus curve is smaller. Another interesting point brought out in this test was the effect of the increased amount of oxygen on the rate of deterioration of the stock. It was found that

⁸ Williams, *IND. ENG. CHEM.*, 19, 674 (1927).

⁹ Subsequent issue, *IND. ENG. CHEM.*

the higher the amount of oxygen carried in the stock by the black the more rapid the deterioration, although this deterioration was only approximately a direct function of the amount of oxygen present.

Table IV—Relation between Oxygen Content of Mixtures of G and M Blacks on Properties of Rubber Compounds (100-minute cure at 140° C.)

BLACK	G	M	MODULUS AT 500% ELONGATION	TENSILE AT BREAK	OXYGEN ON BLACK	% OF ORIGINAL TENSILE, AGED 4 DAYS AT 70° C. (Best Cure)
						Kg. per sq. cm.
0	100		165	298	5.2	20
25	75		183	288	4.2	25
50	50		198	269	3.2	33
75	25		222	269	2.2	59
100	0		232	248	1.2	66

Table V—Effect of Various Blacks on Time of Cure

BLACK	TIME OF CURE AT 140° C.	MODULUS AT 500% ELONGATION	TENSILE AT BREAK	% OF ORIGINAL TENSILE, AGED 6 DAYS AT 70° C.
	Minutes	Kg. per sq. cm.	Kg. per sq. cm.	
B	160	169	288	9
M	160	191	304	10
G	100	220	274	26
D	100	223	273	26
Acetylene	80	219	250	45
Lampblack	140	113	201	8
Theratomic	120	113	225	35

Another series of tests was made using the same amount of accelerator and changing the time of vulcanization to give the maximum physical properties. The compounds used for this test contained 100 parts of pale crepe, 5 zinc oxide, 4 sulfur, 1 stearic acid, 25 of black, and 0.75 diphenylguanidine. These results (Table V) again show the very great difference in the rate of vulcanization of compounds containing the same amount of black but different amounts of oxygen and also show the difference in the maximum physical properties produced under these conditions. It will be seen that the

data agree very well with those presented previously. The figures for the ink black are omitted, since it was too much under-cured to give satisfactory results. The more rapid deterioration of these stocks compared with those shown in Table II is due to the fact that diphenylguanidine does not have so great an antioxidant action as Grasselerator 808.

Conclusion

The data presented herein show that in general the presence of oxygen on carbon black retards the rate of vulcanization in direct proportion to the amount of oxygen present and also decreases the maximum physical properties obtainable with a given amount of accelerator. The aging data show that the presence of this oxygen on the black increases the rate of aging as the amount of oxygen increases, but not in direct proportion to the per cent of this oxygen present. It can be concluded, therefore, that compounds which contain a small amount of oxygen, such as theratomic, G black, or acetylene black, will give better aging stocks than compounds containing higher amounts of oxygen such as lampblack and standard channel blacks. No correlation could be found between the acetone extract, iodine adsorption, or oil adsorption, and the effect of these blacks on the rate of cure or aging.

Acknowledgment

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Paper Pulp from Logging Waste in the Douglas Fir Region¹

Allen H. Hodgson²

OFFICE OF FOREST PRODUCTS, U. S. FOREST SERVICE, PORTLAND, ORE.

THE Douglas fir region is located west of the Cascade Range in Oregon, Washington, and British Columbia, but this discussion is confined to Oregon and Washington. Within this region are found some of the heaviest stands of timber known to man. This timber represents 25 per cent of all the remaining softwood saw timber in the United States. It is being cut at the rate of over 12 billion feet board measure per year. The timber is composed for the most part of very large trees, many of which are 6 to 10 feet in diameter and 250 to 300 feet high. Small trees, 10 to 20 inches in diameter, are usually found under the large ones. The large timber is usually Douglas fir, western red cedar, and Sitka spruce. The small trees most frequently found are western hemlock and white fir, both species in little demand for lumber but having high values for paper pulp. Most of the remaining timber within the region is situated in rough, mountainous country.

The combination of very large logs and very rough country has forced the logger to develop and use the largest and most powerful logging machinery in the world. To make this huge equipment, which is costly to purchase and to operate,

an asset rather than a liability, quantity production is the all-important factor. Small logs cannot be economically handled by the large logging units, and for this reason the undersized trees, together with broken and defective logs from the larger ones, are left in the woods in the form of slash, to rot or to be burned. In extreme cases the volume of timber taken from the forest as merchantable logs amounts to only 25 per cent of the original stand.

Furthermore, as the lumber cut in Oregon and Washington increases during the next few years, the amount of waste wood available in connection with the lumber industry will become proportionately greater. More and more as the operations go back into the higher mountains, they will encounter stands of timber with higher percentages of pulpwood species and lower percentages of the Douglas fir, which is now being sought. If a big demand for pulpwood is built up, this might for some time offset largely, or altogether, a gradual falling off in the production of logs in Oregon and Washington, the beginning of which may be less than a decade ahead.

There is no reason, other than lack of pulpwood markets, why there should not be operations in Oregon and Washington designed primarily to secure pulpwood, or why operations in stands containing a large percentage of pulp species

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² Associate Forester, U. S. Forest Service.

should not be designed to secure saw timber from the material most suitable for that purpose and pulpwood from the remainder of the stand. There are great possibilities in the integration of the lumber and pulp industries, which would make entirely feasible large use of both logging and sawmill waste pulp. A good start toward such a combination, both at the mills and in the woods, has already been made. The use of waste wood from mills has temporarily taken the lead because of the ease with which it can be secured. As time goes on, however, the use of woods waste for pulp will come into its own since these supplies are composed of a better grade of material.

Utilization of Mill Waste

In years past only a negligible amount of mill waste was used by the pulp and paper industry. The raw material was taken in the form of saw logs, which were also suitable for



Photos by Author

Woods Losses in the Douglas Fir Region

A yearly accumulation of 4.1 billion board feet of such material is left to rot or burn by the loggers of the Douglas fir region

lumber. Now, nearly all of the pulp plants of these states are using some mill waste; in 1926, 18 per cent of the pulpwood used in the state of Washington where the production of pulp has been the greatest, was in the form of mill waste; almost without exception, new pulp plants have been located with reference to the utilization of mill waste. In a few cases the lumber mill and pulp and paper mills are integral parts of the same plant and practically complete integration is attained. This is the universal rule in Sweden and Finland, the important pulp and paper producing countries of Europe.

At several pulp mills in Washington, sawmill waste, which is purchased, constitutes the total supply of pulpwood. The one at Bellingham, for example, depends upon waste hemlock and spruce box trimmings. This plant is located between and near two sawmills operating box factories. The waste from the two factories is hauled to the pulp plant by auto trucks. Box trimmings from a third factory, 22 miles distant,

are delivered by rail. The trimmings, dumped into a trough, are conveyed by machinery to a huge bunker. They are then moved by gravity to the wood room, where they are converted into chips. Black knots, bark, and other defective material is sorted out and sold as fuel. Thus every piece of wood, no matter how small, is utilized.

Mill waste is delivered to the pulp plants in various forms, such as slabs, sawmill and box-factory trimmings and edgings, for which a fair price is received. In some cases the waste wood is converted into pulp chips at the sawmills, with equipment installed and owned by the pulp manufacturers, and is delivered in this form to the pulp plant.

System Developed by One Company

As suggested above, it is predicted that the pulp mills will soon turn more and more to that great supply of raw material which is now left by the loggers in the woods. Already some paper-pulp mills are looking to this source of supply and becoming more interested in machinery by means of which it can be profitably salvaged. The problem contains many involved economic and mechanical factors, but these can be overcome, as has already been demonstrated by at least one company within the region.

The Crown-Willamette Paper Company has been interested for a number of years in the proposition of saving woods waste. It has finally worked out a highly efficient system of relogging, which follows after the heavy machinery operation. The small logs and chunks are logged by means of newly developed, light, mobile, gasoline-driven machinery which is inexpensive to purchase and to operate. With this equipment about 10,000 board feet of small logs per acre, or about 15 per cent of the original stand, were salvaged and shipped by rail and water a distance of over 100 miles to the pulp mill near Oregon City. It is understood that the material was handled at a profit and that the operation passed out of the experimental stage. During four months in the summer of 1926, the company saved by its relogging operation more than 4 million board feet of wood that would have otherwise been wasted.

Results of Forest Service Survey

Recognizing the importance of the so-called wood waste problem, also the difficulties of even its approximate solution, the Forest Service, during the past two years, has been conducting a general survey of wood waste in the logging camps of the Douglas fir region. The field work is completed and the results are at present being tabulated in preparation for the final report. This field investigation covers the logging operations of twenty-four widely distributed, representative companies, and is based on accurate measurements of material found on one hundred and fifty sample-acre plots. The data represent a good cross section of existing conditions.

The results of the study show that approximately 20 per cent of the timber is being left in the woods in the form of sound material, measured down to cordwood size. In addition there is perhaps 5 or 10 per cent of wood in the form of broken pieces and tops too small for any present commercial use. Upon the basis of 20 per cent of a stand of 100,000 feet board measure per acre, the approximate volume found on the average sample plot, 20,000 feet board measure per acre is left in the woods. The loggers of western Oregon and Washington in 1926 cut over about 145,000 acres of timber land. Upon these premises about 2.9 billion feet board measure or 5,800,000 cords of sound material, cordwood size and larger, was left in the woods as waste that year.

The tremendous quantity of this material left each year to rot or to be burned can perhaps be appreciated when we consider that in 1926 the total pulpwood produced in the United States was 4,394,766 cords, only 75 per cent in vol-

ume as compared with the woods waste in the Douglas fir region of Oregon and Washington.

An analysis of the woods waste shows that nearly 40 per cent (1,121,000,000 feet board measure) is in the form of logs, which under present or slightly improved economic conditions the industry could reasonably be expected to remove from the woods for use as lumber. About one-half of these logs are western hemlock, white fir, and Sitka spruce, while the other half are Douglas fir, cedar, and pine. The remainder of the material (about 60 per cent) left in the woods is in the form of smaller logs, culled logs, and tops. About one-third of this is made up of hemlock, white fir, and Sitka spruce, while two-thirds is represented by Douglas fir, cedar, and pine.

Summing up, we find that of the yearly accumulation of 5,800,000 cords of woods waste, 2,320,000 cords are western hemlock, white firs, and Sitka spruce, woods in demand for sulfite and mechanical pulp, and 3,480,000 cords are Douglas fir, cedar, and pine, woods best suited for lumber and having inferior pulping properties even by the sulfate or soda processes, but which are being made into pulp to some extent by these processes.

Conclusion

In conclusion it may be stated that when the combined quantities of sawmill waste and logging waste are considered, the raw material in these forms for the paper-pulp industry of Oregon and Washington at present and for a number of years to come is practically without limit.

There are three ways by which the life of the lumbering and wood-using industries, including the production of paper pulp, of Oregon and Washington can be extended: (1) revised tax laws which will encourage the protection and growth of young forests; (2) prevention of forest fires in virgin and second-growth forests as well as on cut-over lands; (3) better and closer utilization of the wood which the lands are producing.

If the pulp industry continues to develop practical means for making greater use of the sawmill and logging waste, it will be doing a great deal toward helping itself as well as assisting to establish continuous prosperity in the states of Oregon and Washington, where the forests give employment to some 168,000 local men and pay nearly 65 per cent of the entire industrial payroll.

Dew Points of Air-Gasoline Mixtures from Distillation Curves^{1,2}

Oscar C. Bridgeman

BUREAU OF STANDARDS, WASHINGTON, D. C.

ONE of the basic properties of liquid fuels, which determines their suitability for use in automotive engines, is volatility. The accepted laboratory test for volatility is the A. S. T. M. distillation, a non-equilibrium process conducted under definitely specified conditions at atmospheric pressure. The difficulty of interpreting the results of this test in terms of engine performance and the lack of a suitable method for estimating volatility more directly in such terms led to the inauguration of an extensive study of volatility which has been in progress during the past few years at the Bureau of Standards in cooperation with the petroleum and automotive industries.

From the industrial standpoint the problem of the volatility of gasoline can be depicted simply in the manner shown in Figure 1. The upper solid line is the corrected A. S. T. M. curve of the fuel, which does not cut either the lines of 0 or 100 per cent evaporated. The gap at the lower end is due to loss of the very volatile constituents at the beginning of the distillation, for which correction is made in all of this volatility work, while at the upper end of the curve the residue remaining in the flask at the end of the distillation prevents the evaluation of the temperature of complete vaporization. The upper dotted line represents the probable curve for equilib-

Gasoline was vaporized by a dynamic method in the presence of known amounts of air at temperatures permitting successive approach to complete vaporization. For each mixture and gasoline, the temperature-percentage evaporated curve extrapolated to 100 per cent gave the dew-point temperature. These equilibrium distillation values agreed well with values obtained by the method of Stevenson and Babor and with the results of these investigators. The dew-point temperatures at 1 atmosphere pressure, of gasoline vapor, and of mixtures from 1:1 to 30:1 were found to be simply related to the 90 per cent A. S. T. M. points, corrected for loss, and to each other.

rium distillation at 1 atmosphere pressure in the absence of air. The hatched area covers the field of interest in connection with automotive engines—namely, air-vapor mixtures from 8:1 to 20:1. The abscissa of 0 per cent evaporated represents the true vapor-pressure line, for along it the composition of the liquid remains unchanged. At the other extreme the abscissa of 100 per cent evapo-

rated is the dew-point line and along it the composition of the vapor remains unchanged. Until recently the study of volatility at the Bureau of Standards has been confined almost exclusively to the automotive range. This study has included the design of an apparatus by Sligh³ for determining volatility under conditions simulating those existent in the engine manifold, the relation between data obtained with this apparatus and the ease of engine starting,⁴ and recently a correlation between volatility data by this method and the A. S. T. M. distillation curves of the fuels.^{5,6} The present study is concerned mainly with dew points as obtained with the Sligh apparatus and corroborated by experiments with an apparatus analogous to that employed by Stevenson and Babor.⁷ An investigation of the vapor pressure of gasoline is now in progress.

¹ *J. Soc. Automotive Eng.*, **18**, 393; **19**, 151 (1926).

² Cragoe and Eisinger, *Ibid.*, **20**, 353 (1927).

³ Bridgeman and Cragoe, *Am. Petroleum Inst. Bull.*, January 31, 1928, p. 54.

⁴ Bridgeman, *J. Soc. Automotive Eng.*, **22**, 437 (1928).

⁵ *IND. ENG. CHEM.*, **19**, 1361 (1927).

¹ Presented before the Division of Petroleum Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² Publication approved by the Director of the National Bureau of Standards.

Considerable interest has been shown in the problem of the dew points of gasolines, both at various pressures in the absence of air and when mixed with air in various proportions. The pioneer work of Wilson and Barnard⁸ was followed by the investigations of Gruse⁹ on the dew points of various air-fuel mixtures by a dynamic method and of Kennedy¹⁰ on gasoline vapors at various pressures by a static method. Recently Stevenson and Babor⁷ have measured

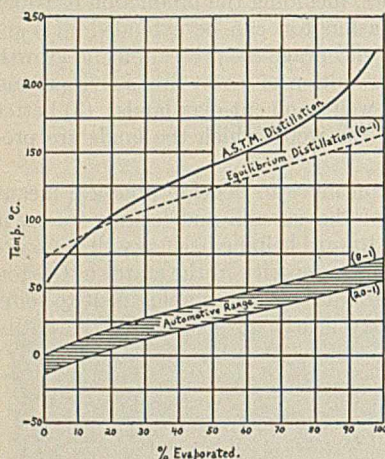


Figure 1—A. S. T. M. and Equilibrium Distillation Curves

the dew points for seven gasolines of mixture ratios from 1:1 to 30:1. The determination of the normal dew point¹¹ of gasoline vapor in the absence of air at a pressure of 1 atmosphere has been studied by a number of methods. Wilson and Barnard⁸ determined the equilibrium solution temperature of a number of gasolines at 1 atmosphere, which is equivalent to the normal dew point, while Whatmough¹² employed a similar method with a number of British fuels. James¹³ and recently Brown¹⁴ determined the amount of gasoline vaporized under equilibrium conditions at 1 atmosphere by passage through a heated tube or spiral. Plots of temperature against percentage evaporated, when extrapolated to 100 per cent give the normal dew points. While the principle of this method is very excellent, the question of attainment of equilibrium is a serious one and the technic necessary for accuracy is extremely difficult. Using the same principle, but working with a static system, Stevenson and Stark¹⁵ published one curve covering the range from 0 to 100 per cent evaporated. This method avoids the difficulties inherent in the dynamic method used by James and by Brown, but requires an excessive amount of time. The phase-change method of Stevenson and Stark¹⁵ takes considerably more time than the more recent one, proposed by Stevenson and Babor,⁷ employing a platinum black surface for detecting the normal dew point.

The dew point of a mixture is the temperature at which the vapor is in equilibrium with an infinitesimal amount of the liquid phase at a given pressure. For each gasoline this temperature is uniquely defined by the pressure of the vapor, or by its equivalent, the mixture ratio at a given total pressure. Since it is obviously impossible to determine when only an infinitesimal amount of liquid is present, the most logical procedure is to make measurements at various percentages evaporated and extrapolate to 100 per cent. This is the main procedure used in the present work.

Dew-Point Determinations by Sligh Method

The apparatus employed (Figure 2) was that designed by Sligh³ and has been described in detail previously,^{3,5,6} so

⁸ *J. Ind. Eng. Chem.*, **13**, 906 (1921); **17**, 428 (1925); *J. Soc. Automotive Eng.*, **12**, 287 (1923).

⁹ *IND. ENG. CHEM.*, **15**, 796 (1923).

¹⁰ *Bur. Standards, Sci. Paper 500* (1925).

¹¹ This point was called the Deppé end point by Stevenson and Stark, and the equilibrium end point by Stevenson and Babor.

¹² *IND. ENG. CHEM.*, **18**, 43 (1926).

¹³ *J. Soc. Automotive Eng.*, **18**, 501 (1926).

¹⁴ *University of Michigan, Eng. Bull.* **7** (May, 1927).

¹⁵ *IND. ENG. CHEM.*, **17**, 679 (1925).

that a brief description will suffice here. Gasoline is fed from the reservoir *H* into the vaporization helix *A* by means of a plunger operated by clockwork. At the same time air, dried with calcium chloride, passes through the orifice meter *N*, is preheated or precooled by passage through the small coil *B*, and flows down through the vaporization helix with the gasoline. These coils are immersed in a liquid bath, the temperature of which can be controlled. At the bottom of the vaporization helix, the mixture is led into a separating chamber, *C*, the air-vapor phase passing out through the exhaust pipe *E*, while the residual liquid drains down into the tube *D*, where it is measured in a volumetric flask. Various rates of gasoline feed are obtained by interchange of the drums *K* on the clock spindle, while the mixture ratio is varied by the use of different orifices in the flowmeter.

Ordinarily feeds of 2 or 3 ml. per minute were used and air-fuel ratios of 0.5:1 to 16:1 were readily obtainable. The known gravity of the original fuel and the experimentally determined gravity of the residue obtained in each measurement permitted a computation of the weight percentage evaporated, according to the relation

$$P = \frac{V_1 d_1 - V_2 d_2}{V_1 d_1} \times 100 \quad (1)$$

where V_1 and V_2 are the volumes of liquid supplied and collected, respectively, per unit of time, d_1 and d_2 are their gravities at the temperatures of the reservoir and bath, respectively, and P is the percentage evaporated. The air-fuel mixture, M_s , supplied is computed from the relation

$$M_s = \frac{k\sqrt{H}}{V_1 d_1} \quad (2)$$

where k is the orifice constant and H is the head of water in the manometer. The volume of liquid supplied per unit of time is proportional to the displacement of the plunger, the diameter of the drum on the clock spindle, and the clock

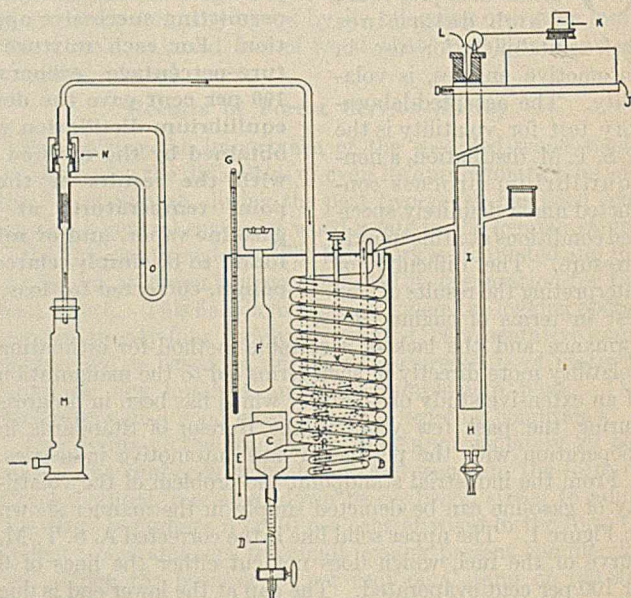


Figure 2—Sligh Apparatus for Equilibrium Air Distillation

rate. The resultant air-vapor mixture, M_r , formed from M_s supplied is given by equation (3).

$$M_r = \frac{M_s}{0.01P} \quad (3)$$

Careful attention was paid to the calibration of the orifices in the flowmeter, the plunger displacement, the effect of torque on the clock rate, and the accuracy of the stopwatch. Experiments with various rates of feed at a number of tem-

peratures and with different mixtures indicated the extent of the departure of the dynamic system from equilibrium, and all results were corrected by means of expression (4).

$$P = P_0 (1 + 0.0125V_1) \quad (4)$$

P represents the corrected and P_0 the observed percentages evaporated for the feed V_1 . Additional experiments with toluene showed that the results corrected by this relation closely approximated equilibrium values. All measurements with this apparatus were made at a total pressure of 1 atmosphere.

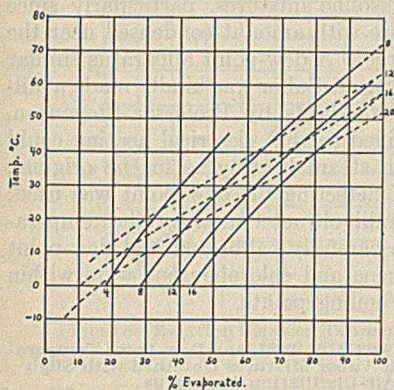


Figure 3—Equilibrium Air-Distillation Curves

and 20:1 formed from the supplied mixtures and are drawn through points computed from the continuous curves by means of equation (3). These dotted lines are the ones of interest, since they indicate the temperature at which a given mixture will form when a certain amount of the fuel evaporates. The dew points of these mixtures are obtained by a slight extrapolation to the line of 100 per cent evaporated. In doing this, there is a safeguard on the extrapolation, for the supplied mixture line of 16:1, for example, meets the resultant 16:1 mixture line at 100 per cent and in effect this amounts to a double smoothing of the experimental data and it increases the accuracy with which the dew point temperatures may be obtained.

The type of curves obtained with the Sligh apparatus is shown in Figure 3 for U. S. motor gasoline. The continuous lines represent air-fuel mixtures supplied of 4:1, 8:1, 12:1, and 16:1, and indicate the temperatures at which various percentages are evaporated from these mixtures. The dotted lines show the resultant air-vapor mixtures of 12:1, 16:1,

No.	DESCRIPTION	
1, 2, 3	Atlantic Refining Co., straight run	
1A, 2A, 3A, 4A	Atlantic Refining Co., special blends for starting tests	
6, A	Bureau of Standards current supply, U. S. motor	
B	Army Air Corps, domestic aviation	
C	Blend of 50% A and 50% B	
D, E, F	The Texas Corporation, special blends for acceleration work	
L	Standard Oil Co. of N. J., laurel oil	
RH, RL	Vacuum Oil Co., Russian naphthas, Grozny crude	
RPC	Midcontinent crude	
J	Universal Oil Products Co., Dubbs process cracked	
K		Smackover crude
N		Panhandle crude
O		California crude
G	Wyoming crude	
H	Blend 60% No. 6 and 40% motor benzene	
I	Blend 80% A and 20% c. p. benzene	
M	Blend 60% A and 40% c. p. benzene	
M	Blend 80% A and 20% kerosene	

A description of the gasolines used in this work is given in Table I and the government specification data are given in Table II. There are 5 cracked gasolines, 1 aviation, 2 Russian naphthas, 2 U. S. motor gasolines, 1 blend with motor benzene, 2 blends with c. p. benzene, and 1 blend with kerosene, while no information is available on the composition of the other samples. The range of temperatures for the specification points are as follows:

	° C.
Initial point	30 to 112
20 per cent	80 to 127
50 per cent	102 to 164
90 per cent	136 to 224
End point	155 to 263

Table II—Specification Data for Gasolines

No.	DISTILLATION				E. P. ° C.	GRAVITY	LOSS %	RESIDUE %
	I. P. ° C.	20% ° C.	50% ° C.	90% ° C.				
1	89	127	156	202	223	0.764	1.3	1.7
3	59	121	159	199	222	0.730	1.8	1.2
1A	50	104	141	202	226	0.733	2.3	1.7
2A	53	106	141	198	225	0.739	1.5	1.5
3A	58	110	141	196	218	0.738	1.0	2.0
4A	55	112	141	189	215	0.731	1.5	1.5
A	38	100	136	199	220	0.768	1.2	1.3
B	32	80	102	136	155	0.714	2.0	1.0
C	36	87	116	173	215	0.741	1.2	1.3
D	48	103	122	204	227	0.754	0.8	1.2
E	47	103	138	201	222	0.762	0.7	1.8
F	43	103	164	199	223	0.766	1.0	1.0
RH	51	99	126	169	204	0.739	0.5	1.1
L	112	118	126	152	180	0.751	0.3	1.2
RPC	38	88	135	200	222	0.747	1.0	1.5
2	45	74	113	198	224	0.730	1.4	1.6
6	58	107	139	192	222	0.768	1.0	1.0
G	65	92	108	181	216	0.807	1.0	1.5
H	47	85	114	191	213	0.776	1.8	1.2
I	56	83	95	183	210	0.805	1.7	1.3
J	30	80	138	210	224	0.751	1.6	1.4
K	36	85	123	178	204	0.735	1.0	1.2
M	47	111	153	224	263	0.776	0.7	1.3
N	60	114	151	205	221	0.771	0.6	1.2
O	46	103	148	201	216	0.755	0.6	1.4
RL	46	84	105	148	188	0.724	0.3	1.2

Table III—Temperature Ratios for 16:1 Resultant Mixtures

No.	10%	20%	30%	40%	50%	60%	70%	80%	90%
1	..	1.34	1.35	1.36	1.37	1.38	1.39	1.40	1.43
3	..	1.32	1.35	1.37	1.38	1.39	1.40	1.41	1.44
1A	1.32	1.34	1.35	1.37	1.38
2A	1.30	1.33	1.35	1.36	1.38
3A	1.32	1.35	1.36	1.38	1.39
4A	1.31	1.35	1.36	1.37	1.38
A	1.38	1.38	1.39	1.40	1.42	1.45
B	1.37	1.37	1.38	1.40	1.43
C	1.37	1.37	1.38	1.40	1.45
D	1.29	1.33	1.35	1.37	1.38	1.38	1.37	1.38	1.48
E	1.29	1.33	1.35	1.36	1.37	1.37	1.39	1.42	1.46
F	1.29	1.31	1.34	1.36	1.37	1.38	1.38	1.39	1.43
RH	1.32	1.34	1.35	1.35	1.36	1.37	1.38	1.40	1.43
L	..	1.35	1.35	1.35	1.35	1.36	1.37	1.39	1.42
RPC	..	1.33	1.33	1.34	1.36	1.37	1.39	1.42	1.45
2	..	1.31	1.33	1.34	1.37	1.39	1.42	1.44	1.47
6	..	1.32	1.33	1.34	1.36	1.37	1.39	1.41	1.44
G	..	1.33	1.34	1.34	1.35	1.36	1.39	1.42	1.47
H	1.34	1.36	1.39	1.42	1.45
I	1.38	1.37	1.36	1.38	1.41	1.47
J	..	1.31	1.33	1.35	1.37	1.38	1.40	1.43	1.46
K	..	1.31	1.34	1.36	1.37	1.38	1.39	1.40	1.43
M	1.29	1.33	1.35	1.36	1.37	1.38	1.39	1.42	1.45
N	1.31	1.34	1.35	1.35	1.36	1.37	1.38	1.41	1.44
O	1.30	1.33	1.34	1.35	1.36	1.37	1.39	1.41	1.43
Av.	1.304	1.330	1.345	1.359	1.369	1.374	1.388	1.410	1.451
Av. Δ	0.011	0.010	0.008	0.011	0.008	0.008	0.008	0.011	0.014

Total average deviation = ±0.010

Comparison with A. S. T. M. Data

In previous publications^{5,6} it was shown in a preliminary manner that the volatility data obtained with the Sligh apparatus for 12 gasolines could be correlated with the A. S. T. M. curves of these fuels. For any given mixture, over the range studied, the ratio of the absolute temperatures on the A. S. T. M. and resultant equilibrium curves at the same percentage evaporated was found to be a constant independent of the sample of gasoline used. Since that time information on a considerable number of additional gasolines has been obtained, which verifies the original generalization as to the possibility of computing volatility data from the A. S. T. M. distillation curves. Since these data are necessary for the determination of the dew points by extrapolation and are very important of themselves, the temperature ratios for 16:1 resultant air-vapor mixtures at every 10 per cent from 10 to 90 per cent, inclusive, are given in Table III for 25 gasolines. It is seen from the average deviations that the ratios are independent of the particular gasoline within reasonable limits. Similar ratios were obtained for 20:1 and 12:1 mixtures, the averages of which are shown in Table IV, where for comparison those for the 16:1 mixture are also included. An equation has been obtained for the 16:1 averages as a function of the percentage evaporated and is as follows:

$$R_{16} = 1.366 \pm (3.8 + 0.014P) \times 10^{-6} (P-50)^2 \quad (5)$$

where the plus sign applies above and the minus sign below 50 per cent evaporated. At the same percentage evaporated, the 16:1 ratio is practically the mean of the 20:1 and the 12:1 ratios, although more accurate relations are: $R_{20} = 1.013 R_{16}$, and $R_{12} = 0.983 R_{16}$. The average deviation between the observed values and those computed from these relations is ± 0.003 . In view of the number and diversity of samples of gasolines used, it is believed that the volatility data of interest in engine operation may be computed¹⁶ with considerable accuracy from the A. S. T. M. distillation curve of any gasoline commercially available at present, if these curves are corrected for distillation loss.

Table IV—Averages of Observed Temperature Ratios

Per cent	20:1	16:1	12:1
10	1.326	1.304	1.280
20	1.349	1.330	1.314
30	1.362	1.345	1.327
40	1.376	1.359	1.338
50	1.381	1.369	1.347
60	1.391	1.374	1.358
70	1.407	1.388	1.368
80	1.430	1.410	1.389
90	1.469	1.451	1.425

The dew-point temperatures of 21 of these gasolines for 8:1, 12:1, 16:1, and 20:1 mixtures have been obtained by extrapolation of the air-vapor and air-liquid gasoline curves

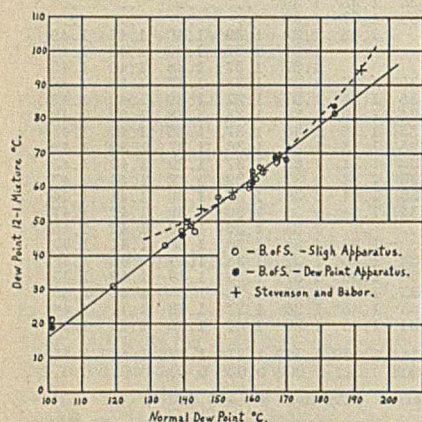


Figure 4—Relation between Dew Points of 12:1 Mixtures and Normal Dew Points

in the manner previously described. Since it is impossible to obtain with accuracy the temperature of 100 per cent evaporated on the A. S. T. M. distillation curve, an attempt was made to relate the dew-point temperatures for these various mixtures with the 90 per cent A. S. T. M. point. For each gasoline, the absolute temperature of this point on the A. S. T. M. curve, corrected for loss, was divided by the absolute temperatures of the dew points of these various mixtures, and these ratios are shown in Table V together with the 90 per cent temperatures in degrees Centigrade. The ratios for each mixture are quite constant and appear to be independent of the particular gasoline used.

Direct Measurement of Dew Points

Recently Stevenson and Babor⁷ have developed an ingenious apparatus for the direct measurement of the dew points of various mixtures from zero air to a 30:1 mixture at a pressure of 1 atmosphere. The criterion chosen for indicating the condensation of liquid was the sudden change in appearance of an illuminated platinum-black surface cooled internally by an adjustable stream of air, and the temperature at which initial condensation began was read by means of a thermocouple soldered to the platinum cone. This apparatus requires careful calibration and a standardized technic must be developed in order to obtain accurate dew-point temperatures. Obviously, the point at which the first infinitesimal trace of liquid separates cannot be detected by this method, and supercooling of the portion under observation always occurs. On the other hand, owing to lag in

¹⁶ A copy of a chart for the graphical evaluation of these data may be obtained on request from the Bureau of Standards.

heat transfer, the thermocouple may not indicate the true temperature of the portion of the cone under observation. Further, although a band of light flashes up very rapidly with rich mixtures, the time factor becomes important with lean mixtures and it is necessary to decide on the intensity of light to be taken as a criterion of the dew point. Careful placing of the thermocouple junction so that heat lag will counterbalance the supercooling, and use of pure substances or mixtures with known dew points as a means of choosing the proper criterion, permit an accurate determination of the dew points of air-gasoline mixtures, particularly since the change in temperature with amount condensed near the dew point is not very large. A dew-point apparatus similar to that used by Stevenson and Babor was kindly made available to the Bureau of Standards by Professor Stevenson. The apparatus was modified so that electrical heating could be employed rather than steam heating as in the original, but the same method of detecting the dew point was used. The thermocouple and millivoltmeter used for the temperature measurements were carefully calibrated and dew-point determinations with toluene and chlorobenzene were within 0.5° C. of their normal boiling points.

Table V—Relation between 90% A. S. T. M. and Dew-Point Temperatures in ° A. of Various Air-Vapor Mixtures Obtained with Slight Equilibrium Air-Distillation Apparatus

FUEL	90% A. S. T. M. ° C.	TEMPERATURE RATIOS			
		8:1	12:1	16:1	20:1
I	199	1.37	1.39	1.41	1.43
3	197	1.37	1.40	1.42	1.45
A	196	1.38	1.41	1.42	1.44
B	132	1.35	1.38	1.43	1.48
C	174	1.37	1.39	1.42	1.45
D	200	1.37	1.40	1.42	1.45
E	199	1.39	1.41	1.43	1.45
F	198	1.39	1.40	1.42	1.44
RH	168	1.37	1.40	1.42	1.44
L	152	1.37	1.40	1.42	1.43
RPC	198	1.37	1.39	1.42	1.45
2	195	1.38	1.41	1.43	1.46
6	190	1.37	1.40	1.43	1.45
G	178	1.39	1.41	1.44	1.46
H	186	1.37	1.39	1.41	1.44
I	177	1.38	1.40	1.42	1.45
J	207	1.39	1.41	1.43	1.45
K	176	1.37	1.40	1.41	1.43
M	222	1.37	1.40	1.42	1.44
N	204	1.38	1.40	1.42	1.44
O	200	1.38	1.40	1.42	1.44
Average		1.375	1.400	1.422	1.446
Average Δ		0.008	0.005	0.006	0.009

The first series of measurements made with this apparatus were on the normal dew points of 15 gasolines. These data are shown in Table VI. The ratios are very constant and it appears that the normal dew point of any gasoline commercially available at present may be obtained directly from the A. S. T. M. distillation curve without recourse to additional experimentation.

Table VI—Relation between the 90% A. S. T. M. and Normal Dew-Point Temperatures in ° A. of Gasoline Vapor at 760 mm.

FUEL	N. D. P. ° C.	90% A. S. T. M. ° C.	RATIO
B	101.2	132	1.082
C	138.4	174	1.086
D	162.5	200	1.086
E	161.7	199	1.086
F	160.0	198	1.087
H	151.0	186	1.083
I	143.0	178	1.085
J	164.8	204	1.089
K	143.0	177	1.081
L	120.2	152	1.080
M	186.8	222	1.078
RH	133.4	168	1.084
RL	113.2	147	1.087
RPC	162.2	198	1.082
Average			1.084 ± 0.003

Comparison of Ratios by Various Observers

A comparison with the ratios computed from the published data of other observers is given in Table VII. The agreement of the Bureau of Standards results with those of Steven-

son and collaborators by three methods is very good, as is also the agreement with the average value obtained from the equilibrium distillation data of James, although the deviations are considerably larger in the latter case. Ratios computed from the work of Brown by an analogous method are much higher, while those obtained from the equilibrium solution data reported by Wilson and Barnard and by Whatmough are lower. However, the average of the values for the last three sets of observers is 1.08. It was suggested

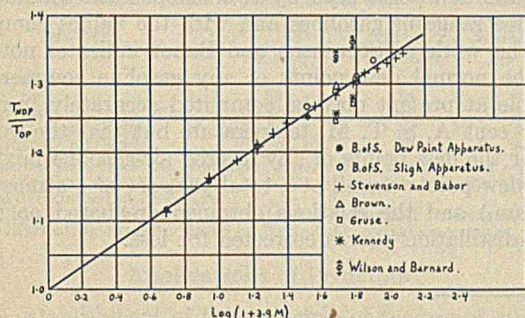


Figure 5—Relation between Temperature Ratio and Air-Fuel Mixture

by Wilson and Barnard that the equilibrium solution temperature was approximately equal to the 85 per cent A. S. T. M. temperature, although later work published by them on 14 gasolines and kerosenes indicated that the latter temperature was consistently higher by an average value of 11° C. The average error introduced by assuming this equivalence is 24° C. for the 15 gasolines used in the present work. The lack of agreement with this 85 per cent rule is in accord with the work of Whatmough, who concluded that, for British fuels, the equilibrium solution temperatures were equal to points on the A. S. T. M. curves considerably lower than the 85 per cent temperatures.

Table VII—Comparison of Ratios between 90% A. S. T. M. and Normal Dew-Point Temperatures Computed from Data by Various Observers

OBSERVER	METHOD	RATIO	SAMPLES
Bureau of Standards	Dew-point apparatus	1.084 ± 0.003	15
Stevenson and collaborators	Dew-point apparatus	1.084 ± 0.007	7
Stevenson and collaborators	Phase-change method	1.080 ± 0.006	6
Stevenson and collaborators	Equilibrium distillation	1.077	1
James	Equilibrium distillation	1.08 ± 0.02	12
Brown	Equilibrium distillation	1.13 ± 0.02	5
Wilson and Barnard	Equilibrium solution	1.05 ± 0.01	14
Whatmough	Equilibrium solution	1.06 ± 0.01	5

On the completion of the normal dew-point measurements, observations were made on the dew points of 5 diverse gasolines using various air-fuel mixtures. These data are shown in Table VIII. Although small consistent deviations from the averages are observable, there does not seem to be any real justification for assuming a relation between the temperature ratios and the normal dew points. An alternative method of stating this is that the dew point of any mixture can be represented as a linear function of the normal dew point, or of the 90 per cent A. S. T. M. point, since these latter are related by a simple ratio.

Table VIII—Ratio of Normal Dew-Point Temperature to Dew-Point Temperatures in ° A. of Various Air-Gasoline Mixtures (Bureau of Standards data with dew-point apparatus)

FUEL	1:1	2:1	4:1	8:1	16:1	N. D. P. ° C.
B	1.110	1.154	1.202	1.247	...	101.2
C	1.115	1.159	1.205	1.247	1.305	138.4
A	1.120	1.180	1.210	1.261	1.300	156.6
J	1.112	1.150	1.203	1.241	1.290	164.8
M	1.109	1.162	1.214	1.253	1.310	186.8
Av.	1.113	1.157	1.207	1.250	1.301	
Av. Δ	0.003	0.004	0.004	0.006	0.006	

A graphical illustration of the linearity of this function is shown in Figure 4 for a 12:1 mixture. The values of

the Bureau of Standards and of Stevenson and Babor are represented, and a straight line is seen to reproduce the points with considerable accuracy. There is some evidence that a slightly curved line would give a little better reproduction but in view of the fact that the equation of the straight line is $T_{NDP}/T = 1.290$ and that the equation for the curve, if used, would be much more complicated, it seems advisable to adopt the simpler relation, particularly since the loss in accuracy is very slight. The dotted curved line is the one proposed by Stevenson and Babor, and although it reproduces the dew points very well over part of the range, it appears to have too large a curvature and if extrapolated would apparently result in very large errors. This plot for a 12:1 mixture is typical of all studied, so that for every mixture there is a specific constant relating the absolute temperature of the dew point of any gasoline to the absolute temperature of the normal dew point or of the 90 per cent A. S. T. M. point. These constants for the various mixtures were found to be a function of the mixture ratio, the relation being given in equation (5).

$$T_{NDP}/T_{DP} = 1 + 0.1707 \log(1 + 3.9M) \quad (5)$$

The average deviation between the temperature ratios calculated from equation (5) and the observed values of the Bureau of Standards by two methods and those computed from the data of Stevenson and Babor is ±0.004, which is equivalent to about ±0.3 per cent. A plot of these temperature ratios against the logarithmic function of mixture ratio is shown in Figure 5 to illustrate the agreement of the observed values with the equation. The Bureau of Standards values obtained with the Sligh apparatus are the ratios shown in Table V divided by 1.084 to transform from the 90 per cent A. S. T. M. temperatures to normal dew points as a reference state. One value computed from the work of Brown is also included and is the average of measurements made on 26 gasolines with a modified Sligh apparatus. Ra-

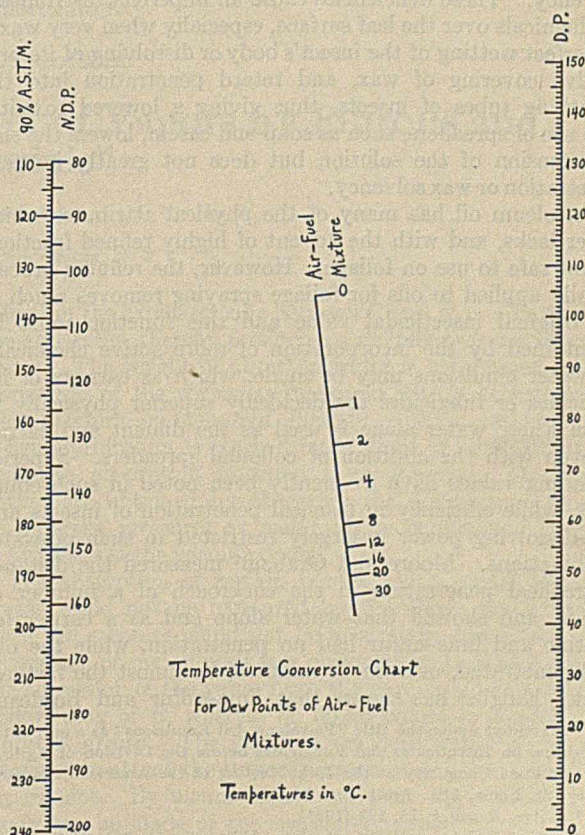


Figure 6

tios calculated from the data of Gruse, of Kennedy, and of Wilson and Barnard show considerable deviation from the line, the average difference in dew-point temperatures between the observed values and those computed from equation (5) being 9°, 7°, and -14° C., respectively.

Chart for Determination of Dew Points

Numerical computation of the dew points by means of equation (5) or its analog in terms of the 90 per cent A. S. T. M. temperature may be obviated by use of the alignment chart shown in Figure 6. The duplex scale on the left represents 90 per cent A. S. T. M. temperatures and the corresponding normal dew points, the former being on the left side of the scale and the latter on the right. From this scale the normal dew point of any gasoline may be accurately estimated if the 90 per cent A. S. T. M. point is known. The middle scale represents mixture ratios while that on the right represents dew-point temperatures. To determine for a given gasoline the dew point of any mixture, connect by means

of a straight edge the 90 per cent A. S. T. M. temperature (or the normal dew-point temperature) with the point on the middle scale representing the mixture ratio of interest and extrapolate the line to the scale on the right. The intersection is the dew-point temperature of the particular mixture for the gasoline in question.

Conclusion

The close agreement with one another of the Bureau of Standards dew-point data by two independent methods on a diverse range of gasolines and with the values computed from the work of Stevenson and Babor indicates not only that the normal dew points of any gasoline commercially available at present may be computed accurately from the 90 per cent A. S. T. M. temperature but that the same is true for the dew points of any desired air-gasoline mixtures. These dew points are all at a total pressure of 1 atmosphere (760 mm.) and the relations obtained are based on A. S. T. M. distillation curves corrected for loss.

Petroleum Oil as a Carrier for Insecticides and as a Plant Stimulant¹

E. R. deOng

FIRST NATIONAL BANK BUILDING, BERKELEY, CALIF.

FOLIAGE applications of chemicals as controls of fungi and insects have been made almost universally with water as the diluent and carrier. Further study of spraying problems showed that water alone was poorly adapted for such functions because of its high surface tension, lack of cohesion between the liquid and solid, and lack of solvency. These deficiencies cause an imperfect distribution of chemicals over the leaf surface, especially when very waxy, imperfect wetting of the insect's body or dissolving of its protective covering of wax, and retard penetration into the breathing tubes of insects, thus giving a lowered toxicity. The use of spreaders, such as soap and casein, lowers the surface tension of the solution but does not greatly increase penetration or wax solvency.

Petroleum oil has many of the physical attributes which water lacks, and with the advent of highly refined fractions is now safe to use on foliage. However, the refining process usually applied to oils for foliage spraying removes much of the original insecticidal value and this function must be maintained by the incorporation of more active chemicals. Oil-water emulsions may be made, which as carriers of insecticides or fungicides are decidedly superior physically to those where water alone is used as the diluent and carrier or even with the addition of colloidal spreaders. Superior spreading values have frequently been noted in such emulsions, while efficiency in tracheal penetration of insects and wax-dissolving power is largely restricted to such oil-water combinations. Moore and Graham² measured the distance of tracheal penetration in the cockroach of a number of liquids, and showed that water alone and as a carrier for nicotine and lime-sulfur had no penetration, while the oils used penetrated, even in 30 minutes, to almost the farthest point. Knight³ has shown that lime-sulfur and Bordeaux

solutions as commonly diluted with water do not penetrate the tracheae of the red scale (*Chysomphalus aurantii*) but when combined with oil emulsions give a fair rate of penetration and "the wax-dissolving power of water, the external phase of stable emulsions, is nil; hence stable emulsions are less toxic to scale-covered insects than quick-breaking emulsions where oil comes in contact with the insect."

Use of Dye Solutions in Oil

A study of the action of oils on leaf surfaces has shown a high degree of penetration, irrespective of viscosity, which affects the rate rather than the degree of penetration. Saturated solutions of Sudan III (a colloidal dye) in oil penetrate leaves readily, while the same dye suspended in water does not penetrate the epidermis or even through the cellular structure of leaves with broken epidermis. The behavior of dye solutions in oil suggested that nicotine and other active insecticides could be added to the oil, carried into the body of the insect, and thus increase the toxicity of the application. For such work the uncombined free nicotine should be used rather than nicotine sulfate such as "Black Leaf 40." The latter form, however, may be readily converted into free nicotine (the alkaloid nicotine as distinguished from nicotine sulfate) by the addition of a small amount of alkali.

Experiments with Nicotine-Oil Mixtures

Coöperative work with the research department of the Tobacco By-Products and Chemical Corporation has shown that nicotine is miscible in certain kerosenes up to 12 per cent. The rate of volatility from light oils is similar to that from water. Nicotine-oil combinations when emulsified yield a certain amount of nicotine to the water until equilibrium is attained. (Table I) But the oil, when penetrating the insect tracheae, carries the remaining nicotine directly into the body of the insect, thus giving an increased toxicity. Experiments with the Brown Apricot scale (*Lecanium corni*) using 2 per cent emulsions of oils alone and with nicotine

¹ Presented under the title "Petroleum-Oil Emulsions" as a part of the Symposium on Insecticides and Fungicides before the Division of Agricultural and Food Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² *J. Agr. Research*, 13, 523 (1921).

³ deOng, Knight, and Chamberlain, *Hillgardia* II, 351 (Calif. Expt. Sta.).

showed an average mortality of 79.5 per cent for kerosene alone and 92.4 per cent for kerosene containing 0.01 per cent of free nicotine. Other experiments with more viscous oils gave similar toxicities until the viscosity reached 100 to 110 seconds Saybolt, when the toxicity began to drop. This shows nicotine to be a more important factor in toxicity than oil and that the oil may be varied within wide limits as desired, or, in other words, the oil acted as a carrier for the active chemical, nicotine.

Table I—Distribution of Nicotine in Oil and Water Mixtures^a

OIL USED	Viscosity at	TOTAL NICOTINE IN:	
	100° F. (38° C.) ^b	Oil layer	Water layer
	Seconds	Per cent	Per cent
Commercial Kerosene	345	56	44
Lubricating oil, very light	50 to 60	48	52
Lubricating oil, light	75 to 80	44	56
Lubricating oil, light	100 to 110	42	58

^a Equal volumes of oil, containing 1 per cent of nicotine, and water were shaken together at room temperature for 5 minutes, and the amount of nicotine determined in each layer.

^b Viscosity of kerosene determined by Saybolt thermoviscosimeter; that of lubricating oils determined by Saybolt Universal viscosimeter.

Applications of Principle

The establishment of this principle of the use of oil for its physical properties, as being equal to or superior to its insecticidal value, makes possible the use of the more volatile and cheaper oil fractions than when dependence is placed alone on the oil for toxicity.

Volatile oils are safer to use on foliage, other factors being uniform, than those which persist in the leaf for long periods of time. The general trend in California field practice is toward the use of light fractions having a viscosity of 70 to 80 seconds rather than 100 seconds or more. Much remains to be worked out in choosing the exact type of oil and the most satisfactory combining chemicals, but the progress made indicates a wide range of usefulness in the combinations of oil and active insecticides, fungicides, and herbicides.

The most common application of the principle of oil as a carrier and also solvent for some other active insecticide

is that of pyrethrum extract, the basis for many commercial fly sprays. Para-dichlorobenzene is another standard insecticide readily soluble in oil which is useful for some purposes. There are also reports of increased efficiency from lime-sulfur sprays when combined with compatible emulsions. Such reports can well be credited when the increased penetration of such a combination is known.

Effect on Plant

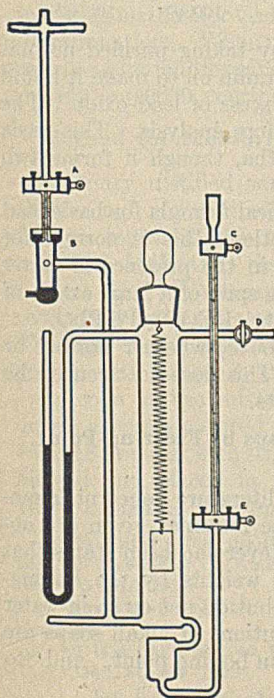
The use of oil on foliage, either alone or in combination, must always be studied with reference to compatibility with the plant. Acute injury is seldom seen with the type of oils now commonly used, but there is still grave danger of interference with normal functions, including the inhibition of starch formation, from the presence of oil in the cell structure, and disturbances of the transpiration rate. Dormant spraying of the tree is now sufficiently understood so that the blooming date may be either retarded or stimulated, as desired, with a fair degree of certainty. Prune trees in central California sprayed the latter part of November nearly always show a retardation of blooming dates amounting to 5 to 7 days. Oils applied in December, during the period of the nearest approach to dormancy, cause but little change in blooming time, but spraying during January gives an early bloom while later applications retard the bloom. It is now a debated question whether it is not possible to secure a continued uniform increase in the set of fruit year after year without too great a drain on the vitality of the trees. Still another beneficial physiological reaction of oil sprays has been noted in southern California—viz., the reduction of injury on lemons and oranges from desiccating winds.

Some of the values now attributed to oil applications may be discredited later, but at least this field should not be overlooked. It is hoped also that the plant physiologist and horticulturist will assist the entomologist and chemist in determining the true value of mineral oil in our diversified problems of horticulture.

McBain-Bakr Balance for Sorption of Vapors by Fibrous and Film Materials^{1,2}

P. T. Newsome

EASTMAN KODAK COMPANY, ROCHESTER, N. Y.



THE McBain-Bakr³ quartz fiber spring balance has been found very useful for measuring the sorption of vapors by fibrous and film materials such as cellulose and cellulose esters. The apparatus shown in the figure is placed inside a carefully controlled air thermostat.

Samples of the material are suspended from the calibrated spring and evacuated through *D* by means of an oil pump to constant weight at a pressure of <0.01 mm. of mercury. When *E* is opened, a small amount of the water con-

tained in the capillary tube between *C* and *E* is admitted to the apparatus, thereby producing a definite pressure of water vapor. The weight of absorbed water is determined by the elongation of the spring as measured with a cathetometer. The pressure is measured directly with a cathetometer. When equilibrium is reached more water is admitted and a complete absorption isotherm thus obtained. Desorption curves are obtained by observing the equilibrium weights at different pressures as water vapor is removed through *D* by means of the vacuum pump.

The absorption of certain liquids which attack stopcock grease could not be measured by the above manipulation, since the pressure could not be accurately controlled. The absorption of such liquids was quite definitely determined by the admission of the vapor from the pure liquid stored in the hollow plug of *B*, wherein no liquid comes in contact with stopcock grease. The vapor of the liquids used showed no tendency to attack the stopcock grease during the course of an experiment. By means of the complete apparatus a rapid study can be made of the successive absorption of two different liquids.

¹ Received March 16, 1928.

² Communication No. 343 from the Kodak Research Laboratories.

³ McBain and Bakr, *J. Am. Chem. Soc.*, 48, 690 (1926).

Chemistry of Lead "Soaps" Made from Litharge and Neutral Fat¹

S. H. Diggs and F. S. Campbell

STANDARD OIL COMPANY (INDIANA), CASPER, WYO.

WHEN fats are "saponified" by lead oxide in the absence of water apparently no glycerol is formed, nor is any appreciable water or aldehyde liberated. Careful work showed that the weight of the fat plus lead oxide was nearly the same as the weight of the resulting "soap." This soap contained no detectable glycerol. Aldehydes, including, of course, acrolein, have very marked odors. The absence of such odors during saponification is in itself good evidence that they are not formed in appreciable quantities, and careful tests proved that only traces of aldehydes are formed.

The "saponifications" were made in a 1-gallon mixer. The fat and litharge were weighed on a torsion balance, accurate to 0.1 gram. The reaction was carried out at 149° C. (300° F.), the time being about 3 hours. After the reaction was complete, the soap was removed from the mixer as completely as possible and weighed on the same balance. The amount of soap left on the stirrer or in the mixer did not exceed 1 gram. Four runs were made weighing all materials in and out of the mixer. In no case did the loss in weight exceed 0.4 per cent of the charge.

When oleic acid is used, the loss is nearly that calculated from the theoretical water formed. For example, an actual experiment showed 2.1 per cent loss as compared with 2.2 per cent calculated loss. This seems to show conclusively that the essential reaction between lead oxide and fatty acids is:



as is usually given.

The quantitative data given above show that the essential reaction between a neutral fat and lead oxide is an addition without elimination of either water or aldehydes. Also it is known qualitatively that glycerol is not formed. Hence, the reaction may tentatively be written



when the amount of lead oxide used is calculated to be that required to make true normal soap. This was approximately what was done in the experiments described above.

Analyses of such "soaps" showed that the reaction given above is not correct, because about one-half of the fat originally used was found unchanged in the "soap." For example, a lead soap made in this way from winter bleached (nearly neutral) fish oil analyzed as follows:

	Per cent
Fatty acid from lead compound	37.84
Unchanged neutral fat	32.94
Glyceryl radical	1.58
PbO from lead compound	27.04
	99.40

Several analyses of different samples of "soap" by different chemists all showed that somewhat less than half of the fat charged to the mixer remained unchanged after the reaction had reached equilibrium. It therefore seemed fair to write as the tentative reaction:



¹ Presented before the Division of Petroleum Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

This, of course, tells us nothing of the way in which the fat and litharge are combined.

When an attempt was made to use 3 mols of lead oxide to 1 mol of fat, the reaction could not be carried out satisfactorily, because the "soap" became too viscous (nearly solid) to continue operating the mixer. It was already known that the "soap" as first made was diluted with unchanged fat, which of course would render it much more liquid. Therefore the proportion was changed to 3 mols lead oxide, 1 mol fat, and enough light paraffin oil (Saybolt viscosity, 95 to 100 at 38° C.; flash, 171–176° C.), to be equivalent to 1 mol of fat. The paraffin oil was unchanged and remained as a diluent just as the unchanged fat did in the first case. The resulting "soap" had all the appearance and superficial qualities of that made from 3 mols lead oxide and 2 mols fat. It analyzed as follows:

	Per cent
Fatty acid from lead compound	41.22
Unchanged neutral fat	1.60
Glyceryl radical	1.72
PbO	32.48
Paraffin oil	22.33
	99.35

Tests showed that after hydrolysis the glyceryl radical was always present, though there was no free glycerol in the "soap."

For comparison samples of normal and basic lead oleate were made from litharge and oleic acid. Both of these soaps are soluble in petroleum ether. On analysis the oleates showed:

	NORMAL LEAD OLEATE		BASIC LEAD OLEATE	
	Found	Theory	Found	Theory
	Per cent	Per cent	Per cent	Per cent
Fatty acid	74.67	74.21	56.00	56.95
Lead oxide	28.88	29.37	44.97	45.07
TOTAL	103.55	103.58	100.97	102.02

The basic lead oleate was made by taking purified normal lead oleate, adding enough light paraffin oil to make it liquid at 300° F. (149° C.) and a large excess of lead oxide. The unused lead oxide was removed before analysis. This basic soap is soluble in petroleum naphtha, though it forms two distinct layers on long standing.

According to Beilstein, the empirical formula for basic lead oleate is $(\text{RCOO})_2\text{Pb} \cdot 2\text{PbO}$; doubtless, this is correct for such soap as usually made—i. e., in the presence of water and alcohol; but our basic oleate, in spite of a large excess of unchanged lead oxide, corresponds to $(\text{RCOO})_2\text{Pb} \cdot \text{PbO}$.

True oleates of lead made as above, whether normal or basic, tend to gel in oil solution. This does not seem to be the case for "soaps" from neutral fats.

Molecular Weights of Lead Soaps by Freezing-Point Method

Nothing can be found in the literature concerning molecular weights of lead soaps. The formulas given are obviously based on analysis only. Meyer-Jacobson states that soda soaps give normal molecular weights by the boiling-point method in alcoholic solution, but do not do so in water solutions. Concentrated water solutions of alkali soaps are said "to give only a minimum rise in boiling point," and "to act like colloids."

We would therefore expect lead soaps to show more or less tendency to associate into double or triple molecules, particularly in benzene solution, which very commonly causes association for solutes which do not associate in water.

Pure lead oleate should have the formula $(C_{17}H_{33}COO)_2 Pb$, and its molecular weight should be 769.8. By the freezing-point method experimental results were as follows:

SOLUTION	MOL. WT.
Benzene	2629
Bromoform	1210
Dichlorobenzene	1559
Naphthalene	1416

In all cases three or more concentrations were used. Agreement of molecular weight for different concentrations in same solvent was very close. The results indicate a triple

molecule in benzene solution, and a double molecule in the other solutions.

Lead soap made from dry litharge and neutral fat after purification had an apparent molecular weight of 1603. It dissolved readily in benzene, showing no indication of colloidal nature, as did the oleates from oleic acid. Assuming the hypothetical formula already given—viz., $(C_{17}H_{33}COO)_3 Pb_3 O_3 H_5$ —the molecular weight should be 1554. This is in very fair agreement with the 1603 actually found by the freezing-point method.

Acknowledgment

The writers wish to acknowledge the assistance of R. Buhman and K. L. Warner, who made most of the analyses given in this report.

Effect of Previous History upon the Viscosity of Gelatin Solutions^{1,2}

Clarke E. Davis and Henry M. Salisbury

NATIONAL BISCUIT COMPANY, 85 NINTH AVE., NEW YORK, N. Y.

IN 1921 Davis, Oakes, and Browne³ measured the viscosity of solutions of various gelatins at 25° C. In 1922 Davis and Oakes⁴ showed that at temperatures above 40° C. the viscosity of gelatin solutions did not change with age and also⁵ determined the viscosity of gelatin solutions at 60° C.

Subsequent research in this laboratory, in collaboration with a research laboratory operating in a large gelatin factory, has developed the following method for viscosity determinations. When using the method of viscosity measurements as herein described, the precision measure is approximately ± 0.0030 centipoise.

Method for Measuring Viscosity of Gelatin Solution

Ordinary distilled water was added to sufficient gelatin to give a 1 per cent solution (dry basis) when made up to 200 cc. together with the amount of acid (0.1 M/HCl) or base (0.1 M/NaOH) that gave a solution of the desired pH value. The pH measurements were made by use of indicators, the hydrogen electrode, and the quinhydrone electrode. The age of the solution was reckoned from the time the gelatin was placed in contact with the water.

As soon as the mixture was made, the flask was placed on an asbestos-covered hot plate and brought to 75° C. in 15 to 18 minutes with stirring. The solution was then rapidly filtered and placed in the thermostat at 40° \pm 0.02° C. When cooled to this temperature, 5 cc. were pipetted into

An accurate method has been developed and tested for determining the viscosity of gelatin solutions. It was found that viscosity measurements were more reproducible at 40° C. than at 25° C. This is considered due to the gelatin staying in the sol form at 40° C. and that at 25° C. there is a gradual transition to the gel form.

Viscosity measurements were made on gelatins of different histories, such as raw material used in its manufacture and the method of extraction. The gelatins of highest jelly strength produced the higher viscosity-pH curves. Viscosity-pH curves are shown to have a maximum viscosity at pH 2.5-2.6.

It is shown that the short duration and low temperature of heating required to put gelatin in solution has no effect on the viscosity values.

a well cleansed and dried Ostwald viscometer previously immersed in the thermostat. After 1 hour and 25 minutes the solution was drawn up through the capillary tube into the bulb and above the top mark. The run was then made, timing the flow from mark to mark with a stop watch.

Calculations

The viscometers were previously calibrated using boiled distilled water at the desired temperature. The

viscosity of the gelatin was calculated in absolute units (centipoises) by the usual formula.

Specific gravity measurements of the gelatin solutions were made by means of a pycnometer.

$$\eta_{\text{Gelatin}} = \eta_{\text{for water}} \frac{\text{seconds gelatin soln.} \times \text{sp. gr. gelatin soln.}}{\text{seconds water} \times \text{sp. gr. water}}$$

$$\eta_{\text{for water at 40° C.}} = 0.6560^6$$

$$\eta_{\text{for water at 25° C.}} = 0.8937$$

$$\text{Specific gravity of water at 40° C.} = 0.99225^7$$

$$\text{Specific gravity of water at 25° C.} = 0.99707$$

To simplify the calculations a constant (K) was calculated for each viscometer.

$$K = \frac{\eta_{\text{for water}} \times \text{sp. gr. gelatin soln.}}{\text{seconds water} \times \text{sp. gr. water}}$$

Then

$$\eta_{\text{(gelatin)}} = K (\text{seconds gelatin soln.})$$

Gelatins Used

In order to determine the effect of previous history, gelatins were selected of which the sources of the raw material and extraction methods were known.

Pigskin and ossein gelatins of various plunge values and

¹ Presented before the Division of Leather and Gelatin Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

² Contribution No. 10 from the Research Laboratory, National Biscuit Company.

³ *J. Am. Chem. Soc.*, **43**, 1526 (1921).

⁴ *Ibid.*, **44**, 464 (1922).

⁵ *J. IND. ENG. CHEM.*, **14**, 706 (1922).

⁶ Bingham, *Bur. Standards, Bull.* **298** (1917).

⁷ *Smithsonian Physical Tables*, 7th ed., p. 118.

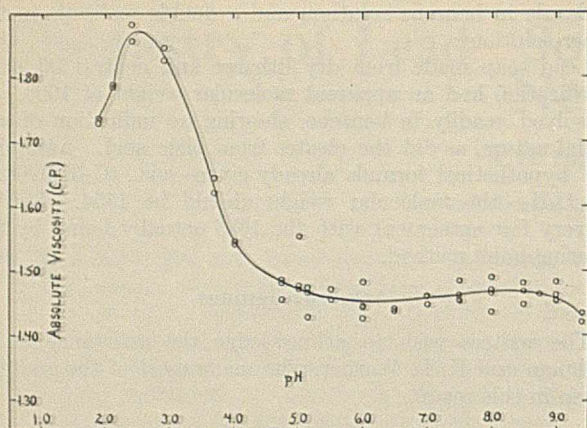


Figure 1—Pigskin Gelatin 16,023
(1% Solution, Dry Basis)
Temperature, 25° C. Moisture, 9.35%
Age, 1 hour, 25 minutes Ash, 1.47%
Plunge, 580 pH, 4.74

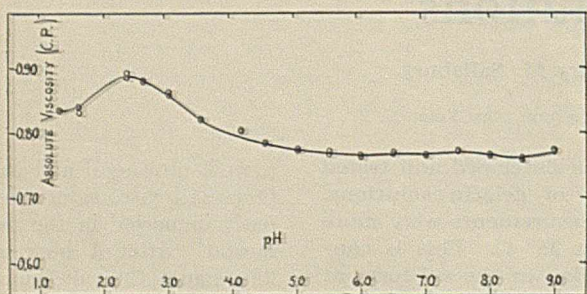


Figure 3—Pigskin Gelatin 511
(1% Solution, Dry Basis)
Temperature, 40° C. Moisture, 10.05%
Age, 1 hour, 25 minutes Ash, 0.87%
Plunge, very slight jelly Acid cook pH, 4.15

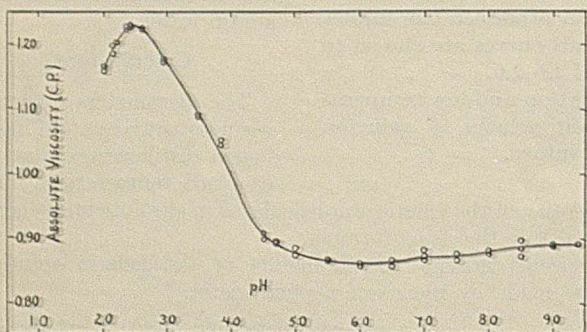


Figure 5—Ossein Gelatin 50
(1% Solution, Dry Basis)
Temperature, 40° C. Moisture, 4.72%
Age, 1 hour, 25 minutes Ash, 0.59%
Plunge, 544 Acid cook pH, 3.82

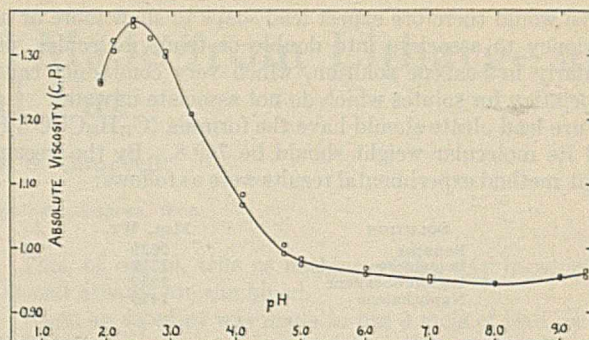


Figure 2—Pigskin Gelatin 16,023
(1% Solution, Dry Basis)
Temperature, 40° C. Moisture, 9.35%
Age, 1 hour, 25 minutes Ash, 1.47%
Plunge, 580 pH, 4.74

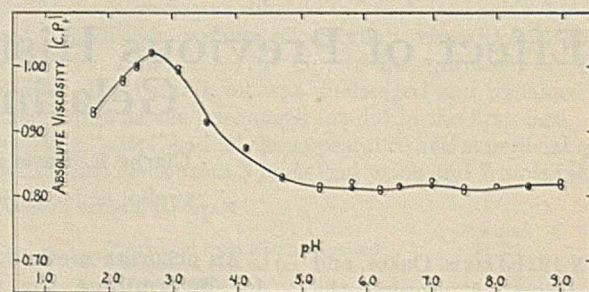


Figure 4—Ossein Gelatin 5649
(1% Solution, Dry Basis)
Temperature, 40° C. Moisture, 6.29%
Age, 1 hour, 25 minutes Ash, 0.48%
Plunge, 80 Acid cook pH, 4.11

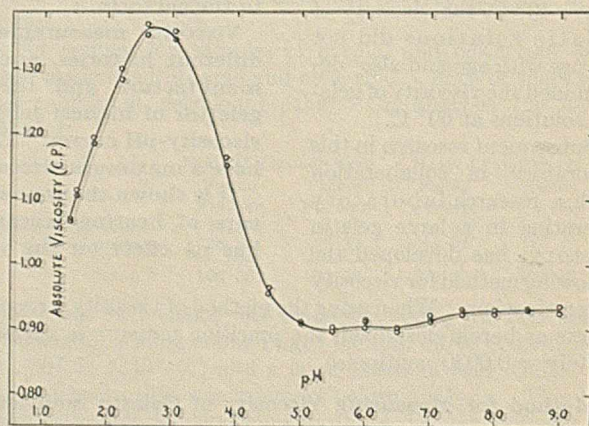


Figure 6—Ossein Gelatin 5648
(1% Solution, Dry Basis)
Temperature, 40° C. Moisture, 6.00%
Age, 1 hour, 25 minutes Ash, 0.52%
Plunge, 815 Acid cook pH, 3.82

different acidities of cooking were used. One gelatin of unknown history is included.

The term "acid cook" when used in reference to a gelatin applies to one cooked at a pH in the vicinity of 4.0 to 4.5. "Alkali cook" refers to a gelatin cooked at a pH approximating 5.2 to 5.5, acid cook being below the isoelectric point of gelatin and alkali cook being above.

All the gelatins were unpurified samples, and the analysis is given with each curve.

The plunge values were determined on the jell-strength testing apparatus as described by Oakes and Davis.⁵

Results

Figure 1 shows a typical viscosity curve at 25° C. and at different pH values. The large variation in values shows

the difficulty of properly evaluating the viscosity at this temperature. This is undoubtedly due to the gradual transition of the sol to the gel form at this temperature since it is certainly below the transition point.

This difficulty led to the adoption as the temperature 40° C. for making viscosity determinations, as this is sufficiently above the transition point to outlaw gelation. The temperature was never allowed to go below 40° C. from the time the solution was made until the completion of the determination.

Figure 2 shows the viscosity-pH curve of the same gelatin as was used in Figure 1, except that the viscosities were run at 40° C. The points were more easily checked and a smooth curve was obtained very similar in general shape to the one at 25° C. but at a lower range of viscosity.

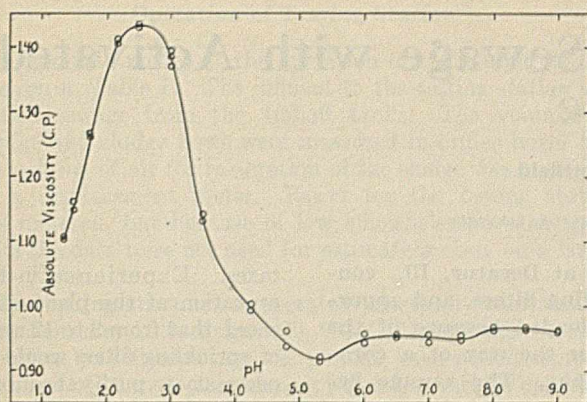


Figure 7—Ossein Gelatin 5650
(1% Solution, Dry Basis)

Temperature, 40° C. Moisture, 9.63%
Age, 1 hour, 25 minutes Ash, 0.63%
Plunge, 865 Alkali cook pH, 5.31

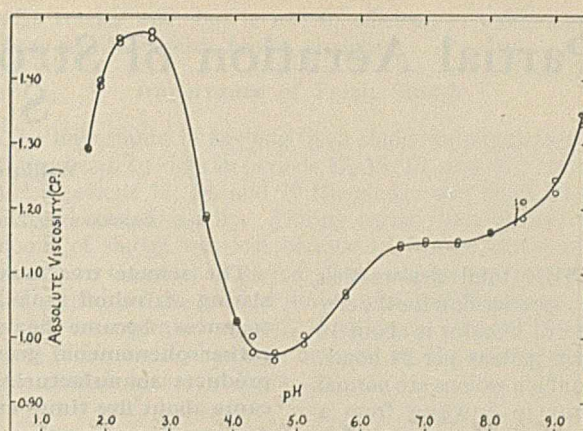


Figure 8—P Silver Label Gelatin
(1% Solution, Dry Basis)

Temperature, 40° C. Moisture, 12.52%
Age, 1 hour, 25 minutes Ash, 1.22%
Plunge, 985 pH, 6.60

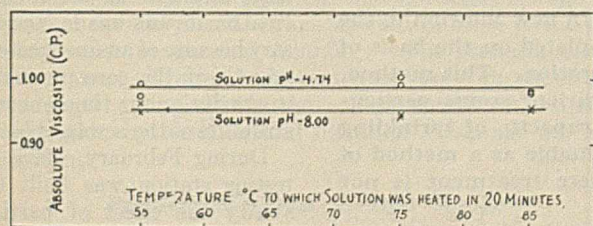


Figure 9—Viscosity—Heating Temperature. Pigskin Gelatin 16,023
(1% Solution, Dry Basis)

Temperature, 40° C. Moisture, 9.35%
Age, 1 hour, 25 minutes Ash, 1.47%
Plunge, 580 pH, 4.74

This gelatin was known to be made from pigskin, but it was not known whether it was cooked at pH 4.74 or adjusted to this value.

The following viscosities were all determined at 40° C. since the foregoing experiments had indicated that reliable results suitable for interpretation could best be obtained at this temperature.

Figure 3 shows the viscosity-pH curve obtained with an acid-cooked pigskin gelatin. This gelatin had a plunge value so low as to be incapable of measurement on the instrument used. It shows a maximum viscosity near pH 2.5-2.6 and tends to flatten out after passing pH 5.5.

Figures 4, 5, and 6 represent three acid-cooked ossein gelatins; Figure 4 is a gelatin of low plunge value, Figure 5 is one of an intermediate plunge value, while Figure 6 shows one of high plunge value. The maximum viscosity in all three cases is from pH 2.5-2.6. The curves show that with a decrease in plunge value there is a corresponding decrease in the viscosity.

Figure 7 is the curve obtained from an ossein stock very similar to the one shown in Figure 6. In this case, however, the gelatin was extracted at an alkali-cook pH value—namely, pH 5.31. This gelatin shows a similar maximum near pH 2.5-2.6, but also shows a tendency towards a minimum around pH 5.5.

Figure 8 shows the viscosities obtained with a high-grade gelatin of unknown history.⁸ It has the maximum at pH 2.5-2.6, corresponding with all of the other gelatins, but has a decided minimum at about pH 4.7. From this point on to pH 9.4 there is a very marked increase in viscosity. At pH 9.4 the viscosity closely approximates the maximum which was noted at pH 2.6. This increase is more striking

in that the other curves show only slight changes beyond the pH value 4.7, their general trend being to flatten out after passing through the isoelectric point, pH 4.7.

For some reason the acid side of all the curves (below pH 4.7) is quite definite in the tendency toward a maximum viscosity around pH 2.5. This tendency is independent of the stock used and the method of preparation. The alkali side of the curves (above pH 4.7) is certainly a function of the salt content and the history of the gelatin such as the stock and the method of preparation.

The alkali-cooked gelatin (Figure 7) definitely shows a minimum viscosity at about pH 5.5. From then on to pH 9.0 the curve is comparatively flat, very similar to those of the acid-cooked gelatins. The gelatin of unknown history (Figure 8) shows that there still may be tendencies above pH 4.7 other than those shown in the cases of the acid-cooked and alkali-cooked gelatins. This would lead one to expect many different shapes of curves above pH 4.7 according to the different histories involved. In other words, it would be expected that the acid portion of the curves would have similar shapes with the maximum viscosity at about pH 2.5 and that above pH 4.7 the history of the gelatin would be recorded.

Effect of Heating Gelatin Solutions

Manning⁹ has criticized the method used by Davis and Oakes⁴ for determining viscosity, which was very similar to that used in this paper. Manning stated: "It is well known that in determining the viscosity of a gelatin solution the pre-treatment of the solution is of first importance. Subjection to a high temperature even for a short time produces an irreversible decrease in viscosity."

Figure 9 shows the inappreciable variation in viscosity produced by heating a pigskin gelatin to various temperatures when making the solutions. The effect has been investigated at the pH values 4.74 and 8.00. This was the same gelatin that was used in producing the curves in Figures 1 and 2.

If Manning's criticism were warranted, one would expect variations in these measurements. When it is considered that in the process of manufacture the gelatin solution has been subjected to high temperatures for many hours, a subsequent exposure of the gelatin solution to heat for the short space of 18 minutes during which time 75° C. is reached only momentarily could not be expected to degrade the gelatin more than the excessive heating above these temperatures for many hours.

⁸ Gelatin furnished by Z. C. Loebel from stock used by him in a study published in *J. Phys. Chem.*, **32**, 763 (1928).

⁹ *Biochem. J.*, **18**, 1085 (1924).

Partial Aeration of Strong Sewage with Activated Sludge¹

William D. Hatfield

SANITARY DISTRICT OF DECATUR, ILLINOIS

THE total dry-weather sewage flow for the city of Decatur is about 10 million gallons per 24 hours. Six million gallons are normal domestic sewage from a sewered population of 40,000 people and the normal industrial wastes from a city of 50,000. The population equivalent of this so-called domestic sewage is about 50,000. The remaining 4 million gallons of the total sewage is industrial waste from a large corn-products factory. The waste contains large quantities of soluble and colloidal matter from the corn, 25 to 50 p. p. m. of sulfur dioxide, and has a summer temperature of about 100° F. The population equivalent of this waste calculated from the 5-day biochemical oxygen demand has averaged between 250,000 to 350,000.

The existing sewage-treatment plant consists of grit chambers and Imhoff tanks of sufficient capacity to treat the total sewage received, and three acres of sprinkling filters. The ultimate plan provided for doubling the Imhoff tank capacity and for 12 acres of sprinkling filters. It was anticipated that 3 more acres of sprinkling filters would be built the second year of operation when sufficient funds were available from

¹ Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

The sewage treatment plant at Decatur, Ill., consisting of Imhoff tanks, sprinkling filters, and appurtenances, became heavily overloaded because of the rather phenomenal growth after the war of a corn-products manufacturing company. The sewage became about five times as strong as normal city sewage. An experiment station to study partial aeration as a method of increasing the capacity of the existing plant and to reduce the odor hazard was operated for 15 months. Complete operating and chemical data are given which indicate that the process could be used to triple the capacity of the filters. A new addition to the sewage plant has now been completed on the basis of the data presented and is in operation. This method, which has been termed pre-aeration, seems particularly adopted to increasing the capacity of sprinkling filters, but should also prove valuable as a method of partial treatment where complete treatment is not advisable until later.

taxes. Experience in the operation of the plant indicated that from 9 to 12 acres of sprinkling filters would be necessary to purify the mixed sewage, but such an increase of filter area was hazardous because of the strong odor of hydrogen sulfide coming from the existing 3 acres. This large addition of secondary treatment was made necessary because of an unexpected growth of the corn-products works during the time of construction of the sewage plant.

During February, 1925, a testing station was built to study the effect of partial aeration with activated sludge

on the sprinkling filter rates. This particular application of a short period of activated-sludge treatment originated in Birmingham, England,² and was reported to have increased the capacity of the sprinkling filters from 2.5 to 3.0 times and to have greatly decreased odors from the plant. The testing station consisted of a Simplex aerator, settling tanks, and a 14-foot diameter sprinkling filter of 6-foot depth of stone. With a sewage flow of 78,000 gallons per day the aeration period was 2 hours and the sedimentation period 1.5 hours. The sprinkling filter was operated by an automatic siphon at rates from 0 to 4.5 million gallons per acre per 24 hours.

² Whitehead, *Surveyor*, 68, 449 (1925).

Table I—Operating Data

No.	TIME	SLUDGE		SIM- PLEX RE- AER- ATION	SLUDGE RE- AER- ATION	SET- TLING TANK DETN.	FILTER RATE PER DAY	B. O. D., 5 DAYS 20° C.				B. O. D. REMOVAL BY:			
		Return	Waste					Crude sewage	EFFLUENT			Imhoff tanks	Aera- tion	Filter	Total
									Im- hoff	Aera- tion	Sprink- filter				
		%	%	Hours	Hours	Hours	Mil. gal.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	%	%	%	%
1	Feb.	6.0	0	5.2	3.2	1.0	1.24	(397)	318	190	52 ^a	20	40		
2	Mar.	25.0	12	4.3	2.8	1.1	2.51	(305)	244	104	24	20	57		
3	Apr.	22.2	0	7.2	5.8	1.6	3.00	(303)	243	152	28	20	38		92
4	Apr.	16.3	1	3.5	3.1	0.8	3.05	(352)	282	148	28	20	48		
5	May	36.0	15.8	3.1	1.7	...	3.05	(450)	360	130	28	20	64		
6	May	21.0	13.7	3.4	...	2.1	3.00	457	371	128	37	19	65	71	92
7	June	34.0	25.0	4.1	...	Var.	3.10	487	408	185	48	16	55	74	90
8	June	25.0	20.8	4.5	...	3.0	3.10	488	366	128	58	15	65	55	88
9	July	34.0	5.2	6.0	...	3.7	3.20	374	256	103	25	31	60	76	93
10	Aug.	10.0	14.8	7.0	...	4.1	3.30	495	340	122	37	31	64	70	93
11	Sept.	25.0	(?)	3.3	...	1.8	3.5 ^a	452	328	146	31	28	56	79	93
12	Sept.	13.7	0.3	3.3	...	1.6	3.78	543	405	195	44	26	52	77	92
13	Oct.	13.7	1.9	3.3	3.4	1.6	3.5 ^b	761	551	237	38	28	58	84	95
14	Oct.	13.7(?)	0.9	3.3	...	1.6	3.36	745	560	269	52	25	52	81	93
15	Nov.	10.0	1.1	2.5	...	1.1	3.36	787	640	387	67	19	39	83	91
16	Dec.	10.0	0.9	2.5	...	1.1	1.75	790	608	317	69	23	48	78	91
17	Dec.	10.0	1.0	2.5	...	1.1	2.52	785	633	430	72	19	32	83	91
18	Jan.	11.0	0.9	3.4	...	1.6	2.52	760	645	425	103	26	34	76	86
19	Jan.	13.5	(?)	3.4	...	1.6	2.37	770	607	340	58	21	44	83	92
20	Feb.	11.0	1.9	3.4	...	1.6	3.00	783	606	284	54	23	53	81	93
21	Feb.	13.0	2.4	6.7	...	3.3	3.00	640	570	118	41	11	79	65	94
							3.33								
							4.32								
							5.00								
22	Mar.	13.0	2.5	9.3	...	4.5	4.28	640	535	110	39	16	83	64	94
							2.2								
23	Apr.	16.0	4.8	11.2	...	3.1	3.30	536	491	46	16	11	91	65	97

^a The B. O. D. data in parentheses are calculated by factors from Oxygen Consumed and Nitrogen.

Operation of Testing Station

A complete record of the operation of the testing station is given in Table I. The influent to the testing station was settled sewage from the Imhoff tanks. The volumes of sewage and sludge flows were measured in orifice boxes and the volume of air for re-aeration of the sludge was measured by a displacement meter. Power for the testing station was metered, but because of low efficiencies on such small units the data were not used for estimating costs on a large-scale plant.

The testing station was operated practically continuously from February 23 to August 20, 1925. During this time the operation was divided into ten periods, each period comprising a run of 12 to 25 days during which the various operating conditions were kept constant. During the first nine periods the sewage was diluted with about 6 million gallons per 24 hours of refinery condenser water. Operation was resumed on September 11 and continued without appreciable interruption until April 7, 1926. During this time there were thirteen additional operating periods and the crude sewage was typical of normal mixed sewage without dilution of the condenser water or unusual rainfall. The strength of the sewage increased owing to increased grind of corn, the strongest sewage coming during the coldest weather when rates of oxidation by aeration and filtration of sewage are at a minimum.

Problem of Under-Aerated Sludge

The major problem in the operation of the testing station was the handling of the under-aerated sludge obtained by this method of partial aeration. The sludge is not typical of true activated sludge. Its color may vary from a light gray through light brown to black septic sludge. The gray sludge is very fresh and flocculent, and settles well. This sludge is usually obtained on starting the process. If the aeration period is long enough this will turn into typical brown activated sludge, but with a somewhat shorter aeration it becomes a light brown, is very fluffy, and will not settle in settling tanks satisfactorily. At times this bulking of the sludge was so bad that it would not settle appreciably in 2 hours in glass cylinders. With short periods of aeration the sludge was black and sometimes septic. This black

sludge settles well, but is not so efficient in purifying the sewage as the lighter brown sludges.

Importance of Fresh Sludge

The importance of keeping fresh sludge in circulation was clearly shown by data in periods 17, 18, 19, and 20 (Table I). During periods 17, 18, and 19 the sludge was black, flocculent, and settled rapidly. During period 19 a considerable amount of sludge was lost because of frozen sludge pipes. Just before the start of period 20 the sludge line broke and all sludge was lost, so that during this period the aeration tanks were operated entirely with fresh sludge. The removal of biochemical oxygen demand by the process during these periods was as follows:

PERIOD	NOTES	B. O. D. REMOVAL (5-Day) Per cent
17	Black septic sludge	32
18	Black septic sludge	34
19	Loss of much black sludge	44
20	Entirely fresh sludge	53

Experience showed that the sludge must be kept in a fairly fresh condition by regular and frequent wasting of excess sludge, and that not more than 10 per cent by volume of the sludge after settling one hour should be kept in the aeration liquor.

Effect of Time of Aeration

The number of hours of aeration has a very definite relation to the amount of purification as measured by the removal of 5-day biochemical oxygen demand. Figure 1 shows the percentage reduction of B. O. D. for different periods of aeration. The points are averages from Table I, omitting those runs that were not typical of normal operation. Within the limits of these experiments the percentage removal of B. O. D. was not influenced by variations in the strength of crude sewage. The results at Birmingham, England, indicated that with a sewage requiring 6 hours' aeration for complete treatment 60 per cent of the purification was obtained in the first hour. At Decatur, although the longest aeration period was 11.2 hours, the trend of the operating data indicated that 16 hours might be required for complete treatment of the Imhoff tank effluent by aera-

at Testing Station

STABILITY	NITRATE-NITRITE-NITROGEN	TOTAL NITROGEN BY KJELDAHL					OXYGEN CONSUMED KMnO ₄ , 30 MIN.				SUSPENDED MATTER GOOCH				SETTLABLE MATTER IMHOFF CONE				
		Crude sewage	EFFLUENT			Crude sewage	EFFLUENT			Crude sewage	EFFLUENT			Crude sewage	EFFLUENT				
			Im-hoff	Aera-tion	Sprink-filter		Im-hoff	Aera-tion	Sprink-filter		Im-hoff	Aera-tion	Sprink-filter		Im-hoff	Aera-tion	Sprink-filter		
%	%	%	%	%	%														
69	1.6	47	37	34	..	207	153	95	53	216	92	79	55	2.2	0.4	0.3	0.8		
90+	8.1	32	28	26	..	151	133	52	35	270	100	123	142	2.7	0.6	13.6	6.3		
90+	6.7	28	28	29	..	150	111	76	44	215	77	197	130	3.6	0.4	16.9	2.7		
90+	8.7	26	25	23	..	174	114	74	44	248	76	164	105	4.0	0.7	39.0	12.0		
90+	6.8	32	28	21	..	210	138	65	43	269	75	131	93	4.2	0.7	93.0	37.0		
70	5.0	32	28	26	9	210	108	85	38	251	78	48	82	4.0	0.6	7.7	2.8		
80+	7.2	34	22	22	10	205	219	81	44	266	68	83	114	4.7	0.7	16.7	5.5		
80+	5.8	42	38	28	15	191	102	83	56	244	73	107	99	4.0	0.5	39.0	14.5		
90+	6.3	30	25	17	6	140	69	44	25	197	61	36	52	3.3	0.6	90.0	7.6		
88	9.0	32	154	87	63	35	280	89	3.7	0.9	58.0	17.3		
53+	5.9	45	..	38	22	199	125	67	39	322	61	50	28	5.8	0.8	0.3	0.5		
85+	11.0	55	58	42	..	231	133	80	39	293	79	45	56	4.7	1.2	0.3	2.5		
79+	7.6	60	60	43	..	375	196	96	36	354	95	88	36	4.6	0.9	0.2	1.2		
90	8.9	69	63	49	..	439	249	116	57	367	127	99	86	4.8	..	0.1	3.3		
54	6.6	79	76	62	..	396	254	125	54	356	124	77	59	5.0	1.8		
89	14.0	72	69	59	..	382	257	106	62	294	118	73	101	4.1	0.9	0.2	6.3		
33	3.3	82	77	62	..	398	264	112	63	315	115	57	70	4.4	0.6	0.2	2.1		
11	3.3	68	67	59	..	415	270	120	74	306	124	61	67	4.3	0.6	0.1	2.2		
87	12.0	69	65	52	..	393	251	112	60	377	154	42	94	5.3	0.6	0.1	3.7		
77	10.6	51	48	41	..	403	265	103	58	350	140	46	78	4.0	0.7	0.1	3.1		
99	17.8	50	48	35	..	354	254	79	45	282	122	64	47	3.7	0.8	0.1	1.6		
25.0																			
17.0																			
13.0																			
99	19.6	33	50	37	..	319	260	73	52	310	141	84	40	4.5	0.9	10.4	1.6		
99	18.0	43	51	16	..	328	263	71	40	289	147	49	23	2.9	1.0	2.7	0.4		

^b Filter rates were variable, average rate given.

tion. Fifty per cent of the B. O. D. in the settled sewage was removed by 3 hours of aeration. Although the Decatur sewage requires much more aeration than the Birmingham sewage, the purification curve in Figure 1 very closely resembles that given for the Birmingham sewage.

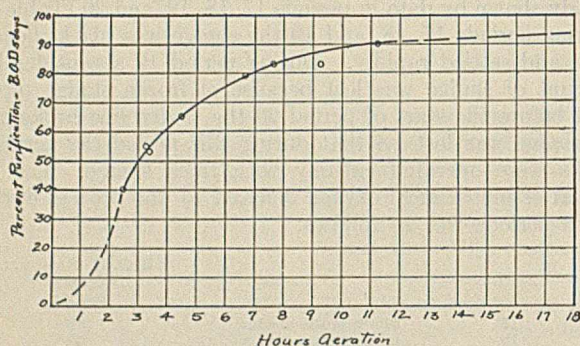


Figure 1—Aeration Efficiency

1-hour aeration required 4.12 horsepower per million gallons per day

The results of re-aeration of the returned sludge from 1 to 6 hours indicated no improvement in the quality of the sludge. Therefore, re-aeration was discontinued. The practice in Birmingham is to re-aerate the sludge for 16 hours, while American practice tends toward more liberal aeration periods in the aeration tanks rather than re-aeration. The new aeration plant at Decatur has been so designed that a long period of re-aeration may later be added if found advisable.

Effect on Sprinkling-Filter Loadings

Partial aeration of sewage in the presence of the pseudo-activated sludge formed not only removes a considerable amount of the biochemical oxygen demand, but also breaks down the remaining soluble and colloidal organic matter, so that it may be applied to sprinkling filters at a much greater rate than can the settled Imhoff effluent. Since it is the function of a sprinkling filter to oxidize the organic matter and nitrogen in the settled sewage, it is logical to use as a loading factor the quantity of B. O. D. in pounds per 24 hours which an acre of filter will satisfactorily handle. The results of the operation of the testing station filter are given in Table II, with the loading in pounds per 24 hours of 5-day B. O. D. With the exception of the data for periods 17, 18, and 19, when experiments with the black sludge were in progress, these data show that an acre of 6-foot filter can handle about 7500 pounds of 5-day B. O. D. per 24 hours.

Data on the large sprinkling filters treating the settled Decatur sewage during the same period are given in Table III, which show that without pre-aeration the filters were only able to handle 4500 pounds of 5-day B. O. D. per acre

per 24 hours. These figures show that partial aeration almost doubles the quantity of organic matter that can be applied to the filters satisfactorily, and since aerating greatly reduces the organic matter in the sprinkling filter influent, the sprinkling filter rate in million gallons per acre per 24 hours may be tripled or quadrupled according to the amount of aeration given the settled sewage.

This fact makes this treatment very promising as a method for increasing the capacity of existing sprinkling filter plants that are overloaded, or the combination of aeration and filters to reduce the power cost of complete treatment by aeration alone, or as a method where an intermediate degree of treatment between Imhoff tank and sprinkling filter effluent is all that is required.

Pre-aeration Plant at Decatur

Figure 2 shows the amount of treatment by aeration that is necessary to prepare Decatur sewage of various strengths for complete treatment on the existing 3 acres of sprinkling filters. This figure was prepared to predict the amount

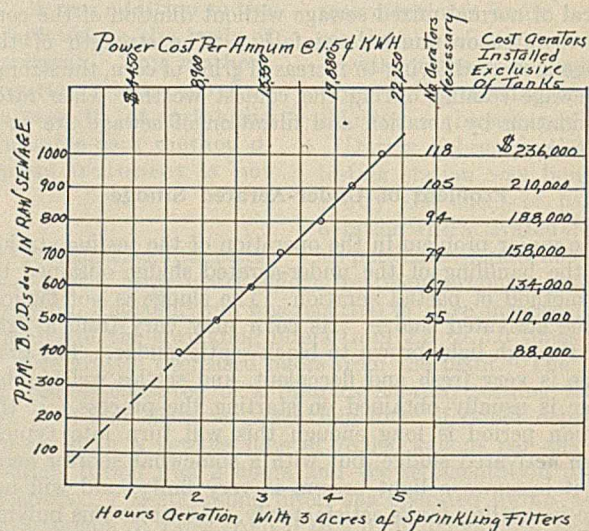


Figure 2—Data for Complete Aeration Treatment of Decatur Sewage

Data calculated on basis of 10 million gallons sewage per day, 1 m. g. d. sludge return, 20 per cent removal of B. O. D. by Imhoff tanks, and 22,500 lbs. B. O. D. per day handled by 3 acres of sprinkling filters

of aeration necessary when certain recoveries of the starch waste were made by the corn-products company. Since the testing station experiments were made, excellent recoveries have been made by the company and the new "pre-aeration plant" is designed for a 2.5-hour aeration at an expected sewage concentration of 300 p. p. m. of 5-day B. O. D. According to Figure 2 an aeration period of 1.2 hours should be sufficient for a sewage of 300 p. p. m. B. O. D. Thus the

Table II—Experimental Sprinkling-Filter Loadings

PERIOD	B. O. D. CRUDE SEWAGE	AERATION	B. O. D. FILTER INFLUENT	FILTER RATE PER DAY	B. O. D. PER ACRE PER DAY	SPRINKLING FILTER EFFLUENT DATA ^a			AV. TEMP. CRUDE SEWAGE
						B. O. D.	Nitrate	Stability	
	P. p. m.	Hours	P. p. m.	Mil. gal.	Lbs.	P. p. m.	P. p. m.	%	° F.
11	452	3.3	146	3.5	4250	31	5.9	53	95
12	543	3.3	195	3.78	6150	44	11.0	85	95
13	761	3.3	237	3.5	6900	38	7.6	79	90
14	745	3.3	269	3.36	7550	52	8.9	90	88
15	787	2.5	387	3.36	10800	67	6.6	54	82
16	790	2.5	317	1.75	4620	69	14.0	89	82
17	785	2.5	430	2.52	9030	72	3.3	33	82
18	760	3.4	425	2.52	8920	103	3.3	11	76
19	770	3.4	340	2.37	6720	58	12.0	87	76
20	783	3.4	284	3.00	7100	54	10.6	77	74
21	640	6.7	118	3 to 5	2950 to 4910	41	18 to 13	99	74
22	640	9.3	110	4.28	3920	39	19.6	99	72
23	536	11.2	46	3.3	1260	16	18.0	99	..

^a The testing station had no secondary settling tank. With secondary sedimentation the B. O. D. of the sprinkling filter in most cases could have been reduced 50 per cent.

new plant will have an additional hour of aeration to take care of an increased growth of the city or of the corn-products industry.

The number of Simplex aerators necessary for different aeration periods of the Decatur sewage is shown in Figure 2. It was found that a plant could be built much more economically with forced aeration through porous plates than with Simplex aerators. The power consumption of the Simplex aerator is somewhat lower than that for the forced aeration, but under the conditions at Decatur this did not justify the larger initial cost of construction. The experiments show, however, that the Simplex aeration unit is efficient as a method of aeration.

The new pre-aeration plant of Decatur is now in operation. It comprises six aeration tanks of the Manchester type, two 76-foot Dorr clarifiers, sludge pump house, blower house, and appurtenances. The capacity is for a dry-weather flow of 10 million gallons per 24 hours. The aeration period is 2.5 hours and the sludge-settling period 2.6 hours. The old plant had a population equivalent of 60,000. The pre-aeration plant increases the capacity to 150,000 population. The construction cost of the new plant was under \$250,000 and the yearly power cost is estimated at \$15,000 to \$18,000. The new plant has not been in operation long enough to make any prediction regarding power costs except that it will run well within the estimate. The excess sludge from the

pre-aeration plant is being returned to the influent of the Imhoff tanks and is digested with the fresh sludge in the digestion compartment.

An interesting feature of the new plant is that the air is heated before compression by a gas-fired boiler which also heats the buildings. The boiler is operated on gas obtained from the digestion compartments of the Imhoff tanks.³ Heating the influent air lowers the power consumption in very cold weather.

Table III—Sprinkling-Filter Loadings on Main Plant

PERIOD	RATE OF APPLI-CATION	B. O. D. OF INFLUENT SPRINK. FILTER	B. O. D. LOAD-ING	QUALITY OF EFFLUENT			Remarks
				B. O. D.	Ni-trate	Sta-bility	
	Mil. gal./day	P. p. m.	Lb./acre/24 hrs.	P. p. m.	P. p. m.	%	
11	1.35	328	3690	16	11	99	Good
12	1.35	405	4550	29	12	95	Good
13	1.2	551	5500	78	2	33	Poor
14	0.9	560	4200	102	5	17	Bad
15	0.6a	640	3200	61	15	96	Poor or bad (?)
16	0.7	608	3540	78	16	74	Poor (?)
17	0.88	633	4630	70	22	95	Poor (?)
18	1.17	645	6280	83	23	80	Poor (?)

^a The large filter was rested during the first 9 days of period 15 to give it a chance to recover and because the river elevation was such that the under-drains were submerged with about 1 foot of effluent. This rest period was followed by effluents high in B. O. D., but with high enough nitrates to produce a high stability toward methylene blue. The general appearance of these latter effluents was not good.

³ Hatfield, *Pub. Works*, 58, 204 (1926).

Comparative Tests with Certain Fumigants¹

L. F. Hoyt

LARKIN CO., INC., BUFFALO, N. Y.

A comparison has been made of the efficiency of seven fumigants—calcyanide, chloropicrin, ethylene dichloride-carbon tetrachloride mixture, ethylene oxide, Lethane 23, Lethane 22, and trichloroethylene—against three species of insects and a few varieties of food products and seeds, upon exposure for 24 hours in a tight room at 75–80° F.

SEVERAL fumigants have been compared under conditions as nearly uniform as possible of temperature and contact period in a "gas-tight" room. The effect of these fumigants on three species of insects, on food products, on the germinating power of certain seeds, and on metals has been noted. The fumigants compared were calcyanide, chloropicrin, ethylene dichloride-carbon tetrachloride mixture (3:1), Lethane 22, Lethane 23, trichloroethylene, ethylene oxide, and vinyl chloride.

The fumigation tests were all carried out in a gas-tight Plymetl vault designed for the fumigation of furniture. The interior dimensions of this vault are length 10 feet, width 8 feet, and height 6 feet. The vault is equipped with an electrically heated hot-water radiator. The fumigant used, if a liquid, is ordinarily poured through a 6-inch orifice in the top of the vault into a long, shallow trough suspended inside the vault just below the top of the vault, the orifice being subsequently closed with a threaded plug. The wide metal doors of the vault close tightly against compressible rubber strips around these doors, which retain the fumigant well. This vault may be considered gas-tight for all practical purposes, since leakage of the fumigant can scarcely be detected even when a substance of the intense lachrymatory power of chloropicrin is being used.

In the case of some of the fumigants whose dosage was unknown or uncertain, preliminary trials were made with carefully measured quantities of the fumigant in tin cans of 0.32 cubic foot capacity. Live insects (*Tribolium confusum*, confused flour beetle) were placed in cloth bags, suspended in these cans, and a predetermined quantity of fumigant added. The cans were quickly closed and kept at about 80° F. for 24 hours, when they were opened and the insects examined. On the basis of these small-scale tests the probable effective dose for the 480-cubic foot vault was computed and tried.

It is obvious that dosage for a given insect is a function of both the duration of the exposure and the temperature, and of course the dosage required to kill different insects under the same conditions varies. In miscellaneous fumigations, where temperature and the available time often cannot be controlled by the operator, the dosages of the same fumigant under different conditions will necessarily vary over a considerable range, as has been clearly pointed out by Safro.² It should, however, be noted that the comparative tests herein reported are all based on a contact period of 24 hours at a temperature of 75–80° F., a combination of conditions which is both easy and practical to obtain for routine fumigations of either furniture or small lots of infested material in the Plymetl vault. These conditions of time and tem-

¹ Presented as a part of the Symposium on Insecticides and Fungicides before the Division of Agricultural and Food Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² *J. Econ. Entomol.*, 20, 261 (1927).

Table I—Properties of Fumigants Used

FUMIGANT	FORMULA	MOLECULAR WEIGHT	BOILING POINT ° C.	SPECIFIC GRAVITY	DOSAGE Lbs./1000 cu. ft.	DOSAGE FOR PLYMETL VAULT Cc.
Calcyanide	CaH ₂ (CN) ₄ ^a	146	(Dry powder)	0.5	4 oz.
Chloropicrin	C ₂ Cl ₂ NO ₂	164	112	1.65	0.8	6.4 oz.
Ethylene dichloride	(CH ₂ Cl) ₂ (3 vols.)	99	84	1.32 (mixture)	14.0	7 lbs.
Carbon tetrachloride	CCl ₄ (1 vol.)	154	77			
Ethylene oxide	CH ₂ CH ₂ —O	44	13.5	0.88/10° C.	2.0	1 lb.
Lethane 23	138-142	1.16	1.5	12 oz.
Lethane 22	126-127	1.24	0.5	4 oz.
Trichloroethylene	C ₂ HCl ₃	131	88	1.47	7.0	3.5 lbs.
Vinyl chloride	CH ₂ :CHCl		-14		8.0 ^b	...

^a Metzger, IND. ENG. CHEM., 18, 161 (1926).

^b Dosage used for laboratory small-scale test; not used in 500-cubic foot vault because of unsatisfactory result obtained on small scale.

perature can often be duplicated in large-scale fumigations of warehouses, flour mills, and grain elevators.

Table I shows dosages and some of the properties of the fumigants tested.

Fumigants Used and Method of Application

CALCYANIDE—A brown powder, resembling cocoa in appearance; generates hydrogen cyanide very quickly by reaction with atmospheric moisture; not objectionable for a skilled operator to handle, but dangerous to human life in the hands of an ignorant or careless operator.

Application. Spread in thin layer on papers on floor of vault.

CHLOROPICRIN—A heavy, colorless liquid; the pure liquid is disagreeable to handle on account of the severe lachrymatory effect of its vapors; reasonably safe and gives ample warning of its presence, now available from the Isco Chemical Company under the name of Larvacide in convenient form in cylinders of various sizes.

Application. Poured into small metal pan suspended just above hot-water radiator.

ETHYLENE DICHLORIDE-CARBON TETRACHLORIDE MIXTURE (3:1)—A water-white liquid of pleasant odor, non-inflammable, safe, and easily handled by an unskilled operator.

Application. Poured into trough at top of vault.

ETHYLENE OXIDE—A gas at ordinary temperature, having a rather faint odor suggestive of ether; supplied in a cylinder under pressure by the Carbide and Carbon Chemicals Corporation.

Application. Cylinder placed in vertical position on a scale. Gas allowed to flow through flexible hose into vault through 3/4-inch thermometer opening.

LETHANE 23—A water-white liquid, whose odor is at first pleasant and ethereal, but which on continued respiration is irritating to the nose and throat; as used for fumigation purposes it can be considered non-inflammable.

Application. Poured into small metal pan suspended just above hot-water radiator.

LETHANE 22—A water-white liquid whose vapors are similar to but more irritating than those of Lethane 23; both Lethane 23 and 22 were supplied by Rohm and Haas.

Application. Poured into small metal pan suspended just above hot-water radiator.

TRICHLOROETHYLENE—A heavy, water-white, non-inflammable liquid with a sweet odor resembling that of chloroform, supplied by Roessler and Hasslacher.

Application. Poured into trough at top of vault.

VINYL CHLORIDE—A gas at ordinary temperature having a characteristic garlic-like odor.

Insects Used

(1) Adults and larvae of the confused flour beetle, *Tribolium confusum*, in wheat flour; infested flour confined in small cloth sack, buried in 5-pound bag of pastry flour.

(2) Larvae of the Indian meal moth, *Plodia interpunctella*, confined in rolled oats in sealed cartons.

(3) Larvae of the clothes moth, *Tineola biselliella*. Most of the larvae were at the adult stage and were confined, on raw wool, in pasteboard pill boxes.

Articles Fumigated

(1) Food products, exposed in open containers: dried prunes, shelled almonds, walnut meats, powdered cocoa (25 per cent cocoa fat), unsweetened chocolate (50 per cent cocoa fat), unwrapped bacon, pastry flour in 5-pound open bag, and rolled oats in sealed cartons.

(2) Seeds exposed in open cartons: oats, wheat, white beans, raw shelled peanuts, and clover.

(3) Polished metals, exposed to determine whether or not corrosion or tarnishing would occur during 24-hour fumigation at 75-80° F.: aluminum, brass, chromium (plated on steel), copper, nickel (plated on steel), silver, steel cutlery, steel piano wire, tin, and zinc.

Procedure of Tests

The products to be subjected to fumigation—insects, foods, seeds, and metals—were placed on the floor of the vault, which was heated to 75-80° F. before the fumigant was released. The vault was then locked and kept at 75-80° F. for 24 hours, ventilated by means of its suction fan system for 20 to 30 minutes, and the products then removed. The insects and metals were examined without delay. The food products were tasted, most of them within half an hour after removal from the vault, and if a taste of the fumigant was detected they were exposed to the air and tasted again at intervals. Prunes, nut meats, cocoa, and unsweetened chocolate were tasted without cooking; the bacon was fried and tasted. Seeds after fumigation were exposed to the air for at least a week before germination tests were started and can therefore be considered to have been thoroughly aerated.

Effect on Insects

The following dosages of fumigants (calculated to a basis of 1000 cubic feet) used at 75-80° F. for 24 hours in the Plymetl vault were found to give a 100 per cent kill of all insects used, which included larvae of the clothes moth, larvae of Indian meal moth, and adult confused flour beetles:

	Pounds		Pounds
Calcyanide	0.5	Ethylene oxide	2.0
Chloropicrin	0.8	Lethane 23	1.5
Trichloroethylene	7.0	Ethylene dichloride-carbon tetrachloride	14.0

Lethane 23 when used at the rate of 1.0 pound per 1000 cubic feet failed to kill larvae of the Indian meal moth and killed only 35 per cent of *Tribolium* adults, but when the fumigation was repeated, using 1.5 pounds per 1000 cubic feet, 100 per cent kill was obtained. Lethane 22 used at the rate of 0.5 pound per 1000 cubic feet killed all clothes moth larvae but only 30 per cent of *Tribolium* adults and no Indian meal moth larvae.

Table II—Effect of Fumigants on Food Products

FUMIGANT	UNWEETENED CHOCOLATE					
	PRUNES	SHELLED ALMONDS	WALNUT MEATS	POWDERED COCOA	CHOCOLATE	BACON
Calcyanide	0	0	0	0	0	e,3
Chloropicrin	i,1	e,1	i,3	i,2	i,4	e,4
Ethylene dichloride-carbon tetrachloride	0	0	i,3	e,1	i,6	e,2
Ethylene oxide	0	0	0	e,1	i,3	i,3
Lethane 23	e,1	e,1	e,2	e,2	i,4	i,3 ^a
Lethane 22	0	0	e,1	0	i,3	i,3 ^b
Trichloroethylene	e,1	e,1	i,3	e,2	i,4	i,4

0 = No taste or odor of fumigant detected.

e = Tastes or smells mildly of fumigant; edible but not palatable.

i = Tastes or smells strongly of fumigant; inedible.

1, 2, 5, etc. = Days aeration required to remove all obvious taste and odor of fumigant so that product was edible and palatable.

^a Tested after 2 weeks' exposure to air; still inedible.

^b No bacon included in this fumigation, by error.

Table III—Effect of Fumigation on Germination of Seeds

FUMIGANT	DOSAGE Lbs./M cu. ft.	WHITE SHELLED				CLOVER
		OATS	WHEAT	BEANS	PEANUTS	
Blank, not fumigated	None	85	85	74	42	86
Calcyanide	0.5	89	85	58	60	86
Chloropicrin	0.8	93	85	44	63	81
Ethylene dichloride-carbon tetrachloride	14.0	81	83	58	52	85
Ethylene oxide	2.0	77	30	20	41	78
Lethane 23	1.5	86	88	53	65	83
Lethane 22	0.5	88	86	61	61	80
Trichloroethylene	7.0	84	88	34	55	85

Laboratory experiments with vinyl chloride,³ a liquid boiling at -14° C. and whose vapor has peculiar garlic-like odor, indicated that it had only low toxicity. A fumigation based on a dosage of 8 pounds per 1000 cubic feet equivalent to a concentration of about 7.5 per cent by volume of the vapor in air, with a contact period of 48 hours at $75-80^{\circ}$ F., killed only 30 per cent of *Tribolium confusum* confined in flour.

Effect on Metals

In the fumigation tests with seven different fumigants in the Plymetl vault in which different polished metal surfaces

³ Dana, Burdick, and Jenkins, *J. Am. Chem. Soc.*, **49**, 2801 (1927).

were exposed no corrosion whatever was detected and the only discoloration noted was a "red" tarnish on the copper after fumigation with calcyanide.

Effect on Food Products

Table II indicates the effects of the seven fumigants used on six different food products. In this 24-hour fumigation in a tight room, chloropicrin was found to be absorbed and retained to a much greater degree than had previously been noted in large-scale fumigations with chloropicrin.⁴ Hydrocyanic acid gas appears to be little absorbed by various food products and the U. S. Department of Agriculture⁵ has indicated that removal of meats and other food products during fumigation of premises with hydrocyanic acid is unnecessary.

The absorption and retention of fumigants, which are themselves good fat solvents, by food products rich in fat, such as bacon, unsweetened chocolate, and walnut meats, are noteworthy. Shelled almonds, though rich in fat, have a rather thick protective skin and appear to resist absorption of the fumigant.

Pastry flour exposed to these seven fumigants acquired their characteristic odors to varying degrees but lost these odors again after relatively short exposure to the air. In the case of calcyanide and ethylene oxide less than 24 hours were required, while with the other fumigants from 2 to 4 days' exposure was necessary.

Effect on Germination Power of Seeds

With the exception of ethylene oxide, which seems to have distinctly deleterious effect on germinating power, particularly of wheat and beans, none of the six other fumigants had any consistent effect on germinating power of five varieties of seeds exposed to fumigation in the Plymetl vault. (Table III) The germination tests were run simultaneously under identical conditions and hence are strictly comparable.

⁴ Hoyt and Ellenberger, *IND. ENG. CHEM.*, **19**, 461 (1927).

⁵ Bur. Animal Industry, Service and Regulatory Announcements, January, 1921.

Treatment and Disposal of Distillery Slop by Anaerobic Digestion Methods¹

S. L. Neave with A. M. Buswell

STATE WATER SURVEY DIVISION, URBANA, ILL.

THE increasing importance of industrial wastes in river-pollution and sewage-disposal problems makes desirable more information regarding the behavior of many wastes in the ordinary sewage-treatment processes. Distillery slop, resulting from the production of industrial alcohol, seems to have received little attention in this country, though a number of patents dealing with the recovery of its potash are to be found in the literature; the feasibility of this recovery evidently depends upon market conditions and an abundant supply of slop. The British Royal Commission on Sewage Disposal² has satisfactorily treated the diluted neutralized wastes from a whisky distillery on a percolating filter and used the effluent to maintain a salmon hatchery. No reference has been found to the anaerobic treatment of such wastes. As collected from the alcohol stills, the slop has a deep brown color and an inoffensive caramel odor; on dilution and exposure to the air, however, it is highly putrescible with the production of foul odors.

¹ Received April 13, 1928.

² Littlefield, *Chemistry & Industry*, **3**, 860 (1925).

Experimental

Anaerobic digestion tests have been made under conditions resembling those used for sewage sludge to determine the extent of bacterial degradation, the quantity and nature of the gases evolved, and the character of the resulting sludge. Through the courtesy of the U. S. Industrial Chemical Company, of Baltimore, a sample of slop, showing the following composition, was obtained:

	Mg. per liter		Mg. per liter
Total solids:	126,338	Ammonia nitrogen	24
Ash (20.7%)	27,415	Organic (Kjeldahl) nitrogen	1,920
Organic matter	98,923	Acidity (as acetic acid)	9,360

In accordance with the technic followed in this laboratory, all digestion mixtures were made up to a volume of 1 liter to fill completely a 1-liter brown-glass bottle connected to a gas reservoir filled with saturated salt solution. Dilutions were made with settled domestic sewage and de-oxygenated tap water, and were inoculated with well-digested Imhoff tank sludge, thus:

- (A) 100 cc. slop + 200 cc. sludge + 400 cc. sewage + 300 cc. water
 (B) 200 cc. slop + 200 cc. sludge + 400 cc. sewage + 200 cc. water + 1 gram CaCO₃
 (C) 300 cc. slop + 200 cc. sludge + 400 cc. sewage + 100 cc. water
 (D) Control 200 cc. sludge + 400 cc. sewage + 400 cc. water

The progress of digestion was judged by the gas evolution; this criterion indicated practically complete digestion in bottle (A) after 73 days, as shown in the accompanying graph, and the tests were discontinued at this time, although bottle (B) was still actively fermenting. Bottle (C), containing 300 cc. of unneutralized slop, failed to ferment. The quantity of gas given by the control (D) was small and no correction of the other gas volumes has been made for it.

At the conclusion of the tests, the resulting sludges and liquors were separated by vacuum filtration and analyzed separately. The following summary shows their characteristics:

Bottle	DRY SLUDGE IN BOTTLE			TOTAL DRY SOLIDS IN BOTTLE			
	Initial	Final	Change	Initial	Final	Over-all loss	Loss of slop alone
	Grams	Grams	Per cent	Grams	Grams	Per cent	Per cent
(A)	15.5	16.0	3.2 (increase)	28.13	22.28	20.8	55.4
(B)	15.5	17.3	5.2 (increase)	41.77	33.17	20.6	68.3
(C)	15.5	19.1(?) ^a	(?)	40.77	40.77	0.0	0.0
(D)	15.5	14.7	5.2 (loss)	15.90	15.50	2.5	..

^a (C) could not be filtered.

Bottle	COMPOSITION OF FINAL SLUDGE		Remarks
	Ash	Nitrogen	
	Per cent	Per cent	
(A)	56.7	2.13	Drains and filters readily; faint tarry odor
(B)	52.9	1.76	Filters slowly; marked kerosene odor
(C)	46.5	2.38(?)	Gelatinous; failed to filter; putrid odor
(D)	59.7	1.92	Filters readily; faint tarry odor

Bottle	COMPOSITION OF FINAL LIQUOR				Remarks
	Dissolved solids	Nitrogen	Volatiles acids as acetic	pH	
	Mg./liter	Mg./liter	Mg./liter		
(A)	6,284	274.4	174	7.0-7.2	Yellowish brown
(B)	14,322	358.4	1,554	6.6-6.8	Deep brown
(C)	32,814	613.2	4,374	About 4.4	Nearly black
(D)	799	121.8	66	7.0	Colorless

Since the solids in the slop are in solution, the usual liquefaction is lacking and a slight increase in sludge results from the precipitation of humus materials. A comparison of the total solids in the bottle, however, shows a decrease, and when these figures are corrected for the Imhoff sludge used, the actual decrease in slop solids is 55 to 68 per cent.

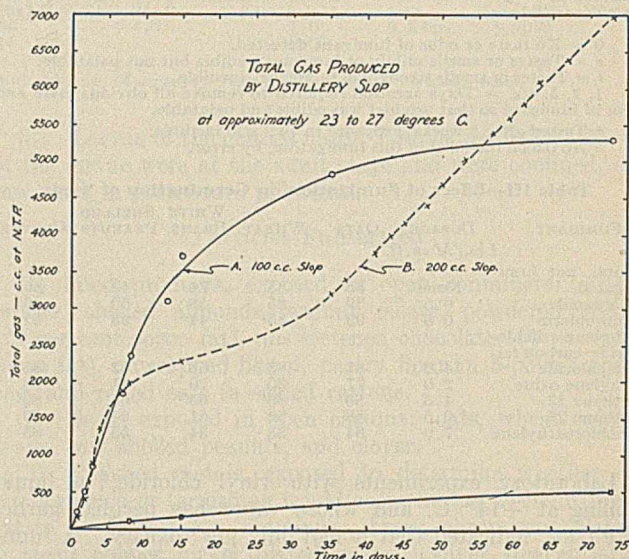
The decrease in total solids approximately equals the weight of gases evolved, thus:

Table I—Gases Evolved in Anaerobic Digestion of Distillery Slop

DAY OF DIGESTION	PERCENTAGE COMPOSITION							
	CO ₂	C ₂ H ₄	O ₂	CO	H ₂	CH ₄	C ₂ H ₆	N ₂
BOTTLE (A)								
1st	31.5	...	1.9	...	3.0	43.0	...	20.6
3rd	53.7	...	0.5	...	16.8	22.6	...	6.4
7th	53.1	...	0.0	...	6.7	40.1	...	0.1
15th	32.4	...	1.4	...	2.4	42.7	5.8	15.3
35th	24.0	...	0.3	3.3	1.3	54.0	5.3	11.8
73rd	30.3	0.0	0.0	1.0	5.6	62.3	1.1	0.0
BOTTLE (B)								
1st	32.2	...	1.2	...	3.3	41.1	...	22.2
3rd	53.2	...	0.0	...	38.7	3.6	0.7	3.8
7th	80.0	...	0.0	...	19.2	0.8	...	0.0
15th	84.1	...	0.0	...	1.5	14.4	0.0	0.0
35th	51.7	...	1.7	1.8	0.7	31.3	3.1	9.7
73rd	28.3	0.0	0.0	1.4	4.3	61.2	3.9	0.9
BOTTLE (D)								
15th	11.9	...	0.5	...	1.1	58.4	5.1	23.0
35th	14.8	0.0	0.6	2.0	4.2	54.2	4.7	19.5
73rd	21.9	0.0	0.0	0.3	5.6	48.4	12.1	11.7

BOTTLE	TOTAL WEIGHT OF GASES			ACTUAL LOSS OF SOLIDS
	CO ₂	H ₂	CH ₄ + C ₂ H ₆	
	Grams	Gram	Gram	Grams
(A)	3.87	0.03	1.87	5.77
(B)	6.02	0.06	2.12	8.20
(D)	0.17	0.002	0.23	0.40

The liquors from the anaerobic digestion have a pronounced color equal to 50 to 60 per cent of the initial color of the diluted slop; these coloring matters are, therefore, only partly attacked under anaerobic conditions. Aerating the liquors for 24 hours in the presence of about 20 per cent by volume of activated sludge also failed to remove this residual color.



The complete composition of the gases is shown in Table I. The total volume of gas evolved is somewhat lower than Rudolfs' value³ of 420 cc. per gram of organic matter: (A) 329; (B) 268+; (D) 82 cc.

Considerable quantities of nitrogen were found in the gases, but since the analytical data showed no loss in total nitrogen during the digestion, this gaseous nitrogen must be attributed to diffusion through rubber connections on the gas reservoir.

Conclusions

- 1—Without dilution the slop will not support a bacterial flora.
- 2—A dilution of 1 part of slop to 4 parts of water still inhibits bacterial growth on account of acidity in the slop.
- 3—Such a dilution will ferment, though slowly, in the presence of an excess of calcium carbonate.
- 4—A dilution of 1 part of slop to 9 parts of water or sewage ferments smoothly and completely, giving an inoffensive, rapidly draining sludge and a destruction of 55 per cent of the total solids in the slop.

³ Fuller and McClintock, "Solving Sewage Problems" (1926).

Rising Italian Production of Sulfate of Ammonia

Italian production of ammonium sulfate totaled 61,000 tons in 1926, or almost four times the 1913 figure and more than double 1925 production, according to reports to the Department of Commerce. The increase is to be attributed almost entirely to ammonium sulfate obtained from synthetic ammonia, it is said. Of the 61,000 tons of ammonium sulfate produced in 1926, 44,000 tons were synthetic ammonia sulfate; the balance, 17,000 tons, having been obtained from gas-works and coke-oven ammonia, from the gasification of peat and lignite, and from the decomposition of calcium cyanamide as follows: from gas-works ammonia, 5570 tons; coke-oven ammonia, 5460 tons; from peat and lignite, 4570 tons; calcium cyanamide, 1200 tons.

Consumption of sulfate of ammonia in Italy in 1927 has been estimated at 81,400 tons, compared with 65,000 tons in 1926 and 35,000 tons in 1913. The 25 per cent increase in the use of ammonium sulfate as between 1926 and 1927 is interesting, since it is the only fertilizer which registered a gain during 1927.

Sulfur Toleration in Gasoline¹

Gustav Egloff and C. D. Lowry, Jr.

UNIVERSAL OIL PRODUCTS COMPANY, CHICAGO, ILL.

THERE is constant pressure on the oil industry to limit the sulfur content of gasoline to 0.1 per cent lest automobile motors be injured by corrosion. Recent research under the aegis of the General Motors Corporation³ and the Standard Oil Company of Indiana⁴ has indicated, however, that corrosion takes place only when the atmosphere is at a temperature of approximately 32° F. or lower. Corrosion, it is stated, does not occur in warm weather. Why, therefore, refine gasoline to an extreme limit of sulfur the year round?

The sharp increase in the amount of high-sulfur crude oils being refined has made it a more serious problem than ever to meet the 0.1 per cent sulfur in gasoline requirement. This will be seen from the estimate made by a prominent petroleum

This study presents an analysis of gasoline consumption in relation to temperature and shows the need for a rational attitude toward sulfur in gasoline. It reveals the fact that over eight billion gallons of gasoline, more than two-thirds of the country's total consumption, are used in warm weather, when according to all published evidence there is no danger of corrosion. It seems absurd to refine this huge amount of gasoline to conform to an arbitrary sulfur specification which in most states throughout the greater part of the year appears to be worthless and to serve only to necessitate wasteful refining practices.² We urge consideration of the only reasonable procedure—regulation of the sulfur tolerance in gasoline by the climatic conditions where it is to be used. At least in warm weather, we see no reason why the sulfur limitation may not well be revoked entirely, as no one has reported any evidence of corrosion under mild temperature conditions.

geologist that 62 per cent of the world's present production of crude oil contains 0.4 per cent sulfur or more. Miller⁵ states:

The question of desulfurizing gasoline is confronting the refinery engineer today in a more acute form than ever before. The increased producing possibilities of the Permian Salt Basin area of West Texas, with a present daily production of 350,000 bbls., and an estimated potential production of 750,000 bbls., constitute a serious problem for the future.

Howe⁶ writes:

Present refining methods for treating high-sulfur crudes result in polymerization, the destruction of certain sulfur compounds, and unfortunately, the partial destruction of the unsaturated compounds which form such a large and essential part of "cracked" gasoline and which some regard as valuable in the anti-knock type of gasoline.*** A gasoline producer estimates that if a higher percentage of sulfur could be tolerated in the gasoline of the country refining losses

¹ Received June 16, 1928.

² Egloff and Morrell, *Oil Gas J.*, 25, 150 (1927).

³ Mougey, *IND. ENG. CHEM.*, 20, 18 (1928).

⁴ Diggs, *Ibid.*, 20, 16 (1928).

⁵ *Oil Gas J.*, 26, 121 (1928).

⁶ *IND. ENG. CHEM.*, 19, 189 (1927).

Average gasoline consumption per motor vehicle by states in 1927, as indicated by tax returns. Figures are gallons

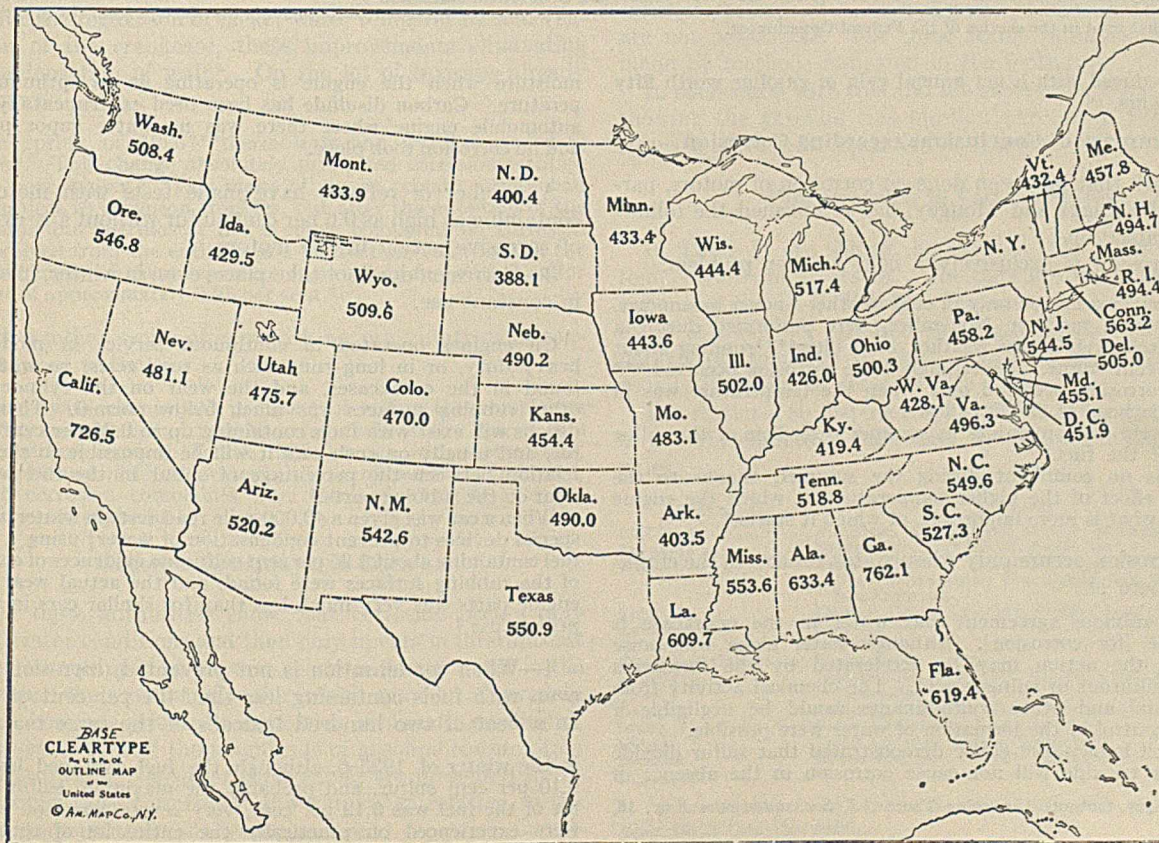


Table II—Mean Minimum Temperatures by Months

STATE	(Degrees Fahrenheit)											
	JAN.	FEB.	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPT.	OCT.	NOV.	DEC.
Alabama	39	40 ^a	48	56	62	69	71	71	66	55	45	39
Arizona	33	36	40	45	51	60	69	67	60	48	39	32
Arkansas	30	32	41	50	59	67	70	69	62	50	40	32
California	40	42	45	47	51	55	59	59	56	51	45	41
Colorado	14	10	23	32	41	50	56	55	46	35	24	16
Connecticut	20	22	28	38	49	57	64	62	55	45	34	25
Delaware	25	24	33	43	53	61	68	66	59	48	38	28
District of Columbia	26	27	34	43	54	63	68	66	59	47	37	28
Florida	53	55	59	64	69	73	75	75	73	67	59	54
Georgia	39	40	47	54	62	68	71	71	67	56	46	40
Idaho	22	26	33	38	48	51	58	56	48	39	31	23
Illinois	21	22	33	43	54	63	69	66	58	47	35	25
Indiana	22	22	33	43	54	62	66	65	58	47	38	25
Iowa	11	13	27	40	51	60	65	62	55	43	30	18
Kansas	15	22	32	43	53	61	67	66	58	45	33	23
Kentucky	26	27	36	46	56	65	68	61	60	48	37	29
Louisiana	43	46	52	59	66	72	74	74	70	60	50	44
Maine	10	10	20	32	42	50	59	55	49	40	29	17
Maryland	27	28	35	45	55	64	69	67	61	49	39	30
Massachusetts	23	22	29	38	48	56	63	62	56	47	37	28
Michigan	13	12	21	34	44	53	59	57	51	41	28	19
Minnesota	1	4	19	34	44	54	60	58	50	38	23	9
Mississippi	37	38	46	53	60	68	70	70	64	53	43	37
Missouri	21	23	34	45	55	64	68	66	59	47	35	25
Montana	9	11	22	33	41	48	55	51	48	33	22	15
Nebraska	12	14	25	38	49	59	64	62	42	38	26	17
Nevada	21	24	29	34	41	49	56	54	46	36	28	22
New Hampshire	12	11	23	33	44	52	59	55	48	39	28	17
New Jersey	26	25	33	42	52	61	67	66	60	50	39	29
New Mexico	22	25	32	39	47	56	61	59	52	41	30	22
New York	16	15	24	36	47	56	62	60	53	43	32	22
North Carolina	35	35	42	49	58	66	70	69	62	54	43	36
North Dakota	6	4	12	26	41	51	56	53	43	32	17	2
Ohio	21	22	30	41	52	61	65	64	57	46	35	26
Oklahoma	28	28	40	49	58	66	69	69	63	50	40	30
Oregon	31	33	36	39	44	48	52	51	47	42	37	33
Pennsylvania	22	22	30	40	51	60	65	63	57	46	36	26
Rhode Island	23	21	29	38	47	61	63	62	57	48	38	33
South Carolina	37	37	45	52	61	68	71	70	69	55	44	37
South Dakota	6	8	21	35	46	56	61	59	50	37	23	13
Tennessee	32	34	42	50	59	66	70	69	62	51	41	34
Texas	40	42	50	56	64	71	73	73	67	59	49	41
Utah	19	23	29	36	42	51	59	58	48	37	30	20
Vermont	8	8	19	32	44	52	59	55	48	38	27	14
Virginia	30	30	38	45	55	63	67	67	61	50	39	32
Washington	31	33	36	40	45	50	55	53	49	43	37	33
West Virginia	33	32	43	51	62	70	73	72	66	56	43	34
Wisconsin	9	11	23	36	47	57	62	60	53	42	26	16
Wyoming	9	11	19	29	37	45	50	48	40	30	20	11

^a Temperatures of 40° F. or over are in italics.

The crankcase oils were badly contaminated with water and iron oxide.³

5—Corrosion may be prevented by equipping cars with devices for the regulation of jacket-water temperature and ventilation of the crankcase, these improvements eliminating the condensation of water. On the lot of taxicabs already mentioned—

in the spring of 1926***thermostats and ventilators [were] installed. This change absolutely prevented corrosion troubles in the next winter.***This make of car in private service had been subject to corrosion troubles, but after the adoption of the ventilator and thermostat not a single complaint on corrosion was received from the entire year's production, regardless of the fact that many of these cars were operated on fuel with a sulfur content of approximately 0.25 per cent.³

With another group of cars with no preventatives of condensation of water—

with fuels with about 0.25 per cent of sulfur the complaints were very numerous and very bad, especially in the case of cars in intermittent service. In the 1925-6 series, with thermostats, ventilators, and oil filters, water in the crankcase was eliminated, and no corrosion complaints were received, regardless of the sulfur content of the fuel.³

Gasoline Consumption Data

Since these authorities show that corrosion occurs only under winter conditions and then only in cars in intermittent service not equipped to prevent condensation of water in the crankcase—the amount of sulfur which may be allowed in gasoline becomes primarily a question of climatic conditions. To give some idea of the magnitude of gasoline consumption in "non-corroding" weather three tables are presented showing gasoline sales throughout the country in relation to the lowest temperatures usually encountered.

Table I shows the gasoline sales in 1927 by months, in the various states. The figures are from reports of the state taxing authorities.⁸ Since in some states there is no gasoline taxation or inspection, exact figures on their use of gasoline are not obtainable. For these states estimates have been made by methods indicated in the footnotes.

In connection with this and the succeeding tables, the map showing the gasoline consumption per car in the different states in 1927 is of considerable interest.

Temperatures in Various States

In Table II are shown, by months, the mean minimum temperatures in all states. The data are taken from publications of the U. S. Weather Bureau covering observations made at their two hundred and eight regular stations over periods of from five to more than fifty years, the figures usually including at least twenty years.

The stations, so disposed as to give a representative picture of the climate of each state, are located in the following cities:

STATE	CITIES
Alabama	Anniston, Birmingham, Mobile, Montgomery
Arkansas	Bentonville, Fort Smith, Little Rock
California	Eureka, Fresno, Independence, Los Angeles, Red Bluff, Sacramento, San Diego, San Luis Obispo, San Francisco
Colorado	Denver, Grand Junction, Pueblo, Leadville
Connecticut	New Haven
Delaware	Wilmington
District of Columbia	Washington
Florida	Jacksonville, Key West, Miami, Pensacola, Tampa, Titusville
Georgia	Atlanta, Augusta, Macon, Savannah, Thomasville
Idaho	Boise, Lewistown, Pocatello
Illinois	Cairo, Chicago, Peoria, Springfield
Indiana	Evansville, Fort Wayne, Indianapolis, Terre Haute

⁸ *Am. Petroleum Inst.*, 9, No. 20 (March 21, 1928); *Natl. Petroleum News*, 20, 29 (May 30, 1928).

STATE	CITIES
Iowa	Charles City, Davenport, Des Moines, Dubuque, Keokuk, Sioux City
Kansas	Concordia, Dodge City, Iola, Topeka, Wichita
Kentucky	Louisville, Lexington
Louisiana	New Orleans, Shreveport
Maine	Eastport, Greenville, Portland
Maryland	Baltimore
Massachusetts	Boston, Nantucket
Michigan	Escanaba, Houghton, Marquette, Sault St. Marie
Minnesota	Duluth, Minneapolis, Moorhead, St. Paul
Mississippi	Corinth, Jackson, Meridian, Vicksburg
Missouri	Columbia, Hannibal, Kansas City, Springfield, St. Joseph, St. Louis
Montana	Billings, Havre, Helena, Kalispell, Miles City, Missoula
Nebraska	Lincoln, North Platte, Omaha, Valentine
Nevada	Reno, Tonopah, Winnemucca
New Hampshire	Concord
New Jersey	Atlantic City, Cape May City, Sandy Hook, Trenton
New Mexico	Roswell, Santa Fe
New York	Albany, Binghamton, Buffalo, Canton, Ithaca, New York, Oswego, Rochester, Syracuse
North Carolina	Asheville, Charlotte, Hatteras, Manteo, Raleigh, Wilmington
North Dakota	Bismarck, Devils Lake, Grand Forks, Williston
Ohio	Cincinnati, Cleveland, Columbus, Dayton, Sandusky, Toledo
Oklahoma	Muskegee
Pennsylvania	Erie, Harrisburg, Philadelphia, Pittsburgh, Reading, Scranton
Rhode Island	Block Island, Providence
South Carolina	Charleston, Columbia, Greenville
South Dakota	Huron, Pierre, Rapid City, Yankton
Tennessee	Chattanooga, Knoxville, Memphis
Texas	Abilene, Amarillo, Brownsville, Corpus Christi, Dallas, Del Rio, El Paso, Fort Worth, Galveston, Houston, Palestine, Port Arthur, San Antonio, Taylor
Utah	Modena, Salt Lake City
Vermont	Burlington, Northfield
Virginia	Cape Henry, Lynchburg, Norfolk, Wytheville
Washington	Blaine, North Head, Port Angeles, Seattle, Spokane, Tatoosh Island, Tacoma, Walla Walla, Yakima
West Virginia	Elkins, Parkersburg
Wisconsin	Green Bay, La Crosse, Madison, Milwaukee
Wyoming	Cheyenne, Lander, Sheridan, Yellowstone Park

To obtain the data in Table II, at each station, the lowest temperature for each day was recorded. The observations made during a month by each station were averaged, giving the monthly mean minimum temperature. An average of these for the number of years the station had been in operation was then made, and the means for all the stations in each state were again averaged to give the state's monthly mean minimum temperatures, which are the figures used in the table. As they show the lowest temperatures normally found, these mean minimum temperatures are the best available index to weather conditions as they affect the sulfur problem.

A mean minimum temperature of 40° F. has been selected as a suitable dividing line between weather requiring low-sulfur gasoline and that in which a sulfur specification should be unnecessary. In view of the statement of Diggs, that "marked corrosion occurred only when the temperature was in the neighborhood of 32° F. or lower," the choice of 40° F. gives an ample margin of safety for irregularities in temperature. In the table figures of 40° F. and above are therefore italicized to denote periods in which the published data indicate that corrosion will not occur. The mean temperature in any state is, of course, much higher than the mean of the minima here given.

Sales of Gasoline in Warm and Cold Weather

To show the relative proportions of warm- and cold-weather gasoline, the sales of gasoline in 1927 in months whose mean minimum temperatures are 40° F. or above, and the sales in months below this temperature, are given in Table III.

It will be noted that approximately 71 per cent of the gasoline consumption reported was in weather warm enough to prevent corrosion. A number of states should experience no corrosion on high-sulfur gasoline at any time of the year, notably California and Texas, both of which consume large quantities of gasoline and produce high-sulfur crude oil in large volume. To be sure, there are mountainous areas to which the climatic generalizations will not apply. But in view of the published data on corrosion, the table would

indicate that for a large part of the gasoline marketed a sulfur specification is superfluous.

At first thought it may not seem feasible to fit gasoline to the weather. But the differentiation of summer and winter gasoline is now established practice. In volatility the Bureau of Mines' semiannual surveys show definite reasonable variation. There should be no insurmountable difficulty in distributing gasoline without regard to sulfur content in the summer months, and reducing the sulfur, in addition to raising the volatility when cold-weather conditions prevail.

Table III—Sales of Gasoline in Warm and Cold Weather in 1927

STATE	MEAN MIN. TEMP. IN 40° F. OR ABOVE		PART OF TOTAL SALES	MEAN MIN. TEMP. IN 40° F. BELOW		PART OF TOTAL SALES
	Months	1000 gallons		Months	1000 gallons	
Alabama	10	129,512	87.3	2	18,713	12.7
Arizona	8	27,174	65.9	4	14,063	34.1
Arkansas	9	77,529	78.0	3	21,865	22.0
California	12	1,017,681	100.0	0	0	0.0
Colorado	5	60,750	46.9	7	68,434	53.1
Connecticut	6	92,866	58.1	6	67,087	41.9
Delaware	7	15,676	64.6	5	8,597	35.4
District of Columbia	7	36,295	63.5	5	21,509	36.5
Florida	12	247,248	100.0	0	0	0.0
Georgia	11	175,892	85.2	1	16,370	14.8
Idaho	5	22,862	52.7	7	20,481	47.3
Illinois ^a	7	452,842	64.2	5	252,350	35.8
Indiana	7	224,395	64.1	5	125,600	35.9
Iowa	7	213,539	69.1	5	95,559	30.9
Kansas	7	177,540	66.3	5	93,075	33.7
Kentucky	7	78,902	66.6	5	39,371	33.3
Louisiana	12	151,605	100.0	0	0	0.0
Maine	6	53,945	72.1	6	20,793	27.9
Maryland	7	84,121	63.0	5	47,379	36.0
Massachusetts ^b	6	183,050	59.5	6	124,130	40.5
Michigan	6	370,286	62.4	6	223,086	37.6
Minnesota	5	154,188	53.2	7	135,498	46.8
Mississippi	9	91,536	76.8	3	26,220	23.2
Missouri	7	208,097	64.6	5	114,122	35.4
Montana ^c	5	27,206	51.1	7	26,042	48.9
Nebraska	5	32,834	48.8	7	36,843	51.2
Nevada	5	6,541	51.4	7	6,179	48.6
New Hampshire	5	25,995	56.8	7	19,727	43.2
New Jersey	7	235,226	63.5	5	135,943	36.5
New Mexico	6	17,007	55.6	6	13,647	44.5
New York ^b	6	554,300	57.2	6	414,659	42.8
North Carolina	9	166,348	75.8	3	53,235	24.2
North Dakota	5	52,141	58.8	7	36,500	41.2
Ohio	7	511,326	66.5	5	259,475	33.5
Oklahoma	9	197,720	72.8	3	53,742	27.2
Oregon	6	78,136	59.4	6	52,749	40.6
Pennsylvania ^c	7	442,204	63.9	5	249,353	36.1
Rhode Island	6	35,874	58.1	6	25,562	41.9
South Carolina	9	79,787	78.4	3	21,985	21.6
South Dakota	5	46,683	53.0	7	41,348	47.0
Tennessee	9	119,005	75.2	3	29,847	24.8
Texas	12	591,447	100.0	0	0	0.0
Utah	5	20,749	49.6	7	21,025	50.4
Vermont	5	19,958	60.5	7	13,209	39.5
Virginia	7	101,893	64.7	5	58,889	35.3
Washington	7	134,238	66.0	5	69,183	34.0
West Virginia	9	86,510	81.1	3	16,145	18.9
Wisconsin	6	199,346	63.5	6	114,240	36.5
Wyoming	4	12,124	46.2	8	14,094	53.8

Totals 8,197,229 Av. 70.8 3,387,923 Av. 29.2

^a See footnote a, Table I.

^b See footnote b, Table I.

^c Figures for sales by quarters furnished by state; sales by months estimated from sales in corresponding months in North and South Dakota.

^d See footnote c, Table I.

^e Sales by quarters reported by state; sales by months estimated from sales in New Jersey.

Conclusion

This proposed elasticity in the sulfur specification may meet objection on the ground that allowing the marketing of high-sulfur gasoline for even part of the year could lead to abuse of this privilege. But there is even now no bar to the selling of any sort of gasoline, except the integrity of reputable oil companies who may be relied upon not to play false to the interests of the motoring public. The improvement in gasoline in recent years, particularly the introduction of fuel of high volatility during the winter months, has not been primarily in response to a demand from the public, but is an advance due to competitive conditions and a real desire to market the best product possible. The same forces would control the putting into practice of changes in the sulfur specification. It would be a great improvement over

existing conditions if the present unnecessarily rigid standard were replaced by regulation of the sulfur tolerance in gasoline in accord with the known facts regarding corrosion.

We are not urging that no attention be paid to the sulfur content of motor fuel. But the elimination of the sulfur requirement in warm weather is in accord with published work on corrosion, and would be a means of effecting economies in refining and of supplying better antiknock motor

fuel. The annual saving to the country which this measure would accomplish is estimated at thirty-five million dollars.

Acknowledgment

The writers wish to express their appreciation of the assistance given by B. Parry, of the New York office of the U. S. Weather Bureau, in obtaining the temperature data used in this paper.

Lubrication Round-Table Discussion

D. P. BARNARD, 4th—Those engaged in supplying lubricants for automobile equipment know that the problems of warm-weather lubrication are by no means so serious as those encountered when cars are operated at low temperatures. Some time ago this laboratory undertook an experimental program for the purpose of determining the viscosities of typical automotive lubricating oils at temperatures down to -17°C . (0°F .) and to study the effects of viscosity and pour test upon the resistance to cranking offered by the oil and upon its circulating characteristics. The results indicate that cranking effort is determined almost entirely by the viscosity of an oil apart from its cold test, while circulation by the lubricating system depends largely upon the temperature of the oil being above its pour test.

The first work to be published on the subject of oil-viscosity characteristics at low temperatures was that

of Parsons and Taylor,¹ who presented the results obtained from two widely varying types of oil, asphalt- and paraffin-base, when compared in a Saybolt viscometer under varying heads. Their results are illustrated in Figure 1, in which the rate of flow has been plotted against the corresponding pressure drop.

It will be noticed that the asphalt-base oil apparently conformed to Poiseuille's law in that the flow varied directly with the pressure drop. The paraffin-base oil, however, behaved quite differently in that the flow increased more rapidly than the pressure drop, indicating that the oil at this temperature was a plastic material the apparent viscosity of which decreased with increasing shearing stress. This characteristic is most important, as it indicates that two oils may have the same viscosity at 38.5°C . (100°F .) but entirely different properties at -17°C . (0°F .) The paraffin-base oil, for instance, although having a comparatively high pour test, actually flowed more readily at high rates of shear than did the asphalt-base oil. In other words, while the paraffin-base oil had the higher apparent viscosity at low rates of shear, this condition was reversed at high rates of shear. Parsons and Taylor did not, however, describe any correlation between these results and actual engine performance.

A similar method was followed in the viscosity experiments at Whiting, the chief difference in procedure consisting in the use of thermocouples placed at the entrance to the metering capillary in place of the thermometer and dummy tube of

Parsons and Taylor, and the substitution of a brine bath for the freezing mixture previously employed.

The results obtained by this method are illustrated by Figure 2, in which the rates of flow have been plotted against the pressure drop for three typical oils. The logarithmic scale was used in this work instead of arithmetical coordinates, as employed by Parsons and Taylor, to afford constant precision in plotting and to offer a wider range of observa-

tions. On such a plot any fluid which follows the laws of viscous flow, or flow directly proportional to pressure, will give a straight line having a slope of 1. However, none of these oils showed such a slope at the lower temperatures indicated.

The deviation in the case of the asphalt-base oil was not great, but in the other two it was marked, the flow increasing more rapidly than in proportion to the pressure. The data for

glycerol have been included for the purpose of demonstrating that the non-conformity with Poiseuille's law was not in apparatus characteristic. The same data plotted as apparent viscosity *vs.* pressure-drop are shown in Figure 3. The slopes of these graphs become equal to $1-\eta$, where η is the slope of the lines in Figure 2.

Departure from Laws of Viscous Flow

The departure from the ordinary laws of viscous flow, as illustrated in Figures 2, 3, and 4, is typical of the different classes of oils examined. It is evidently due to the presence of a colloidal structure which becomes more pronounced as the temperature is lowered. In the case of the paraffin-base oils the solid phase is without doubt mainly wax crystals, but some kind of colloidal particles also appear to be present in the asphalt-base oils.

Figure 4 shows the results of several observations at various temperatures for oils of different viscosities belonging to the three general types. It was observed throughout this work that η is rather erratic, although variations were never so great as to cause overlapping of oils of the different classes. It is probable that deviation of η from unity is in some way related to the pour-test temperature as specified by the American Society for Testing Materials, but the data available at present do not indicate the existence of any definite relation and evidently the deviation persists well above the pour point. Furthermore, there seems to be no direct bearing of viscosity within the limits examined, upon the value of η . In general, this work can be summarized in accordance with Table I.

The Round-Table Discussion on Lubrication was arranged as a joint meeting of the Petroleum and Industrial and Engineering Chemistry Divisions at the St. Louis Meeting of the American Chemical Society in order to provide for the informal presentation of the progress made since the Lubrication Symposium at Tulsa two years ago. R. E. Wilson was appointed chairman of both meetings, but was unable to attend the one at St. Louis. In his absence D. P. Barnard, 4th, served as a substitute and opened the discussion by describing some of the experimental work recently carried out by the Standard Oil Company of Indiana.

Table I—Summary of Observations at Various Temperatures for Oils of Different Viscosities belonging to Three General Types

Oil	Viscosity		A. S. T. M. POUR POINT		η AT POUR POINT	η AT -17° C.
	38.5° C. (100° F.)	98.9° C. (210° F.)	° C.			
	Seconds	Seconds	° C.	° F.		
1	216	45	-16	+3	1.1	1.1
2	331	50	-5	+23	1.3	1.3
3	565	61.5	+4.5	+40	..	1.3
4	109	41	-22	-7
5	185	46.5	-21	-5	1.2	1.2
6	205	46.5	-12	+10	1.1	1.1
7	390	57	-4	+25	1.15	1.2
8	1165	94	+4.5	+40
9	..	161	+4.5	+40
10	325	51	+7	+45
11	565	62	+7	+45
12	308	48	-17	0
13	580	56	-17	0	1.15	1.15
14	1080	70	-12	+10
15	130	42	+7	+45	..	2.4
16	231	51	+4.5	+40	..	1.8
17a	2064	148	+7	+45	1.3	..

Inasmuch as the A. S. T. M. pour test is substantially a determination of the temperature at which the apparent viscosity becomes infinite under the existing conditions of very low shearing stress, it is to be expected that if the foregoing work were extended to include very small pressures a bend in the curves shown in Figures 3 and 4 would result. An example of one such series of observations is given in Figure 5. The upward curvature of the apparent viscosity-pressure drop curves can be taken as indicating the increase in shearing stress necessary to overcome the solid structure, or solid-test effect, in the oil at the temperature noted. The solid-test effect is apparently distinct from the remainder of the pressure-viscosity graph. Figure 5 shows also how the variations in apparent viscosity disappear as the temperature is raised.

One of the most convenient methods of expressing the temperature-viscosity characteristics of lubricating oils is the chart developed independently by MacCoull² and Herschel³ and reproduced in Figure 6. In this chart the scales are so constructed that the temperature-viscosity graph is ordinarily a straight line. If the graph obtained by plotting the viscosities at, say, 99° C. (210° F.) and 38.5° C. (100° F.) be extended to -17° C. (0° F.), the viscosity indicated for this temperature is presumably that of a true fluid free from other plastic effects.

In the case of oils having values of η greater than unity it is to be expected

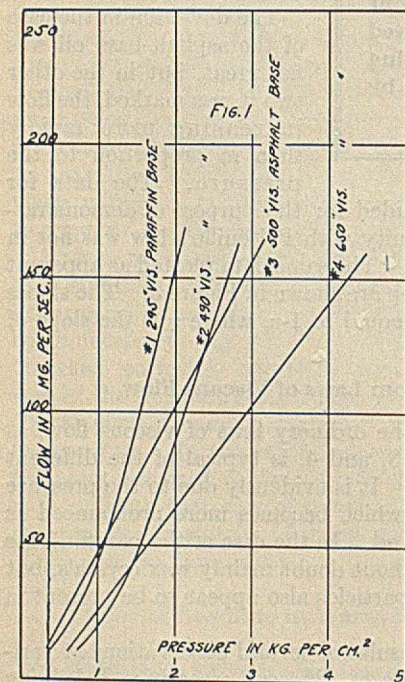
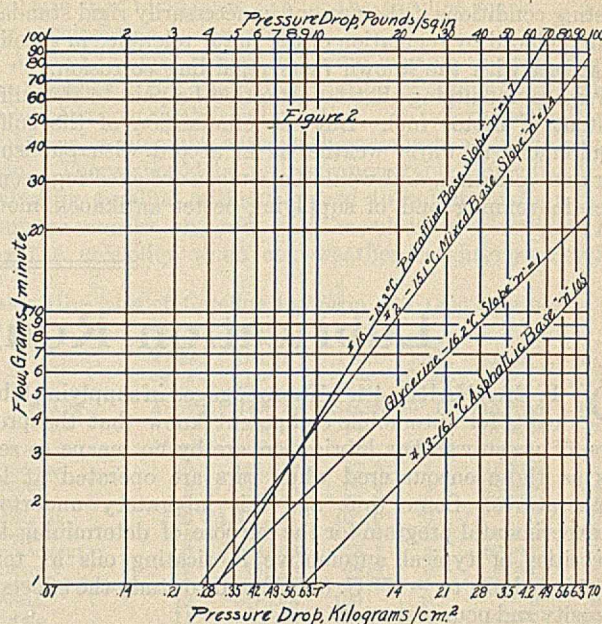


Figure 1—Rate of Flow of Oils through Standard Saybolt Universal Viscometer Capillary at -17.8° C. (0° F.)

No.	Viscosity		Pour Point, ° C.
	38.5° C. (100° F.)	98.9° C. (210° F.)	
1	295	52	+1.7
2	490	63	+1.7
3	500	55	-20.6
4	650	61	-17.8

that observed viscosities will be higher than would be indicated by the chart unless the shearing stress is large enough



to overcome completely the effects of any plastic or semi-solid structure formation. The actual curves indicate that this assumption is approximately correct, apparent viscosities at low rates of shear being much higher than the extrapolated straight line. The magnitude of the deviations is rather minimized by the more highly compressed scale employed, but will be evident by referring to the figures on the ordinates.

Comparison of Viscosities

Table II presents a comparison between the viscosities as predicted from inspection data at 38.5° C. (100° F.) and 99° C. (210° F.) by means of extrapolation on the Herschel chart and actual determinations for several conditions of shearing stress. Evidently, best agreement between estimated and observed viscosities is obtained under a pressure drop of about 14 kg. per sq. cm. (200 lbs. per sq. in.). The checks are by no means perfect and in some instances represent rather large viscosity variations, but when it is considered that the corresponding temperature deviation is in no instance more than 3° C. (5° F.), the agreement appears good enough for most practical purposes, especially if the unstable nature of viscosity at the lower temperatures be taken into account. It will be noted that a relatively small error in the 99° C. (210° F.) determination will make large variations in the estimated viscosity at -17° C. (0° F.) if only the 99° C. (210° F.) and 38.5° C. (100° F.) points are known.

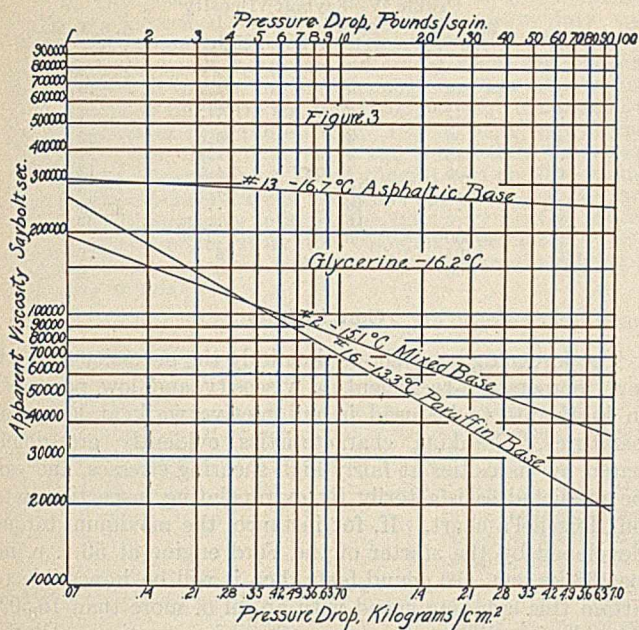
Table II—Apparent Viscosity, Saybolt

OIL	TEMP. ° C.	0.7	1.4	27.7	FROM
		KG./SQ. CM.	KG./SQ. CM.	KG./SQ. CM.	HERSCHEL
		Seconds	Seconds	Seconds	Seconds
1	-17	42,000	39,300	30,000	45,000
2	-16.5	149,000	120,000	49,300	60,000
3	-16	519,000	420,000	169,000	123,750
4	-19	10,500	7,600	..	7,400
5	-17.5	21,200	18,000	8,500	15,000
6	-17.5	40,000	25,000	19,200	19,000
7	-18	158,000	138,000	78,000	46,000
8	-6.7	550,000	355,000	56,000	75,000
9	-2.6	1,870,000	1,370,000	355,000	252,000
10	-16.5	530,000	335,000	45,000	80,000
11	-16	1,480,000	1,300,000	220,000	116,500
12	-17.8	92,000	60,000	84,000	100,000
13	-17.8	540,000	490,000	322,000	450,000
14	-17	1,500,000	1,360,000	910,000	1,575,000
15	-16.3	271,000	122,000	3,800	3,900
16	-18	410,000	252,000	31,000	52,000
17a	-4.3	700,000	530,000	160,000	90,000

In this connection it is interesting to note that, while the temperature coefficient of viscosity does not appear to be

² "Lubrication," published by The Texas Company.

³ Oil Gas J., 24, 146 (1926).



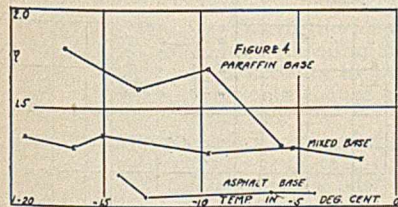
of great importance when one studies only the results at 99° C. (210° F.) and 38.5° C. (100° F.), or 54.5° C. (130° F.), its importance increases rapidly as temperatures decrease. This is illustrated by the comparison made in Table III of two typical asphalt-base oils with corresponding oils of mid-continent origin at widely different temperatures.

Table III—Comparison of Saybolt Viscosity of Asphalt-Base and Mixed-Base Oils at Various Temperatures

OIL	98.9° C.	54.4° C.	38.5° C.	21° C.	0° C.	-17.8° C.
	(210° F.)	(130° F.)	(100° F.)	(70° F.)	(32° F.)	(0° F.)
	Seconds	Seconds	Seconds	Seconds	Seconds	Seconds
Asphalt-base	80	490	1500	6700	115,000	4,000,000
Mixed-base	80	375	920	3000	26,000	360,000
Asphalt-base	55	205	525	1700	15,000	280,000
Mixed-base	55	180	418	1150	7,300	66,000

Table III also brings out in a very striking manner the tremendous rate of increase in the viscosity of oils as the temperature drops, and makes it clear why some dilution is necessary to start any oil of satisfactory viscosity at temperatures around -17° C. (0° F.). While Table II indicates that viscosities under considerable stress can be estimated with fair reliability by the Herschel chart, the apparent viscosities under lower stresses will be greater than such a prediction.

For example, in Figure 6 are plotted the data for two oils having temperature-viscosity coefficients characteristic of (a) asphalt-base and (b) paraffin-base oils. At -17° C. (0° F.) the effect of shearing



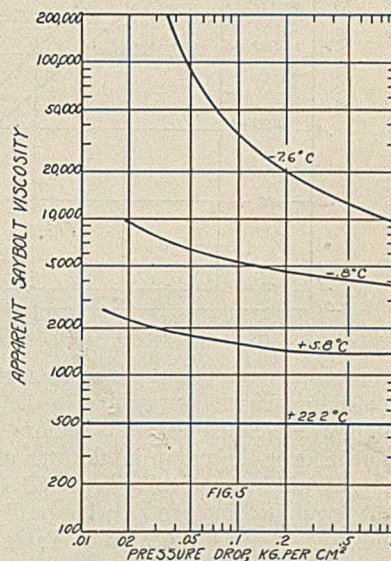
stress on the viscosity of the asphalt-base oil is slight. It is so pronounced in the case of the paraffin-base oil, however, that at the lower stresses it may more than offset the advantage of the lower temperature-coefficient. Under the rapid-shear conditions in oil films on cylinder walls and the like, the effective viscosity might be considerably higher. To extend this information to service conditions, the following engine-cranking tests were made.

Relation between Viscosity and Cranking Effort

To determine the effect of oil viscosity on cranking effort, several engines were subjected to cranking tests in the cold room. These tests were made in the following manner:

The engine under test was placed in the cold room and connected to an electric cradle-dynamometer through a gear box which made it possible to operate the dynamometer at about three times engine speed to secure smoothness. The gear box was mounted outside the cold room and the resistance of the entire cranking train was small in comparison with that of the engine. When testing the Ford Model-T power plant it was necessary to crank from the front end of the engine to reproduce car conditions. The other engines were coupled at the flywheel ends in the conventional way. All tests were made by running the engine first under its own power until thoroughly warmed up, and then draining, flushing, and filling with the oil to be examined. The engine was then motored for 5 to 10 minutes by the dynamometer, after which it was allowed to stand overnight before making observations of cranking effort. Tests were made at the lowest temperature first, and the engine was allowed to stand from 15 to 30 minutes after each observation to equalize temperature changes due to frictional heat. Thermometers were installed in the oil sump and in the water connections and tests were made only when all temperatures were substantially the same. Observations were made of the breakaway torque and the torque required to crank the engine at 35, 50, 70, and 100 r. p. m. No attempt was made to reproduce temperatures exactly. Instead, observations were made at temperatures ranging from 71° C. (+160° F.) to -23° C. (-10° F.), using oils varying in viscosity from 200 seconds at 99° C. (210° F.) to 100 seconds at 38.5° C. (100° F.), and pour tests varying from +7° C. (+45° F.) to -20° C. (-5° F.). In most of the work reported the spark plugs were removed to eliminate pumping losses.

The results of these tests are given in Figure 7, in which the cranking efforts as observed have been plotted against the apparent oil viscosity at high shear rates as estimated from inspection data by means of the Herschel chart and in many cases verified by actual measurements. Experimental errors in work of this sort are necessarily large; nevertheless, the data indicate consistently that the cranking efforts observed were determined by oil viscosity, and evidently by viscosities corresponding to fairly high shearing stresses. The deviations could not be correlated with any pour-test effect and, within the range studied, pour test appeared to have no effect on the ease of starting.



While cranking torque seems to depend on viscosity alone, in no case was proportionality between cranking effort and viscosity observed, the slopes of the curves in Figure 7 varying from 0.3 to 0.6. Evidently the immersion of the flywheel and transmission in the motor oil made the Ford Model-T power plant more susceptible to the effects of oil viscosity than the other engines.

The tests on the Ford power plant were made in high-gear position and correspond to cranking the car in gear but with the propeller shaft disconnected. In general, this work indicates that the cranking-effort characteristics of a motor oil can be estimated with fair reliability from suitable temperature-viscosity data by means of the Herschel diagram. It should be recognized, however, that excessive pour-test effects may modify this conclusion to some extent. Furthermore, viscosities should be determined carefully at three temperatures as far apart as possible before attempting to extrapolate to low temperatures, as a comparatively unimportant error

at normal temperatures becomes very large when extended to -17°C . (0°F).

Oil-Circulation Tests

In addition to its cranking characteristics, it is important that a motor oil circulate freely in the lubricating system even at very low temperatures. The tests reported in Figure 8 were made in the cold room with a four-cylinder, sleeve-valve, passenger-car engine. In these tests the engine was cranked

by the dynamometer and allowed to run at 800 r. p. m. under its own power, the time and the sump temperature being noted with relation to the development of circulation as indicated by

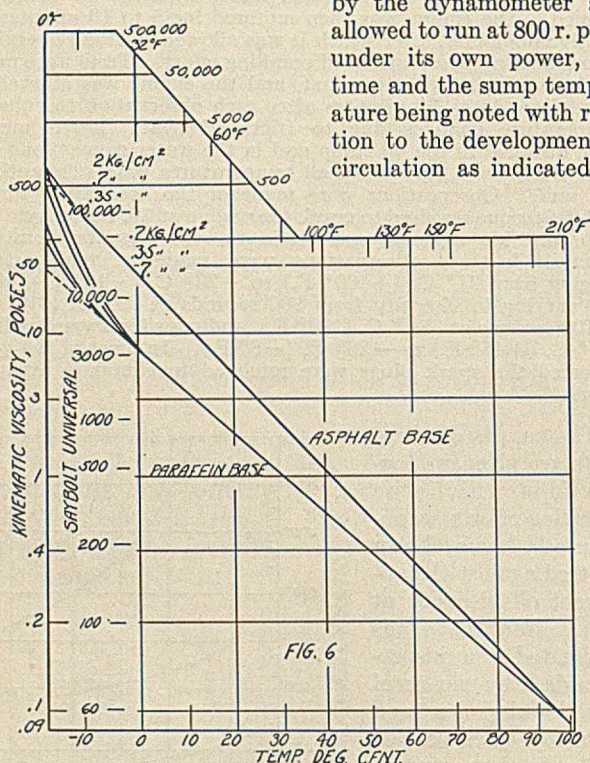


FIG. 6

the oil-pressure gage. The thermometer in the sump was placed as closely as possible to the pump inlet, and the gage line was cleaned carefully before starting each test. The screen over the pump intake was of 12.5 meshes per cm. (32 mesh) and had a total area of 180 sq. cm. (28 sq. in.) The oils examined included a wide range of viscosities and varying cold-tests as indicated in Table IV.

It is obvious from Figure 8 that pour test was the factor determining the establishment of circulation, at least with this type of oil screen. In no case did the pressure gage show a consistent reading until the sump thermometer reached approximately the pour point of the oil. In a few instances the gage would show some pressure at the outset due to the presence of oil in the pump. This pressure, however, would disappear in a moment and no further indication would appear until flow to the pump occurred.

Under the conditions of these tests the establishment of circulation was wholly dependent on pour test and was virtually unaffected by viscosity characteristics at higher shear stresses. However, the rate of circulation after flow had started was undoubtedly influenced by such viscosity characteristics. As yet, no information is available on this point.

Figure 9 shows the effect of lack of lubrication on two of the pistons removed from the engine.

At present, a study is being made of the conditions of flow through typical screen and pump-inlet systems which should establish the relations between screen mesh and viscosity and shearing stress at low temperatures. It appears that screens having coarser mesh will markedly reduce the effect of pour test on oil circulation. It is hoped that this work will be available for publication in the near future.

Table IV—Saybolt Viscosity

OIL	38.5° C.	98.9° C.	SP. GR.	A. S. T. M.
	(100° F.)	(210° F.)		POUR POINT
	Seconds	Seconds	° Be.	° C.
1	216	45	22.7	-19.4
2	331	50	22.9	-5
3	565	61.5	23.8	+4.5
4	109	41	25.5	-22
5	185	46.5	24.4	-21
6	205	46.5	24.2	-12
9	...	161	22.6	+4.5
17	...	165	...	+26.6
18	...	165	...	+32
19	330	57	...	-21
20	105	...	26	-23
25	106	...	25.9	-23

Conclusions

The foregoing work shows definitely the necessity for both low temperature-coefficient of viscosity and low pour test in lubricants to be used in automotive work at low temperatures. Cranking characteristics evidently are dominated by viscosities at fairly high shearing stresses, and can be predicted satisfactorily by extrapolating inspection data on Herschel's chart. If, for instance, the maximum torque developed by the starter of the Ford engine at 50 r. p. m. be 138 kg. cm. (10 pound feet) then it will be impossible to attain this cranking speed with an oil of more than 16,500-second viscosity at the temperature in question. All the values quoted will vary markedly between different engines; but, nevertheless, the general characteristics noted should be correct. At the lower temperatures virtually all the oils examined up to the present have exhibited plastic characteristics and in most cases have not followed at all closely the laws of viscous flow. Those oils in which this deviation is great appear at a disadvantage for automobile-engine work owing to their relatively poor circulation characteristics, this effect being so pronounced under some conditions as to offset otherwise satisfactory temperature-viscosity susceptibilities. The conditions of shearing stress are much less severe at the intake to the circulating system than on the cylinder walls, and free circulation therefore requires satisfactory viscosity under both high and low shearing stresses.

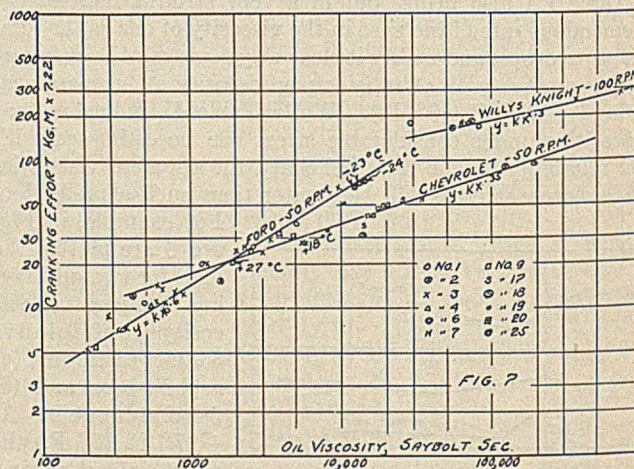


FIG. 7

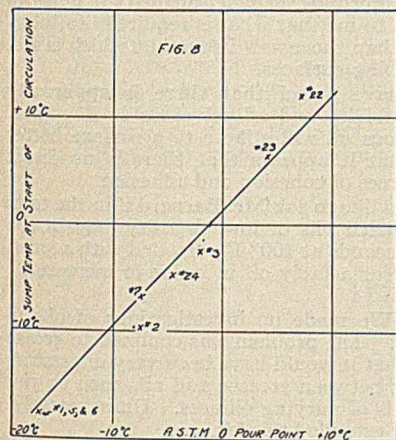
Unfortunately the types of crude which yield oils with a low temperature-coefficient generally tend to give rather high pour tests and, conversely, those oils which naturally have low pour tests also have very large viscosity-temperature-coefficients. Since a low temperature-coefficient of viscosity is of the more fundamental importance, at both low and high temperatures, it appears logical to emphasize this characteristic and to eliminate or minimize the effects of pour test by enlarging pump inlets, which would also help to eliminate clogging by ice crystals. An oil with both characteristics is the ideal for low-temperature operation.⁴

⁴ The work described in the foregoing discussion appears in more detail in the *J. Soc. Automotive Eng.*, 22, 213 (1928).

J. C. GENIESSE—We conducted a series of tests similar to those just described by Mr. Barnard. A heavy-duty truck motor was installed inside of a refrigerated room. To this was connected an electric motor in order to determine the amount of torque required to turn the gasoline engine at low temperatures. Before starting the work, six thermocouples were installed in the rubbing surfaces near the oil film; two of these were in main bearings, two in the cylinder wall, and two of them through the pistons and into the rings. With these it was possible to make sure that the temperature of the whole apparatus was the same. It was found necessary to make the tests very brief in order to prevent the oil temperature from changing appreciably.

About thirty oils were tested for the purpose of studying the following factors:

- (1) *Viscosity.* Oils varying from 100 to 870 seconds Saybolt viscosity at 100° F. were used.
- (2) *Source.* (a) Pennsylvania; (b) Midcontinent; (c) Gulf Coast.
- (3) *Wax Content.* Three oils having pour points of about 70° F. were dewaxed so as to obtain a pour point of 0° F. Both sets were tested.
- (4) *Method of Manufacture.* (a) Straight-run overhead products; (b) blend of overhead and residuum products; (c) long residuum oils.



These oils were placed in the motor and cooled to temperatures ranging from 0° to 30° F. The torque required to turn the motor at speeds ranging from 0 to 120 r. p. m. was determined. The results obtained with all the oils show that the torque required to turn the motor depends only on the viscosity of the oil at the temperature of the test. The viscosity of an oil below the pour-point temperature was obtained from the Texas Company temperature-viscosity chart by extrapolating on a straight line through the points corresponding to the viscosities at the higher temperatures.

In order to get some information on the viscosity range of oils that could be handled by automobile oil pumps, two of them were installed in the cold room, one directly in oil and the other with a 10-inch suction head. Below the pour-point temperature neither pump would handle the oil. At higher temperatures the pumps behaved slightly differently. The one in the oil handled a constant quantity regardless of the viscosity. The one above the oil level pumped less of the more viscous oils because of the friction offered by the inlet pipe. With oils of very low viscosity, such as 30 seconds at 100° F., the volume pumped was diminished, undoubtedly due to slippage in the pump.

T. P. CHASE—What information did you get from the thermocouples?
 J. C. GENIESSE—The thermocouples were placed there to see that the temperature of the oil in all parts of the motor was the same. We found it necessary to make the tests very brief since the oil temperature would change as much as 15° F. if the test was continued 10 minutes.

F. R. STALEY—For a given viscosity at the test temperature, for instance at 0° F., was there any difference noticeable between paraffin-base and asphalt-base oils?

J. C. GENIESSE—Viscosities were determined by extrapolation from normal-temperature inspection data. If the viscosities of the paraffin-base and asphalt-base oils are equal at the test temperature, they will offer the same resistance to cranking.

F. R. STALEY—The results have all been given in terms of viscosity at the test temperature. Was allowance made for variation of test temperature with time?

J. C. GENIESSE—The actual observations required such little time that the temperatures did not vary more than 1° or 2° F.

D. P. BARNARD, 4TH—In reference to Doctor Geniesse's circulation tests, were any observations made with the pump removed from the oil reservoir in the horizontal direction as well as vertically?

J. C. GENIESSE—No. We used only the vertical oil line. However, we did try two sizes of line.

D. P. BARNARD, 4TH—You experienced no difficulty in priming the pump located above the oil level?

J. C. GENIESSE—No.

A. E. BOSS—If you take an oil of high viscosity, say an asphaltic oil, and dilute it to a lower viscosity, would you obtain any abnormal cranking torque values?

J. C. GENIESSE—We tried that. We prediluted some oils 10 per cent, which, I believe, reduces the viscosity by about 50 per cent. In every case the cranking effort with the diluted oil was just as might be expected from its viscosity.

D. C. JENNINGS—You spoke of using a long residuum in your tests. Was it dewaxed at 0° F. or at the usual 30° to 35° F.?

J. C. GENIESSE—The long residuum oil was dewaxed at -10° F. and had a pour point of about +20° F.

E. G. GILSON—At the Lubrication Symposium of the AMERICAN CHEMICAL SOCIETY at Tulsa, attention was directed to the effect of the surrounding atmosphere on the friction in a bearing.⁵ Again at the Oil Power Conference at Pennsylvania State College, April, 1927, attention was called to this strange phenomenon, and some additional facts were presented. These data showed increases in friction of as much as 60 per cent when the bearing, composed of a 3 per cent nickel-steel journal, having 0.035 carbon and a bronze bushing, was run in a surrounding atmosphere of dry hydrogen.

By replacing the hydrogen with air the friction could be brought back to the original value and by changing back from air to a non-oxidizing atmosphere, either by means of a vacuum, or replacing with hydrogen, the friction would again go up. Wet hydrogen acted much the same as air. The whole trend of the work showed that when operated in an oxidizing atmosphere the friction is much lower than when operated in a non-oxidizing atmosphere.

This was with a bearing having a 3 per cent nickel-steel journal, and 0.035 carbon, in a bronze bushing. When a plain steel journal having 0.040 carbon was used, other conditions remaining the same, the results were quite different. In this case, changes of the friction, with the atmosphere, amounted to only a few per cent. In some cases any change at all was very hard to detect. But the changes were always in the same direction as with the nickel-steel journal—that is, the cycle was the same, but the magnitude of change was much less. It was found, however, that the friction with the plain steel journal was much lower than the minimum friction with nickel-steel journal.

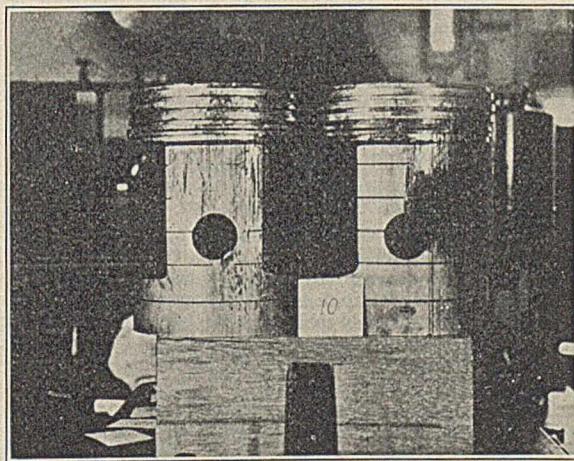


Figure 9—Scuffed Aluminum Alloy Pistons Resulting from Starting under Conditions Which Prevented Free Oil Circulation

This led to the investigation of the effect on the friction, in air, of different combinations of metals in the bearings. Two shafts were used: one 3 per cent nickel steel and 0.035 carbon, the other plain steel, 0.040 carbon. Four sleeves, or bushings, were used—two of bronze and two of white metal. The composition of each is given below.

The bearing was 2 inches (50.8 mm.) in diameter by 5 inches (127.0 mm.) long. The different parts were identical. The clearance conformed to standard practice. The speed was 2000 r. p. m., but the load was very light, only 10 pounds per square inch (7 kg. per sq. cm.).

Each shaft was run with each bushing. The average results are given in the following tabulation:

⁵ Gilson, *IND. ENG. CHEM.*, 18, 467 (1926).

No.	BEARING			SHAFT	FRICTION
	Cu	Composition ^a			
	%	Sn	Zn		%
1	85.3	10.0	4.64	A ^b	100
				B ^c	96
2	59.15	39.81	0.37	A	119
				B	132
3	83.3	8.3	8.3	A	98
				B	100
4	79.0	5.0	16.0	A	79
				B	89

^a Composition of Nos. 1 and 2 by analysis, of Nos. 3 and 4 by specification.

^b Shaft A = 3% nickel steel, 0.035 carbon.

^c Shaft B = plain steel, 0.040 carbon.

It is interesting to note that in the case of No. 1 bronze the nickel-steel shaft gave higher friction than the plain steel, but in all the other cases it was lower.

In considering all these strange results, it should be remembered that these were bearings conforming in every way, both in design and operation, very closely to standard practice; also that they were operating under conditions of fluid-film lubrication, if such conditions ever occur in practice.

With fluid-film lubrication present in these experiments the results tend to discredit the theory that under such conditions the friction is wholly a function of the viscosity of the oil.

As a matter of fact, a study of the results obtained strengthens the conviction that friction in a bearing is the result of a chemical, or probably an electrochemical, reaction between the oil and the metals composing the bearing, in which oxygen plays a very active part.

G. L. BAXTER—Does anyone know if there has been any attempt to substitute oil for the hard grease such as is used in the lubrication of locomotive journals? At the present time operating temperatures are running excessively high with grease. The loads carried are over 100 pounds per square inch and at times grease lubrication leaves much to be desired.

D. P. BARNARD, 4TH—I should think that Mr. Baxter's question would be of considerable interest. Oil lubrication is rather extensively used in European practice, but I doubt if there are many locomotives so lubricated in this country. The newest electric machines, which embody many features of automotive construction, may have provisions for oil lubrication. There is no question that the grease cellar which gave good service in comparatively light locomotives at 45 miles per hour is not satisfactory in the heavy high-speed machines of today.

E. G. GILSON—I think that there is an electric locomotive in service having plain journals and using heavy oil.

F. E. BARTELL—Was the same oil used in all of Mr. Gilson's tests? If so, the cohesive forces within the oil remained the same and the variations in friction probably involved some factor connected with adhesiveness between the oil and the metal. In such a case a measure of the adhesiveness between oil and metal might throw some light on the subject.

E. G. GILSON—The same oils were used in all cases.

F. L. KOERTHEN—I might say a word on the question of lubricating a high-speed reciprocating bearing subjected to a pressure of 200 pounds per square inch as in the locomotive rod bearings. The fact that the motion is reciprocating, and hence the bearing has no opportunity to build up an oil pressure sufficient to support the load, particularly at the ends of the strokes, indicates that we should use a lubricant which will give an actual protective film of plastic or semisolid nature on the surfaces; therefore a grease is better than an oil.

The objection which has developed with grease in modern high-speed, long-run locomotive practice is due to the fact that too heavy and sticky a grease has been used, causing the friction within the film of lubricant itself to be too great. It is not necessary to use such a sticky viscous grease; a softer grease which gives less resistance to high-speed motion, yet has a very high lubricating value by virtue of its plastic soap jelly particles which are adsorbed on the metal surfaces, is the logical solution of the problem. The use of a softer, more nearly fluid grease will, of course, require a change in the device used for applying the lubricant. Such a change would be justified by the results.

The ability of a material to lubricate under severe conditions is dependent, not on the viscosity alone, but also on the presence of semiplastic substances capable of being adsorbed on the surfaces to form a film with strength enough to prevent actual metallic contact.

G. L. BAXTER—In our work on locomotive lubrication we are confronted by the problem of the heavy power used and have run into some trouble. In attempting to eliminate some of our difficulties we experimented with "dry" greases and those containing substantial amounts of moisture. We found that a

"dry" grease containing less than 0.5 per cent of water and which would not drop off a hook enclosed in a test tube when heated to 320° F. gave better service than a grease which melted at a lower temperature. A low-melting grease would run out of the bearing and permit the journal to run without lubrication.

D. P. BARNARD, 4TH—The temperature of 320° F. quoted is very interesting in that it agrees closely with some experimental work at our Whiting laboratory. We constructed a model driving journal, about 4 inches in diameter by 5 inches long, operated it at conventional locomotive rubbing speeds and loads, and noted the brass temperature at which grease commenced to squeeze out at the ends of the perforated plate. We found that a grease which performed satisfactorily on this model bearing at 300–320° F. also gave satisfactory results in service, while one which ran out at 280° F. would not perform properly. The agreement in temperature limits between the two methods indicates that the problem is simply that of providing a grease with a melting point high enough to prevent running out of the box at any temperature it might encounter.

J. W. KIRTH—Those values apply to grease lubrication. It would be necessary, of course, to use a different method of supply in the case of oil lubrication. Grease cannot be adapted to supply a constant flow of lubricant, as when it melts it tends to run away. It would seem to me that what is required is a lubricant which is less viscous than those now in use but which is still more adhesive to the rubbing surfaces.

F. E. BARTELL—We have found that there is apparently no connection between viscosity and adhesiveness to a surface. In many cases a non-viscous oil will adhere to a surface better than a viscous one, so that it appears that there is no direct connection between the forces of cohesion and adhesion.

J. C. GENIESSE—I would like to ask Mr. Barnard if in the tests on his model bearing he tried oils of low viscosity, say in the neighborhood of 60 to 80 seconds at 100° F., blended with a small proportion of a fatty acid or a fatty oil in order to increase its adhesiveness.

D. P. BARNARD, 4TH—We made no investigations of oils in connection with this work. The problem was confined to grease characteristics. I think that it would have been very interesting to have had a comparison between greases and oils such as you suggest, especially with oils of varying oiliness. Unfortunately, however, our work was not extended this far.

The lubrication of locomotive bearings is particularly interesting to all of those in the oil industry. In my opinion it would be of a marked benefit both to the operator and to those who supply lubricants for this service if a more modern and more generally satisfactory system of oil lubrication could be adopted. I believe that in this country the only oiling systems that have been applied to car journals have been of the circulating type, in which they expect a reservoir of oil to feed properly and for the oil to run back to the reservoir with no loss of lubricant. Naturally, this has been extremely difficult to obtain and the principal trouble has been that the systems would run dry in a very short time. Recently, however, considerable success has been attained with fresh oil lubrication, particularly in certain types of internal-combustion engines. It is surprising what a small amount of fresh clean oil is required to lubricate properly a bearing running at a fairly high rate of speed. Some fairly recent work by the Madison Kipp Company and the Waukesha Motor Company has indicated that the main bearing of a truck engine 2 1/4 inches in diameter and running at 1000 r. p. m. could be satisfactorily lubricated with less than 5 drops per minute, which seems to be a remarkably small amount of oil for such a high rubbing speed. This is particularly true when it is considered that the clearances are much larger than those obtaining in locomotive and car journals. It should be possible to incorporate some system of oil lubrication in which the amount of oil delivered will be governed by journal speed.

G. L. BAXTER—There are a number of locomotives in operation at the present time in which force-feed lubricators have been installed.

D. P. BARNARD, 4TH—I am aware that this has been done in the case of cylinder lubrication. I was referring principally to the locomotive journals. Do you think that it is possible to work out a satisfactory journal-lubrication system along these lines?

G. L. BAXTER—Yes, I do.

D. P. BARNARD, 4TH—If such a system could be made thoroughly practical, I believe that if all the oil men present at the meeting today were to urge its adoption both the operators and the oil men would benefit by it.

G. L. BAXTER—Our company is experimenting along this line and expects to be able to try out something of the sort very shortly.

R. R. MATHEWS—The work on fresh oil lubrication which you

mention was, I believe, given in a paper presented before the Society of Automotive Engineers.

D. P. BARNARD, 4TH—Yes.

R. R. MATHEWS—As I remember it, they had worked out a method of feeding fresh oil to the cylinders of the engine, after which the oil dropped into the crankcase and was circulated through the rest of the system. I was very much interested in it, because it has always seemed that we would have better piston lubrication if we could always have fresh oil on the cylinder walls. Has any effort been made to adopt this system generally?

D. P. BARNARD, 4TH—No, I don't believe so. The system to which you refer is the Madison Kipp system and, while it has been successfully applied to the larger types of industrial engines, it has up to the present time received no attention from the manufacturers of automobiles. As Doctor Mathews states, this system feeds fresh oil to the cylinders—that is, oil from a small storage tank which has not previously been in circulation in the engine. I think that this work was a revelation in that it showed what an extremely small amount of oil the cylinders of an automobile engine really require. In connection with a 4 by 5 inch truck engine I believe it was found that 15 drops a minute were sufficient to lubricate all of the cylinders at 1000 r. p. m. This is certainly a long cry from the present system in general use, which involves the throwing of oil in great quantities on to the cylinder walls.

R. R. MATHEWS—I believe that this work indicated that it was possible to keep oil consumption under control and at the same time prevent undue cylinder wear.

D. P. BARNARD, 4TH—I think it is the general experience of all those engaged in dynamometer work that an engine on the block

will show less wear for a period of operation equivalent to 100,000 miles or so than it will actually show in less than one-tenth of that mileage on the road. It is almost impossible to wear out an engine on the block where it does not have to digest the vast quantities of dirt which it must breathe on the road. The fresh oil system supplies to the cylinder oil that contains no grit, and it has been definitely proved that the life of the engine is greatly prolonged by the use of such a system. I am not sure that we oil men should agitate too strongly for the general adoption of such a system, as it is very effective in reducing the oil consumption of an engine and would therefore force us to depend almost entirely on crankcase leakage to keep up the year's volume of business. We have probably nothing to worry about for a year or two at least, as the cost of developing and putting into practice such a system for the various types of production cars would be enormous. It is doubtful if the oil saved by the prevention of excessive consumption would pay for its installation cost. From the point of view of cold-weather lubrication, however, a positive-feed oiling system to the cylinder walls has much to recommend it. I understand that quite beneficial results have been obtained by the use of a modification of this system on some automobile engines in which oil is forced to the cylinder walls when the engine is being cranked. Of course, this supply of oil takes place only when the starting pedal is depressed and as soon as the engine catches it must depend for lubrication upon its regular lubricating system. However, the small shot of oil given the cylinders during cranking period in most cases is probably just enough to prevent damage to the pistons and will lubricate them adequately until the main oiling system can come into play.

Miscible Carbon Disulfide¹

Walter E. Fleming and Reinhold Wagner

JAPANESE BEETLE LABORATORY, U. S. BUREAU OF ENTOMOLOGY, MOORESTOWN, N. J.

THE treatment of soil about the roots of nursery stock with dilute emulsions of carbon disulfide is one of the most effective methods for destroying the Japanese beetle (*Popillia japonica* Newm.) in the soil without causing serious damage to plants. A miscible carbon disulfide which has been perfected recently is equally as effective as emulsions of this compound for destroying the soil-infesting stages of the beetle. It is no more injurious to plants, and furthermore, it has certain physical and chemical advantages.

Properties

Miscible carbon disulfide is a mobile, transparent liquid with a specific gravity of 1.1156 at 15° C. It does not form a heavy foam when shaken, and it can therefore be poured easily and measured accurately in small quantities. It mixes readily with water in all proportions, forming a white emulsion. Unlike emulsions containing soap and water, it does not stratify, but remains homogeneous. It does not disintegrate under normal conditions, and it can be held at a temperature of 32° F. (0° C.) for one week without breaking down.

Ingredients

Miscible carbon disulfide is a mixture of carbon disulfide with castor oil, potassium hydroxide, denatured alcohol, and water. As it can be made satisfactorily only by using high-grade materials, it is necessary to specify carefully the quality of each ingredient.

Carbon disulfide. Use a good grade of technical carbon disulfide which contains only small proportions of free sulfur, hydrogen sulfide, sulfuric acid, or sulfurous acid.

Castor oil. Use a blown castor oil with a specific gravity be-

tween 0.991 and 1.004 at 15.5° C. This oil should have an iodine number² between 60 and 53, a saponification number³ between 205 and 216, and a titer⁴ of 3. The fatty acids of this oil should have an iodine number between 63 and 53 and an acid value between 210 and 225. An unblown castor oil cannot be used with satisfactory results.

Alcohol. Use 190-proof ethyl alcohol. Ethyl alcohol which has been completely denatured according to formula No. 1 of the United States Bureau of Internal Revenue has been found satisfactory and is recommended. This alcohol contains 10 parts by volume of methanol and 0.5 part of benzene to 100 parts of ethyl alcohol. No permit from the United States Bureau of Internal Revenue is required to handle this grade of denatured alcohol.

Potassium hydroxide. Use a high-grade potassium hydroxide. It should be at least 80 per cent pure and contain not more than 4 per cent potassium carbonate. It should be soluble in alcohol, and should have only traces of sulfates, chlorides, nitrates, or silicates.

Water. Use distilled water, rain water, or water containing not more than traces of dissolved salts. Calcium and magnesium salts are particularly objectionable.

Apparatus

The castor oil must be saponified by alcoholic potassium hydroxide in a closed kettle which is equipped with a heating device and a mechanical agitator. In the laboratory small quantities of oil have been saponified in a three-necked flask heated over a water bath. The flask was equipped with a mechanical agitator, a thermometer, and a reflux condenser to prevent loss of alcohol.

Preparation

Dissolve sufficient potassium hydroxide in a solution composed of 7 parts by volume of alcohol and 3 parts of water

² Assocn. Official Agr. Chem. Methods, p. 244 (1920).

³ *Ibid.*, p. 246.

⁴ *Ibid.*, p. 242.

¹ Received April 18, 1928. Contribution No. 40 of the Japanese Beetle Laboratory.

to give a concentration of 24.5 to 25.0 per cent potassium hydroxide. (In the laboratory an excess of alkali was dissolved in the alcohol and water, aliquot samples were taken and were standardized against a normal hydrochloric acid solution, and sufficient alcohol and water were added to obtain the proper concentration of potassium hydroxide.) Then mix 55 parts by volume of castor oil with each 10 parts of alcoholic potassium hydroxide. Close the container, start the agitator, and gradually increase the temperature to 200° F. (93.3° C.). Hold at this temperature and agitate until the alkali has reacted completely with the oil. In small batches, 2 hours at 200° F. were sufficient. Test saponification by withdrawing small samples at intervals, mixing them with half their volume of carbon disulfide, and observing their action in water. When the drop breaks into its component parts in water so that carbon disulfide settles to the bottom in droplets, saponification is not complete; when it breaks into a milky-white liquid which gradually diffuses throughout the water, the proper stage has been reached. The alcoholic soap, when completed, should have the following composition by weight:

	Per cent	Per cent
Total solids:		86.9
Castor oil	83.2	
Potassium hydroxide	3.7	
Total volatile constituents:		13.1
Alcohol	8.6	
Water	4.5	

When the alcoholic castor-oil soap has been prepared, cool it to room temperature and mix with carbon disulfide, using 35 parts by volume of carbon disulfide for each 65 parts of the soap, and stirring the mixture until it is homogeneous. Miscible carbon disulfide can be used immediately, or placed in storage in tight containers. When completed, it should have the following composition by weight:

	Per cent	Per cent
Total solids:		51.7
Castor oil	49.5	
Potassium hydroxide	2.2	
Total volatile constituents:		48.3
Carbon disulfide	40.5	
Alcohol	5.1	
Water	2.7	

The proportion of no ingredient should vary more than 1 per cent from the figure given in the formula.

Analysis

In order to assist the manufacturer in the preparation of a standard product, the following procedure is suggested as a means of analyzing the finished product. Analytical results as obtained in this laboratory are given in Table I.

Table I—Quantitative Analytical Data

ANALYSIS No. of detns.	TOTAL SOLIDS		OIL	TOTAL VOLATILE		ALCOHOL AND WATER
	KOH			CS ₂		
	12	10		12	10	10
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Maximum	52.33	2.29		49.35	41.52	
Minimum	50.65	2.00		47.67	40.20	
Average	51.86	2.10	49.76 ^a	48.14	40.59	7.55 ^a
Theoretical	51.7	2.20	49.5	48.3	40.5	7.8

^a Estimated.

TOTAL SOLIDS—Weigh a 20-gram sample of miscible carbon disulfide on an analytical balance in a glass-stoppered, flat-bottom weighing bottle, and place on a steam bath to remove the readily volatile constituents. Then place in an oven at 105° C. and dry to a constant weight.

POTASSIUM HYDROXIDE—Take a 10-gram sample of the miscible carbon disulfide, drive off the volatile constituents on a steam bath, and dissolve the residue in 500 cc. of boiling distilled water. Add 10 cc. of normal sulfuric acid and boil with vigorous agitation until the fatty acids separate

and the aqueous solution becomes clear. Allow the solution to stand overnight. Filter through a wet filter, wash the fatty acids thoroughly with distilled water, and titrate the filtrate with normal sodium hydroxide solution, using phenolphthalein as an indicator. After deducting from the total volume (cc.) of the normal sulfuric acid used the volume of normal acid neutralized by the sodium hydroxide, there is left the volume of sulfuric acid which reacted with the potassium in the castor-oil soap. The percentage of potassium hydroxide in the sample is determined by using the following formula:

$$R = \frac{M \times 0.0561 \times 100}{W}$$

where R = per cent of KOH in samples
 M = cc. of NH_4SO_4 reacting with KOH
 W = weight of sample, grams
 0.0561 = grams KOH per 1 cc. normal solution

OIL—An approximate quantitative estimation of the oil can be obtained by deducting the percentage of potassium hydroxide from the percentage of total solids in the sample, since these two ingredients, together with traces of impurities in the volatile constituents, form the non-volatile part of the miscible carbon disulfide.

The quality of the oil is determined by the characteristics of its fatty acids. Take a 0.2- to 0.3-gram sample of the washed fatty acids left on the filter paper in the potassium hydroxide determination and determine the iodine number of the fatty acids by Hanus's method.² Determine the acid value by dissolving a 2-gram sample of washed fatty acids left on the filter paper in a known excess volume of standard alcoholic potassium hydroxide, and determining the excess alkali that was added by titrating against standard hydrochloric acid, using phenolphthalein as an indicator. The milligrams of potassium hydroxide reacting with 1 gram of fatty acid is the acid value. Four samples were taken from each of two different batches of miscible carbon disulfide. The following results were obtained:

SAMPLE	IODINE NUMBER	ACID VALUE	SAMPLE	IODINE NUMBER	ACID VALUE
Batch 1			Batch 2		
1	61.0	210	1	53.9	222
2	60.7	210	2	54.1	217
3	60.0	210	3	54.1	220
4	60.0	210	4	56.0	223

Since the fatty acids of the oil should have an iodine number between 63 and 53, and an acid value between 210 and 223, it is obvious that the proper oils were used in the preparation of the material.

TOTAL VOLATILE CONSTITUENTS—Weigh a 20-gram sample of miscible carbon disulfide on an analytical balance in a glass-stoppered, flat-bottom weighing bottle, and place first on a steam bath to remove the readily volatile constituents, and then in an oven at 105° C. and dry to a constant weight.

CARBON DISULFIDE—Dilute a 10-gram sample of miscible carbon disulfide to 1000 cc. with distilled water in a volumetric flask. Take 10 cc. of this dilute solution for analysis and mix with 10 cc. of 20 per cent alcoholic potassium hydroxide. Neutralize with 50 per cent glacial acetic acid, using phenolphthalein as an indicator. Add a slight excess of solid sodium bicarbonate. Dilute to 50 cc. with distilled water, and titrate with a standard iodine solution, using starch as an indicator, until the blue color persists for 30 seconds. One cubic centimeter of the iodine solution required is equivalent to 0.0129 gram of carbon disulfide present.

The total quantity of carbon disulfide cannot be detected by the iodometric method, probably because some is absorbed by the castor oil. It has been found that the total quantity of carbon disulfide can be estimated by multiply-

ing the number of grams of carbon disulfide determined iodometrically by the factor 1.14, which was derived by dividing the weight taken by the weight recovered in a large number of laboratory tests.

ALCOHOL AND WATER—Small quantities of alcohol and water cannot be readily determined quantitatively in miscible carbon disulfide. The appearance and action of the finished product is a fair index of the proper proportions of these

ingredients. If there is too much water, the miscible carbon disulfide will be translucent; if there is too much alcohol, crystals will be formed in the transparent solution; if the proportions are correct it will remain transparent without the formation of crystals. The approximate total quantity of these ingredients can be estimated by deducting the percentage of carbon disulfide from the percentage of the total volatile constituents.

Chipping and Abrasion Tests for Paint Coatings on Metal¹

A. D. Camp

RESEARCH BUREAU, ALUMINUM COMPANY OF AMERICA, BUFFALO, N. Y.

THE selection of paints and varnishes for the finishing of furniture made of strong aluminum alloy has presented problems of a somewhat different nature from those connected with their use on articles composed of other metals and wood. Aluminum, being a silvery white metal, shows a very great color contrast between finish and metal, if the finish is scratched or worn off. Therefore, in addition to considering the color and beauty of finish, the manufacturer of aluminum furniture must select extremely tough and durable paints, which are as resistant as possible to abrasion and chipping.

A diligent search did not disclose any tests for determining those qualities which were exactly suited to our needs, so the methods in this article were developed for the purpose. These tests have been found very serviceable in studying the comparative qualities of paints obtained from different sources and applied to aluminum by different processes.

Note—Since this paper was prepared an article by Vogt [IND. ENG. CHEM., 20, 302 (1928)] has appeared, which describes a machine for testing the abrasion resistance of rubber. The operation of the paint and rubber testing machines is quite similar except that the abrading media and the test specimens exchange positions. Some of the mathematical relationships worked out for the rubber machine might be applied to the abrasion testing of paint films.

The chipping test is hardly exact enough to become a standard test for use by operators working under different conditions, but it is so simple in its application that it should become a valuable means of quickly testing the comparative toughness and adhesion of paint films. The abrasion test, on the other hand, is subject to quite exact control, and with further refinement might well become a standard test for determining the wearing qualities of applied paints. Suggestions from paint users and manufacturers will be welcomed by the author.

Chipping Test

The chipping test is made by dropping on the test panel under standardized conditions a series of standard tools, and observing the extent and character of the impression made on the coating.

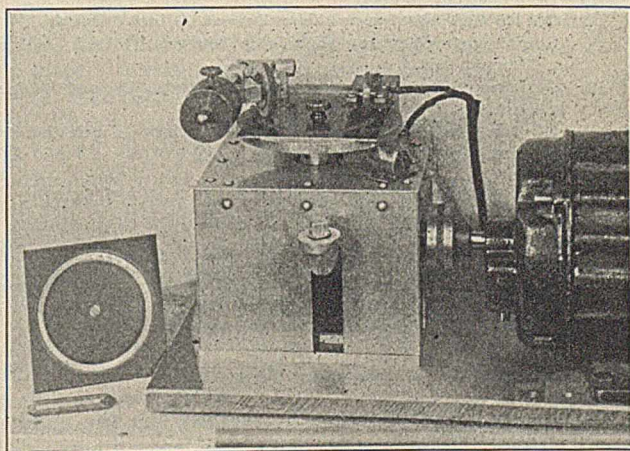
PREPARATION OF TEST SPECIMENS—Since the adhesion of paint to metal surfaces is greatly influenced by their condition before the application of paint, it is of prime importance that a standardized surface condition be adopted for all chipping tests. For aluminum a sand-blasted surface has been found to offer the best foundation for paint, so the test samples are uniformly sand-blasted on both sides. Specimens 4 inches wide by 8 inches long are amply large for both chipping and abrasion tests.

In testing paint films it is desirable to test each element of the finish separately, but since most finishes for aluminum furniture are compounds of primaries, ground coats, and

varnish, it is necessary in most instances to test the complete finish, in order to determine the durability of the finished article, as each coat added has an effect upon those immediately above and below it. In testing finishing varnishes all samples of varnish are sprayed upon uniformly applied backgrounds of primer and ground color. The comparative tests of ground colors are usually applied to primed samples prepared under standardized conditions. It is also desirable to have all paints applied, dried, and tested at the same time, since it is not always possible to duplicate conditions in different series of tests.

The thickness of all panels is measured to 0.0001 inch with vernier micrometer calipers in at least ten spots before and after painting, and the readings are recorded on the backs of the specimens, so that the thickness of the paint film at the point of chipping can be obtained. The total thickness of the paint film for the chipping test has a very great influence on the character of the chip, and for these tests it is maintained between 0.0025 and 0.0030 inch. Other things being equal, the heavier the paint film the greater is the tendency to chip.

Another factor which affects the test is the hardness or temper of the metal composing the sample panel; increasing softness of the metal greatly decreases the tendency to chip.



Courtesy of Roswell Allen
Abrasion Testing Machine

For testing the finishes of aluminum furniture, 16 gage 51 SW alloy is selected for the sample panels. This alloy has a composition of 0.1 per cent silicon, 0.6 per cent magnesium, balance aluminum, and in the heat-treated and quenched condition, denoted by the initial (W), it has a tensile strength

¹ Received April 30, 1928.

of 30,000 to 40,000 pounds per square inch, and a Brinell hardness number of 55 to 70. The thickness of the sheet also affects the results, so that uniformity in this respect should be maintained.

EQUIPMENT—The only special equipment required for the test, outside of that already mentioned, is a piece of metal tubing 24 inches long and $\frac{1}{2}$ inch internal diameter, and three tools $2\frac{1}{2}$ inches long, made of case-hardened $\frac{3}{8}$ inch diameter steel drill rod. The end of one section of drill rod is ground to a sharp edge having a face $\frac{1}{4}$ inch long and a taper angle of 77 degrees. The second tool is pointed in the same way as the first except that the edge is rounded on a $\frac{1}{64}$ -inch radius. The third tool is ground to a ball point $\frac{3}{32}$ inch in diameter. Each tool weighs approximately 1.5 ounces (43 grams), and the shapes of the points were arbitrarily selected. Some other shaped points might work better, but since the ones described above have given satisfactory results no attempt has been made to improve them.

OPERATION—After ascertaining that the thickness of the paint film on the sample to be tested is between 0.0025 and 0.0030 inch, the panel is placed flat upon a firm metal or stone table top, in such a way that the spot being tested is in perfect contact with the support. The 24-inch section of $\frac{1}{2}$ -inch diameter tubing is then erected vertically upon the sample, and the three tools are dropped through it in succession on different portions of the surface of the panel.

The impact of the "sharp" tool is naturally the most severe test, and marks or chips the paint film more or less severely in proportion to the brittleness and adhesion of the paint. The most durable paints show only a slight dent, while very brittle films show chip marks $\frac{3}{16}$ inch in diameter. The ball-pointed tool gives the least severe test, and it breaks through the films of only the most friable paint materials. By studying the marks made by the three tools under a magnifying glass, it is possible after some practice to detect rather fine differences in the resistance to chipping of different paints.

INTERPRETATION OF RESULTS—In order to obtain the best results from the chipping test, the writer has found it desirable to grade, by means of an arbitrary scale, the degree of chipping produced by each tool. It has been found that the marks can be readily divided into six grades, roughly designated as follows:

- (6) Slight dent (best)
- (5) Deep dent but no chip
- (4) Cut through paint but no chip as large as $\frac{1}{32}$ inch diameter
- (3) Cut through paint and slight chip between $\frac{1}{32}$ and $\frac{1}{16}$ inch diameter
- (2) Cut through paint and medium chip between $\frac{1}{16}$ and $\frac{1}{8}$ inch diameter
- (1) Cut through paint and large chip greater than $\frac{1}{8}$ inch diameter (worst)

The total number of points scored by a given sample in all three tests is an indication of its toughness and adhesion, and the number is called the "chipping value." When this test is used repeatedly, it is best for judging purposes to select permanent standard samples representing each grade with which each test specimen can be compared.

Abrasion Test

The abrasion test is made by determining the number of revolutions of the panel under a standard abrading disk which are required to wear through the paint film.

PREPARATION OF TEST SPECIMENS—If a sample 8 by 4 inches is prepared as described for the chipping test, one half can be cut off and used for the abrasion test. The sheet should be as nearly flat as possible and the film to be tested should be between 0.0020 and 0.0035 inch in thickness, preferably 0.0025 inch. The exact thickness of the film should be determined within 0.0001 inch. A $\frac{1}{4}$ -inch hole is drilled

in the center of the sheet for the purpose of fastening it by means of a threaded post and thumb screw to the revolving table of the testing machine shown in the accompanying photograph.

EQUIPMENT AND METHOD OF TESTING—The apparatus has a plate 5 inches in diameter, which is rotated at an approximate rate of 30 r. p. m. by means of a $\frac{1}{6}$ -horsepower 1400 r. p. m. motor, to which it is connected by a 40:1 Boston Gear Company speed-reducing unit. Resting upon the plate, and free to revolve upon an axis, is an abrading disk $1\frac{5}{8}$ inches in diameter and $\frac{1}{4}$ inch thick, made of a standard ink-eraser rubber composition. The revolving abrading disk is attached to a hinged lever arm 3 inches from the hinge or fulcrum, and it is pressed upon the test specimen under a load of 19 ounces (540 grams) consisting of a steel weight sliding upon the lever arm. In most of these tests the weight was fixed at a point 8 inches from the fulcrum. The rubber disk is set at an angle of 45 degrees to the radius of the plate, so that as the plate revolves the abrading disk sweeps across the surface and wears a path about $\frac{1}{4}$ inch wide.

The plate is supplied with a revolution counter, and the abrasion resistance of the finish is determined by the number of revolutions of the rubber disk required to wear through the paint or varnish film. For comparative purposes the observed number of revolutions is always corrected proportionally to correspond with the standard film thickness of 0.0025 inch. In order to relieve the operator of the necessity of constantly watching the test, there is attached to the machine a copper trailer wheel, which follows in the path of the abrading disk and is connected to a transformer, a circuit-breaking relay, and a standard motor starter (not shown in photo), so that when the wheel makes contact with the exposed metal at the conclusion of the test it automatically stops the motor. This attachment is not necessary to the proper working of the apparatus, but it greatly conserves the attention of the operator. Tests can be checked on the same sample within about 500 revolutions when the total number amounts to between 5000 and 8000, so that it furnishes comparisons of satisfactory accuracy on the abrasion-resistance qualities of different paints.

A fresh disk is always started with each sample, and the disks are changed at the end of each 5000 revolutions.²

INTERPRETATION OF RESULTS—When a number of paint samples are being subjected to different tests for the purpose of selecting those of greatest merit, the writer has found the point system most convenient for grading the samples, and it is suggested that the abrasion test be evaluated by giving one point for each 500 revolutions which the paint film withstands.

In selecting the most desirable finishes for furniture and other articles, the abrasion or wear resistance of the paints is a very important factor. Differences in the abrasion quality of paints of the same class and applied under identical conditions have been found ranging from 2000 to 46,000 revolutions, and the writer believes that this test furnishes extremely valuable information to the manufacturers and users of protective surface coatings.

² The disks were furnished on special order by the Eberhard-Faber Co., Brooklyn, N. Y., and the compound used is known as No. 1071.

British Low-Temperature Carbonization Project

It is announced that the British Benzole and Coal Distillation, Ltd., has been formed to take advantage of the preference given by the current budget to domestic motor fuel, that is, the tax of 4 d. per gallon which was imposed on April 25 on imported light oils. The new company proposes to install a coal carbonization plant at Bedwas, Wales, on a site leased from the Bedwas Navigation Colliery Co., Ltd., the plant to include extensive benzene and coal distillation works, as well as a benzene rectification plant and tar distillation plant.

Machine for Testing Rubber Products Used to Absorb Vibration¹

Franz D. Abbott

THE FIRESTONE TIRE & RUBBER COMPANY, AKRON, OHIO

WITHIN the last two years numerous rubber parts, other than tires and tubes, have become widely adopted in the assembly of automobiles. Virtually all of these new rubber parts are used to absorb vibration in one way or another. Nevertheless, no universally accepted laboratory tests, of significance as far as actual service conditions are concerned, have been developed.

The quality and type of rubber products for such service have generally been determined from tensile, modulus, elongation, permanent set, and hardness data. It can easily be shown that such tests not only are inadequate but may be very misleading. Furthermore, most of them cannot be made on the finished product. Although a stock possessing high tensile strength may be considered as of better quality than one possessing low tensile, in the case of rubber products used to absorb vibration there certainly is a value above which increase in tensile does not mean better quality. This is, of course, true of many other products also.

Degree of cure has a decided effect on the degree to which vulcanized rubber withstands various service conditions. Nevertheless, many properties, particularly hardness, show no decided change with relatively large variations in cure. ("Hardness" of a rubber product may be defined as the resistance which the surface layers of this product offer to indentation by a penetrating element under a predetermined load.)

It is also to be noted that motor supports, rubber spring shackles, torque insulators, balls for universal joints, and similar parts, undergo permanent set due, to a greater or less degree, to flexure under compression.

Note—In this paper any force applied toward the interior of the rubber sample will be called a "compressive load." The deflection produced by such a force will, for the sake of simplicity, be called "compression" or "compressibility." In the work on materials used to absorb vibration we are probably little concerned at present, at least, with the true compressibility of vulcanized rubber, since this is so small as to be negligible.

Although there have been static compression tests for permanent set under a definite load and also under a definite distortion, there is a lack of uniformity in procedure and in results. It is shown later in this paper that one of the most common of these tests fails to evaluate such products, and, as far as the writer is aware, no satisfactory dynamic tests have been described in the literature. Mention is made of a repeated compression test in an unsigned article,² but neither

data nor comments are given. None of the above tests simulate service conditions to any extent.

Because of these unsatisfactory conditions a new machine, called a compression flexometer, was designed, which tests the resistance of vulcanized rubber to flexure under compression.

Description of Flexometer

The compression flexometer (Figure 1) consists of a fixed bottom plate with rocker bolts hinged to it which pass through a top plate, which is attached to a driving device. By screwing

nuts down on these rocker bolts the top plate may be made to produce a compressive load on a test piece placed between the two plates. The top plate is made to oscillate at 800 cycles per minute. The oscillations are secured by setting the thrust arms off center with respect to the drive shaft. It is possible to increase the range of oscillatory movement (throw) to over 10 cm. (4 inches) overall by means of the slots cut in the eccentric collar shown at A. Tests recorded in this paper were made with a 0.95 cm. ($\frac{3}{8}$ -inch) over-all throw. The compressive load is produced by the weight of the top plate and

a component part of the thrust arms (a total of 13.6 kg. or 30 lbs.) plus that secured by tightening the nuts shown on the top plate. A standard load is chosen for a given size of test piece. The tests herein reported were run at constant distortion. For a purely technical study of rubber stocks, involving the effect of pigments and other ingredients, tests can also be made under a constant load by means of lead weights fastened to the top plate. This work will be reported in a future paper.

The duration of the tests under various conditions, although arbitrarily chosen, is such that the permanent set developed in various high-quality stocks is great enough to insure a low percentage error. Tests on materials to absorb vibration are stopped far short of complete physical breakdown or blow-out, which is, in general, an explosive rupture of the test piece due to gaseous and liquid products produced by the heat of flexure.

Method of Making Test and Calculation of Results

The test piece, which has been molded, or cut and buffed, to the desired shape and size, is carefully centered on the bottom plate of the compression flexometer. Care is taken that flexure and loading occur in the same respective directions as in service. The top is then carefully lowered onto

A machine for studying the effect of flexing rubber under compression is described. The operation of this machine in the testing of shock insulators, motor supports, and other rubber parts that absorb vibration, or undergo flexure under compression, is given in detail. Ordinary tests such as tensile and elongation are insufficient in evaluating such products. Furthermore, the more recent static compression-set test is not satisfactory. Results of tests on various stocks as given with this device check with dynamometer and service tests.

Under the conditions of test adopted the permanent set is shown to approach a maximum in 3 or 4 hours. The temperature of the test piece rapidly reaches a maximum value.

Data and curves are presented for comparison of set under flexure with tests under tension and with static compression.

¹ Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² *Rubber Age*, 20, 601 (1927).

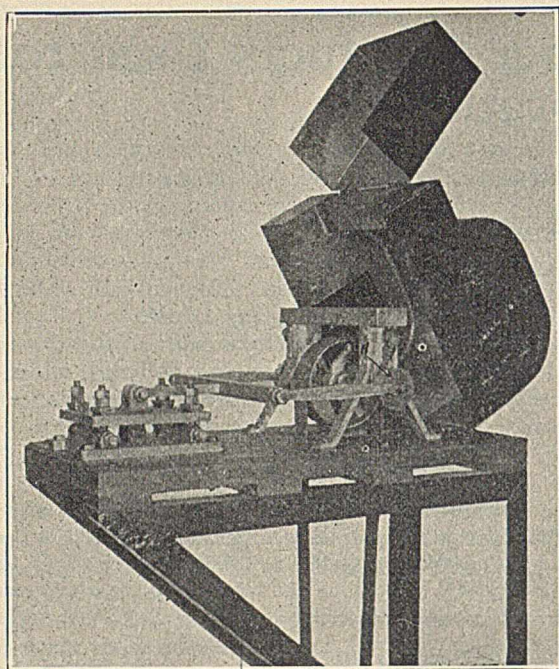


Figure 1—Compression Flexometer

the sample while the machine is at dead center. The desired compression (uniformly secured) is obtained by means of the nuts on the top plate. The flexing is then started. Ordinarily the sample is removed from the flexometer immediately at the conclusion of the flexure and allowed to cool 1 hour. The test piece is then bisected in a vertical plane in the direction of flexure. The least height of this cross section in the direction of the loading is measured. The loss in height is reported as per cent flexure-set.

With stocks of the pure-gum type virtually no set is developed under the ordinary conditions of test. In order to produce flexure-set in such stocks the severity of the test must be increased. This may be done by increasing the pressure, increasing the duration of the flexure, increasing the amplitude of flexure, or, by allowing the test piece to stand under load in the machine at the completion of the flexing. If the last method is adopted the machine should be stopped at dead center. A combination of any of these four methods is, of course, possible.

In all tests reported in this paper the samples rested on a block of oak 3.81 cm. ($1\frac{1}{2}$ inches) high. This resulted in a higher temperature (82° C. in stock No. 1, Figure 6) in the test piece than in service, but was adopted in order to accelerate the tests. Results of tests run on steel plates with resulting lower temperatures, due to conduction, will be reported in a subsequent paper, which will also include tests conducted without the top plate (zero compression).

Accuracy of Test

The accuracy obtained with this machine has been within ± 1 per cent flexure-set. A large portion of the error involved is due to the fact that no effort has been made to measure the recovered height of the sample with an accuracy greater than 1 per cent. A good idea of the accuracy can be secured from the data of Table I. If the flexure-set values of two different stocks check as close as 3 per cent, the tests should be repeated before concluding that one stock is better than the other.

The tests recorded in Table I were made on test pieces cut

from laboratory compression slabs $1.9 \times 4.15 \times 2.54$ cm. ($\frac{3}{4} \times 1\frac{5}{8} \times 1$ inch). (In giving the sizes of test pieces the width, length in the direction of flexure, and height, respectively, are stated in the order named.)

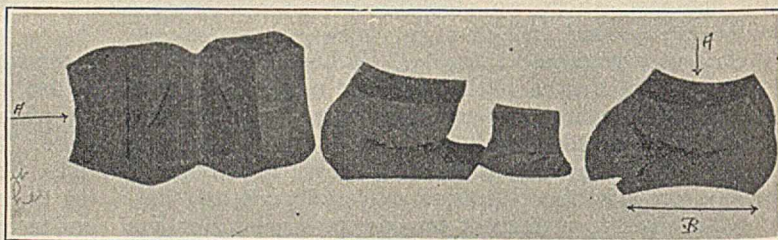
Stock	FLEXURE-SET		TIME OF FLEXURE Hours	DEFLECTION Per cent
	Sample 1	Sample 2		
8	36.0	36.0	2	55.5
3	34.4	34.4	2	50
30	29.5	31.2	2	50
1	43.1	41.7	2	50

Physical Results of Flexure under Compression

Examples of blow-out that occurred during flexometer tests on portions of a solid tire are shown in Figure 2. These test pieces measured $5.7 \times 4.4 \times 6$ cm. ($2\frac{1}{4} \times 1\frac{3}{4} \times 2\frac{3}{8}$ inches) before the test. Failure occurred in a plane almost perpendicular to the compressive load (55.25 per cent deflection). Inspection showed a number of shorter slits parallel to the main opening. All evidence seems to indicate that failure had occurred "along the grain" produced in the process of manufacture.

Less severe tests are desirable for shock insulators and other motor products used to absorb vibration. Consequently much smaller test pieces were used. Under a low compression (10 to 15 per cent) less flexure-set results over a period of several days than is secured at 50 per cent compression in an hour or two. The action in a shock insulator and certain types of motor supports can be simulated very well by proper choice of the load.

Under these less severe conditions of flexure there are produced several residual stresses in the test pieces in addition to sub-permanent set measured after 1-hour recovery. Such effects can be seen in the buckled appearance of the bisected test piece. Figure 3 shows a 1-inch ball before test (A), and after test (2 and 3). Sample 2 is a bisected ball of stock No. 2, and 3 is a bisected ball of stock No. 3. It is easily seen that stock No. 2 undergoes less flexure-set than does stock No. 3. Close inspection will show that the least distance across the cross section of 3 is considerably less than across a similar cross section taken farther from the



A—Compressive load; B—Direction of flexure

Figure 2—Examples of Blow-Out on Portions of a Solid Tire

center of the ball. This phenomenon was hardly noticeable in the case of stock No. 2, and is the best visual evidence of the stresses remaining after flexure has ceased.

Figure 4 shows a torque insulator (A), and a similar insulator (B) from which one arm has been cut for the test piece; also the test piece (C) before test, and flexed samples of stocks Nos. 2, 3, and 16. There are also shown the directions of flexure (YY') and of the compressive load (X). The line MN shows where the insulator is cut for the test piece. It is easily seen that stock No. 2 suffered less flexure-set than either No. 3 or 16, and also gives evidence of less residual stresses ("buckled" to a less degree).

Figure 5 further illustrates the effects of flexure under compression. Stock No. 14, a so-called pure gum, showed

zero flexure-set. Stock 15 showed 45 per cent. This test piece suffered blow-out, so was not bisected. Blow-out had relieved the stresses that would otherwise have remained after flexure.

Table II gives general data pertaining to the types of test pieces shown in Figures 3 to 5, inclusive.

Table II—Test Data for Different Test Pieces

FIG-URE	PART	SIZE OF TEST PIECE	DEFLECTION (LOAD)		TIME OF FLEXURE	
			Per cent	Minutes	Per cent	Minutes
3	Ball (for universal joint)	2.54 cm. (1 in.) diam.	50	45		
4	Torque insulator	2.54 × 3.2 × 3.5 cm. (1 × 1¼ × 1⅜ in.)	54	105; stood 60 min. under load		
5	Laboratory compression slab 1.9 cm. thick	1.9 × 4.15 × 2.54 cm. (¾ × 1⅝ × 1 in.)	50	120		

Effect of Various Factors on Flexure-Set

TIME OF FLEXURE—Flexure-set rapidly approaches a maximum as the test progresses. Temperature rises even more rapidly and probably influences to a considerable ex-

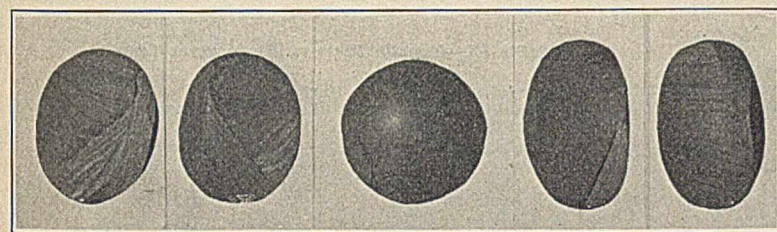


Figure 3—Effect of Flexure of Rubber Ball

tent the slope of the flexure-set-time curve. This is seen by comparing curves I and II, respectively, of Figure 6. The data for the temperature-rise curve (II) were obtained on the 210-minute test (Table III). A copper-constantan thermocouple was inserted in a narrow horizontal slit near the bottom of the test piece before its assembly in the flexometer. Readings on the potentiometer were taken every few minutes for 2 hours.

The data for tests included in curve I are given in Table III. Flexure was at 55.5 per cent compression on test pieces cut from two insulators of stock No. 1, cured 70 minutes at 148° C.

Table III—Effect of Duration of Flexure

TIME OF FLEXURE	FLEXURE-SET	TIME OF FLEXURE	FLEXURE-SET
Minutes	Per cent	Minutes	Per cent
5	12.4	60	36.2
15	23.5	120	43.1
30	30.6	210	44.4

STATE OF CURE—Decided undercure results in a high flexure-set. As the time of cure progresses the resistance to flexing under compression increases. Flexure-set approaches a minimum, as evidenced by the fact that overcures were found to show high flexure-set again. Curve I, Figure 7, shows that flexure-set decreases as the state of cure progresses. The tests were of 1-hour duration on test pieces from shock insulators cured 65, 70, 75, and 80 minutes at 148° C. (stock No. 1) Curve II shows flexure-set resulting from 2 hours' flexure for the same cures. The 2-hour test is too severe to differentiate between the lower cures, but does show the 80-minute cure to be decidedly better than the others. Nevertheless, it has the advantage that all products showing a greater flexure-set than a "standard" adopted value based on this duration are eliminated and a high-quality product is thus assured. The data for these tests

are given in Table IV. Flexure was at 55.5 per cent compression.

Table IV—Effect of Cure

CURE AT 148° C.	FLEXURE-SET	
	1 Hour	2 Hours
Minutes	Per cent	Per cent
65	40.2	43.1
70	36.2	43.1
75	33.3	43.1
80	26.4	33.3

HARDNESS—Hardness is no indication of the resistance of a stock to flexure under compression, as shown by the data in Table V. Motor part 1 had been cured to the proper state of cure as determined by service and by flexure-set data. Motor part 2, of a different size but similar shape, was also cured to the proper hardness values. The test pieces were flexed for 2 hours under 55.5 per cent distortion. All test pieces were 1.43 × 3.8 × 2.86 cm. (9/16 × 1½ × 1⅜ inches). In every case motor part 2 showed excessive flexure-set. These data show the fallacy of using hardness data to indicate that cure which gives the greatest resistance to dynamic fatigue.

Table V—Effect of Hardness

STOCK	MOTOR PART 1		MOTOR PART 2	
	Hardness ^a	Flexure-Set	Hardness ^a	Flexure-Set
	Unit	Per cent	Unit	Per cent
3	49	19.4	51	27.8
4	51	16.7	53	35.0
6	54	25.0	58	41.7
7	54	19.4	56	38.8
8	53	19.4	52	36.0
9	41	27.8	41	38.9

^a Data by Firestone penetrometer.

COMPRESSIBILITY (DEFLECTION)—Data on the deflection of a test piece of standard size by a given compressive load fail to furnish a satisfactory indication of resistance to flexure. (Table VI) In these tests disks 1.9 cm. (¾ inch) in diameter were cut from a slab of 0.63-cm. (¼ inch) gage. These were then subjected to a load of 42.18 kg. per sq. cm. (600 pounds per square inch). Stock No. 4 shows the greatest resistance to flexure, yet it stands about midway in order of compressibility (column 2, Table VI). On the contrary, stock No. 7 shows the greatest deflection but stands midway in order of resistance to flexure under compression.

STATIC-SET AND HYSTERESIS LOSS UNDER COMPRESSION—Permanent set under simple compression does not check with flexure-set, whereas hysteresis loss does give a quite

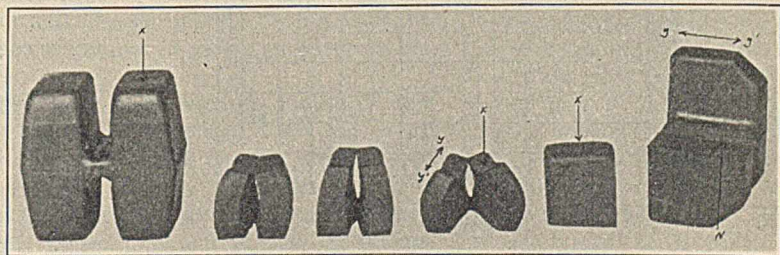


Figure 4—Torque Insulator and Flexed Samples of Stocks Nos. 2, 3, and 16

satisfactory indication of resistance to dynamic fatigue. Some data comparing these tests are given in Table VII. Each stock is seen to stand in the same relation to the others, whether flexure-set or hysteresis data are considered. Static-set (permanent set under static compressive conditions) data are far out of line. The hysteresis values were determined by getting the load-deflection data on circular disks 1.9 cm. in diameter and 0.63 cm. thick. The maximum load was 42.18 kg. per sq. cm. The initial deflection at this

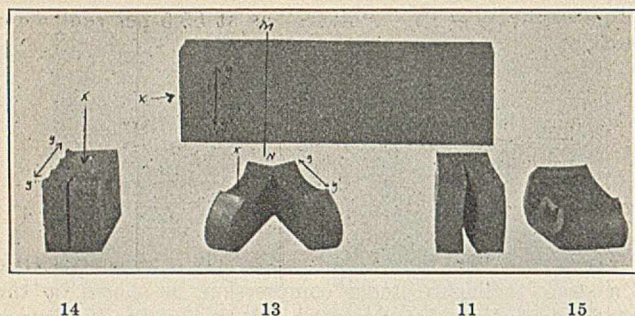


Figure 5—Effect of Flexure of Laboratory Samples

load is given in column 5, Table VII. (A full report of this work together with a description of the instrument designed to study hysteresis loss and permanent-set under either constant deflection or a constant load, will be given in a subsequent paper.) Static-set tests were made on similar disks under the distortion secured by a load of 42.18 kg. per sq. cm. Tests were conducted in an oven at 82° C. for 24 hours.

Table VI—Compressibility vs. Flexure-Set

STOCK	DEFLECTION AT 42.18 KG./SQ. CM.	ORDER OF INCREASING DEFLECTION	FLEXURE-SET Per cent	ORDER OF INCREASING FLEXURE-SET
	Per cent			
3	21.1	4	19.4	2
4	18.5	2	16.7	1
6	19.9	3	25.0	3
7	22.7	5	19.4	2
8	20.5	3	19.4	2
9	14.0	1	27.8	4

Table VII—Hysteresis Due to Compression vs. Flexure-Set

STOCK	STATIC-SET	FLEXURE-SET	RELATIVE HYSTERESIS LOSS	DEFLECTION AT 42.18
	Per cent			Per cent
3	14.5	30	5.85	33.7
10	14.2	21.9	4.8	37.5
11	26.0	10.0	..	51.8
12	14.8	11.0	3.95	43.0
14	8.9	0	3.00	45.0
15	..	45.0	10.55	..

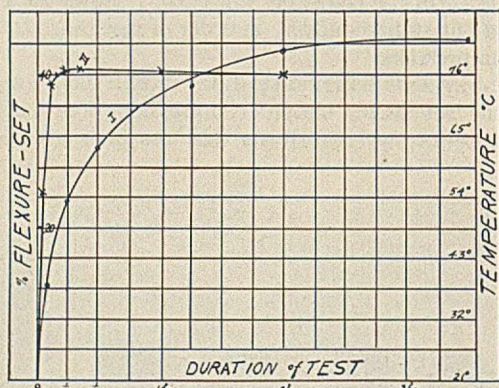


Figure 6

FLEXURE-SET VS. TENSILE STRESSES, ULTIMATE ELONGATION, AND SET AT BREAK—The ordinary data from tests under tension also fail to evaluate satisfactorily the resistance of stocks to flexure under compression. Comparisons of some of these data with flexure-set are given in Table VIII.

Table VIII—Tensile Tests vs. Flexometer Tests

STOCK	ULTIMATE ELONGATION Per cent	STRESS AT 400%		ULTIMATE TENSILE		SET AT FLEXURE-SET	
		Kg./sq. cm.	Lbs./sq. in.	Kg./sq. cm.	Lbs./sq. in.	Per cent	Per cent
		3	580	116	1660	217	3100
4	550	103	1480	166	2370	31	16.7
6	560	92	1310	140	1990	50	25
7	560	94	1340	160	2270	32	19.4
8	500	128	1830	180	2560	40	19.4

It will be noted that the values for ultimate elongation are alike within experimental error (with the possible exception of stock No. 8). Set at break (the increased distance between two marks originally 1 inch apart, measured 10 minutes after the dumb-bell strip has broken) likewise fails in evaluating these stocks. Ultimate tensile likewise is of little value for this purpose. It is to be noted that stock No. 3 possesses the highest tensile (217 kg. per sq. cm.) but suffers a higher flexure set (19.4 per cent) than does stock No. 4, which has an ultimate tensile of only 166 kg. per sq. cm.

At the other extreme is stock No. 6 with the lowest ultimate tensile (140 kg. per sq. cm.), which also shows a still higher flexure-set. Similar discrepancies are to be noted in the case of moduli. Stock No. 3 with the second highest stress at 400 per cent elongation (116 kg. per sq. cm.) and stock No. 6 with the lowest stress at 400 per cent elongation both suffered greater flexure-set than stock No. 4, which possessed an intermediate value for the stress at 400 per cent elongation and also the lowest flexure-set. Table IX shows to much better advantage how poorly data of tests under tension evaluate the above stocks as to their resistance to dynamic fatigue.

Table IX—Tensile Tests vs. Flexometer Tests

STOCK	ULTIMATE ELONGATION	STRESS AT 400% ELONGATION	ULTIMATE TENSILE	SET AT BREAK	FLEXURE-SET
	Per cent	Kg./sq. cm.			
10	620	95	222	37	21.9
11	650	61	200	..	10
12	619	85	188	34	11
13	480	29	65	22	37.5
15	425	155	200	25	45.0

REPEATED-STRETCH SET—Set after repeated elongation does not help in the evaluation of stocks as to their resistance to flexure under compression. It was believed that this test, although under tension instead of compression, might properly evaluate stocks. This certainly should be the case if we believe the same as do Gottlob³ and others.⁴ The data in Table X show conclusively that set after repeated stretch under either constant load or constant distortion does not check set resulting from repeated flexure under compression.

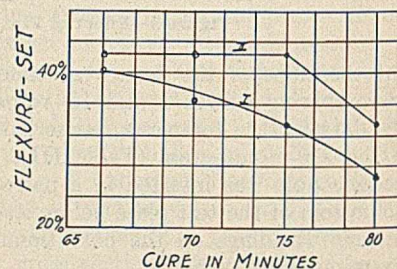


Figure 7

Table X—Set Due to Repeated Stretch vs. Flexure-Set

STOCK	SET DUE TO REPEATED STRETCH		FLEXURE-SET
	Constant load	Constant distortion ¹	
3	20	..	20.0
10	22	15	21.9
11	22	14	10.0
12	20	20	11.0
13	^a	^a	37.5
15	32	^b	45.0

^a Broke during first elongation.

^b Broke during second elongation.

Determination of Stretch under Constant Load—A dumb-bell test strip was stretched five times in a tensile machine at 51 cm. per sec. (20 inches per minute) to 70.3 kg. per sq. cm. (1000 pounds per square inch). The interval between extensions was only that necessary for the machine to reverse. After the fifth return the strip was removed and allowed to recover for 1 hour. Permanent set was measured as the increased distance between two marks originally 2.54 cm. (1 inch) apart.

³ "Technology of Rubber," pp. 199 and 202, English ed., 1927.

⁴ Davies and Norton, *India Rubber J.*, 59, 833 (1920).

FLEXURE-SET VS. DYNAMOMETER TESTS—Flexure-set results check dynamometer tests very satisfactorily.

Dynamometer Tests—Sixteen balls are assembled in a universal drive unit, each under approximately 21.65 kg. (50 pounds) compression. The alternate balls seem to carry practically the whole load of running at 1500 r. p. m. under a torque of 8.9 kg.-meters (64.5 foot-pounds). The generator shaft is at a 5-degree angle to the drive shaft. The test is stopped when the drive unit becomes loose.

It will be noted from the data in Table XI that stock No. 2 in each instance shows a greater resistance to fatigue resulting from flexure under compression than does stock No. 3. These data are typical of the results with other stocks.

Table XI—Dynamometer Test vs. Flexure-Set

Stock	DYNAMOMETER TEST Duration Hours	Condition of ball	FLEXURE-SET		
			Ball for universal joint Per cent	Torque insulator Per cent	1.9-cm. compression slabs Per cent
3	26 ^a	High set, very poor	37.5	31.8	30
2	32 ^{1/4} , 38 ^{1/4} ^b	No set, bad	15.6	20.4	12

^a At 3.5-degree angle of drive.

^b At 5-degree angle of drive.

The fact that flexure-set results for stock No. 2 (or No. 3 as the case may be) do not check within themselves does not discredit the flexometer test. On the contrary, the fact that two stocks line up in the same order although tests were conducted on different volumes and shapes of test pieces as well as under different deflections and different durations of test (Table II), seems an important point in favor of the flexometer test.

Summary

Data have been presented to show that the commonly used physical tests such as stress at break, stress at 400 per cent elongation (modulus), ultimate elongation, set at break, set after repeated stretch, and static compression-set fail to evaluate properly the resistance of vulcanized rubber to dynamic fatigue of flexure under compression, whereas flexure-set as determined in a new machine (the compression flexometer) herein described does evaluate stocks properly as determined by service and dynamometer tests. Accordingly, resistance to flexure under compression (dynamic fatigue) is suggested as a much more important property of rubber products used to absorb vibration under compression than any of the above-mentioned tests.

Jelly-Strength Measurements of Fruit Jellies by the Bloom Gelometer¹

Carl R. Fellers and Francis P. Griffiths

DEPARTMENT OF HORTICULTURAL MANUFACTURERS, MASSACHUSETTS AGRICULTURAL COLLEGE AND EXPERIMENT STATION, AMHERST, MASS.

THE need of an instrument for giving reasonably accurate and reproducible measurements of the jelly strength of jellies has long been recognized.^{2,3,4} Bogue³ described the several types of instruments in use prior to 1922 for testing gelatin and glue products. Sucharipa,⁴ also Baker⁵ and Tarr,⁶ described instruments involving the use of water or air pressure for the testing of pectin jellies. Tarr stated that he found no instrument used for the measurement of gelatin or glue adaptable to pectin jellies.

The Bloom gelometer⁷ as originally described by Richardson⁸ has been used in our laboratory for two years for making jelly strength determinations on fruit jellies, jams, and similar products. It has also proved useful in

With a few minor modifications the Bloom gelometer was found to be very satisfactory for the determination of the jelly strength of fruit jellies and similar products. Jellies may thus be standardized as to consistency within relatively narrow limits. This is of particular significance in the manufacture of jellies and similar products as well as in the grading of commercial pectins.

Jellies for testing should be sealed, stored for at least 24 hours, and tested at a constant temperature, preferably from 20° to 23° C. Weak jellies set more slowly than firm ones. The greater part of the change occurred during the first 24 hours. Jelly strengths decreased with rise in temperature. Owing to skin effect on the surface, uncovered jellies gave unreliable readings.

Considering both top and bottom readings the average per cent deviation of twenty-two series of samples, ranging from very weak to very strong, was approximately 5 per cent.

Jellies of good organoleptic qualities, consistency, and texture usually tested between 60 and 100 grams and strained cranberry sauce tested between 140 and 180 grams.

evaluating the jelly-making quality of fruit juices and commercial pectins. A description of its adaptation and use for the measurement of the jelly strength of fruit jellies should prove of value to both laboratory workers and manufacturers.

The Bloom gelometer is already a standard instrument for the measurement of edible gelatin,⁹ this product being usually sold on the basis of jelly strength as measured by this instrument. The latter may be purchased together with the chill bath required for gelatin testing from the secretary of the Edible Gelatin Manufacturers' Research Society of America.

Operation of Instrument

Three modifications in operation were found necessary in order to adapt the instrument to the testing of fruit jellies: (1) The distance of travel of the plunger was increased to 5 mm. (2) The heavier metal cup receiving the shot was replaced by a light paper cup. (3) The rate of inflow of the shot was adjusted to 100 grams in 10 seconds when the lever arm E_1 was on the second dog from the bottom. (Figure 1)

⁹ Edible Gelatin Manufacturers' Research Society of America, "Standard Methods for Determining Viscosity and Jelly Strength of Gelatin," 1457 Broadway, New York, N. Y.

¹ Received May 2, 1928. Contribution No. 78, Massachusetts Agricultural Experiment Station.

² Paine, *Am. Food J.*, **17**, No. 3, 11 (1922).

³ "Chemistry and Technology of Gelatin and Glue," p. 369, McGraw-Hill Book Co., New York, 1922.

⁴ "Die Pektinstoffe," p. 81, Serger & Hempel, Braunschweig, 1925.

⁵ *IND. ENG. CHEM.*, **18**, 89 (1926).

⁶ *Del. Agr. Expt. Sta., Bull.* **142** (1926).

⁷ U. S. Patent 1,540,979 (1925).

⁸ *Chem. Met. Eng.*, **28**, 551 (1923).

Table I—Accuracy of Jelly-Strength Measurements

No.	No. of Samples	MEAN JELLY STRENGTH		PROBABLE ERROR OF MEAN		AVERAGE DEVIATION FROM MEAN				JELLY	APPARENT CONSISTENCY
		Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom		
		Grams	Grams	Grams	Grams	Grams	Grams	Per cent	Per cent		
1	24	69.0	74.5	0.75	1.5	3.1	4.7	4.5	6.3	Apple	Slightly soft
2	10	119.0	79.5	2.5	1.5	9.9	4.0	8.3	5.1	Apple	Firm
3	12	90.5	82.0	2.0	2.0	6.4	6.9	7.1	8.4	Apple	Firm
4	12	31.0	...	0.5	...	1.6	...	5.2	...	Cranberry-apple	Very soft
5	4	107.5	107.0	3.4	3.6	3.1	3.3	Pectin	Firm
6	3	273.5	303.5	10.5	5.3	3.8	1.7	Pectin	Very firm, rubbery
7	19	91.0	98.5	1.0	1.5	4.3	6.2	4.7	6.3	Pectin	Firm
8	16	269.5	280.1	2.0	3.0	7.2	11.7	4.3	4.2	Pectin	Very firm
9	26	47.0	...	0.75	...	3.9	...	8.3	...	Cranberry sauce	Very soft
10	22	97.0	77.0	1.5	1.0	7.8	5.5	8.0	7.1	Cranberry sauce	Slightly soft
11	18	111.5	97.5	1.0	0.5	4.9	2.3	4.4	2.4	Cranberry sauce	Slightly soft
12	16	86.0	51.5	1.5	1.5	6.6	6.2	7.7	12.0	Cranberry sauce	Soft
13	9	96.5	57.0	1.0	2.0	3.7	7.3	3.8	12.8	Cranberry sauce	Slightly soft
14	21	134.5	108.0	1.0	1.0	5.0	3.7	3.7	3.4	Cranberry sauce	Firm
15	9	142.0	107.0	1.0	2.0	3.3	7.0	2.3	6.6	Cranberry sauce	Firm
16	12	144.5	114.0	1.5	1.5	5.2	6.0	3.6	5.3	Cranberry sauce	Firm
17	21	177	156.5	1.5	1.5	6.9	6.0	3.6	5.3	Cranberry sauce	Firm
18	18	173.5	152.0	1.0	1.0	3.9	4.4	2.25	2.9	Cranberry sauce	Firm
19	20	225.5	201.0	1.5	2.0	6.5	9.0	2.9	4.5	Cranberry sauce	Very firm
20	19	218.0	195.0	1.5	1.5	6.1	6.3	2.7	3.2	Cranberry sauce	Very firm
21	13	227.0	205.0	1.5	2.0	7.0	4.6	3.1	2.2	Cranberry sauce	Very firm
22	12	249.0	228.5	2.0	2.0	6.1	8.5	2.1	3.7	Cranberry sauce	Very firm, rubbery
Av.	15			1.4	1.7	5.6	6.0	4.5	5.3		

For use the contact disk *B* is adjusted by means of spring *F*, so that it just touches the point *A*₂ when the carrier *H* is empty. The cup *K* is then placed on *H* in position to receive the shot and the jelly sample placed on stand *N*, and racked up by means of knobs *O*₁ and *O*₂ until the contact disk *B* touches the upper point, *A*₂. If the arm *E*₁ is now raised, shot pours into the cup from the mouth *E*₂ until the plunger *L* is forced by the weight of the shot 5 mm. into the jelly. Contact is again made by disk *B* with the lower point *A*₂ and the flow of shot automatically shuts off. The cup *K* and its contents are then weighed, this weight being jelly strength or resistance in grams offered by the jelly to plunger *L* during its 5 mm. of travel.

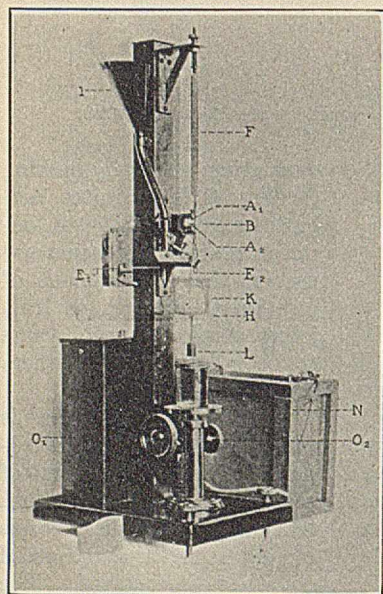


Figure 1—Bloom Gelometer as Modified for Testing Fruit Jellies

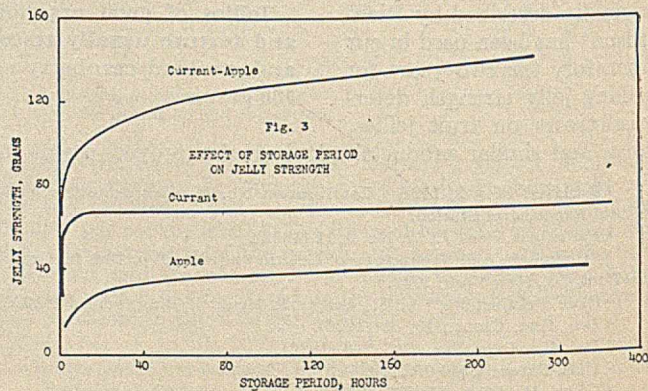
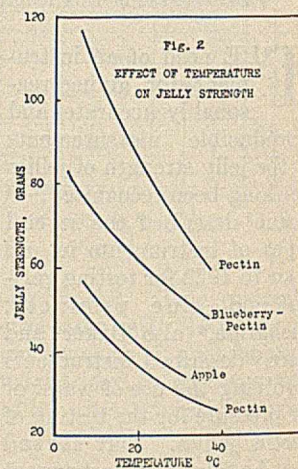
The rate of inflow of the shot is important and in all experiments was kept constant by raising the lever arm *E*₁ to the second dog. The rate of flow should be very close to 100 grams of shot in 10 seconds. The amount of shot in the hopper *l* should be kept nearly constant because variations in head cause differences in the rate of flow.

In a weak jelly the weight of the metal cup caused the plunger to penetrate the jelly before an accurate measurement could be made. For this reason it was found advisable to replace the metal cup with a light paper one and to make the time elapsing between raising the jelly into contact with the plunger and the moment of inflow of shot as short as possible. In work with the instrument, jellies were tested ranging in strength from very weak (30 grams) to very tough and rubber-like (200 to 280 grams). Strained cranberry sauce, a product which is very similar to a jelly was also tested over a range from 47 to 250 grams. At least three samples of each jelly were tested in 2-ounce (57-gram) straight-walled glasses

having an inside diameter of 3.5 cm. and an inside height of 6 cm. In testing the bottom the jelly was carefully removed by loosening with a thin blade or spatula, inverted, and replaced in the glass. The conditions of testing of the top and bottom were therefore comparable. The best fruit jellies usually gave values between 60 to 100 grams, while the best cranberry sauces varied from 140 to 180 grams. Pure fruit jellies and jams varied widely in jelly strength with the method of preparation, variety, and character of the fruit.

Effect of Temperature on Jelly Strength

A number of tests were made on fruit jellies held at different temperatures to determine the effect of temperature of testing on the jelly-strength reading. Figure 2 shows that the jelly strength decreased rather uniformly with increasing temperature between 10° and 30° C., the decrease being approximately 1 gram per degree. Although gelatins are tested with a Bloom gelometer at 10° C. using a specially designed chill bath, this was found to be unnecessary for ordinary work in the case of fruit or pectin jellies. Jelly strength determinations were made at 20° to 23° C. Corrections may be made for slight differences in temperature. For refined and exacting results the use of a chill bath is desirable.



Effect of Storage Period on the Jelly Strength

Jellies increased in strength with length of storage, as shown by Figure 3. A storage temperature of 23° to 25° C. was used and all jellies were paraffined within a few minutes after filling the glasses. The maximum change occurred very soon after making, but a gradual increase took place over a period of several days. This confirms Tarr's⁶ work. It is recommended that jellies be allowed to stand at least 24 hours before testing. Weak jellies were found to set more slowly than firmer ones, but the changes taking place after 24 hours were usually slight.

Contrary to Tarr,⁶ it was found that the surface of uncovered jelly toughened very noticeably on standing. This skin effect or surface hardening became evident as soon as the jelly cooled and increased as long as the jellies remained uncovered. In order that an accurate determination could be made it was found necessary to cover the surface of the jellies with melted paraffin or a hermetic seal soon after making. To illustrate, a current jelly was prepared in the regular 2-ounce (57-gram) jelly glasses. One-half of these were paraffined at once while the rest remained uncovered. After 4½ hours the paraffined jelly tested 93 grams while the uncovered tested 147 grams. After 52 hours' storage at 23° C.

the readings were, respectively, 131 and 174. In every case uncovered jellies showed this surface hardening effect.

Limits of Accuracy of Instrument

Table I shows the results obtained from a large number of determinations. The probable error or the mean of any series of determinations was found in all cases to be within ±3 grams. This was calculated according to the formula:

$$P. E. = 0.6745 \sqrt{\frac{\sum d^2}{n^2}}$$

where P. E. is probable error of the mean, $\sum d^2$ is equal to the summation of the squares of the individual deviations from the arithmetical mean, and n equals the number of determinations.

Considering both top and bottom readings in Table I, the average per cent deviation of twenty-two series of samples was approximately 5 per cent. There was little difference in accuracy between series run on the bottom or on the top of jellies. The jelly strength of the bottoms of the samples of apple jellies and cranberry sauces were usually less than those of the tops. The reverse was found to be the case with artificial pectin jellies. For practical purposes it is not considered necessary to test the bottom of jelly samples.

Note Concerning Thermodynamic Calculations¹

David F. Smith

PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, PITTSBURGH, PA.

INTEREST recently attaching to the thermodynamic properties of hydrocarbons and alcohols makes it desirable to attempt to clear up some apparent misunderstandings which the writer's paper² on the subject seems to have caused. Two interesting articles by Francis³ have since appeared in which the free energies of various hydrocarbons and alcohols have been estimated. The present writer wishes to commend these efforts to present the best available thermodynamic data, uncertain though they may be, in a form that makes them usable for those who would not take the trouble to search the literature, make the calculations, and correlate the data for themselves. Although many of the data that Francis uses are admittedly but rough approximations, his free-energy equations, especially in cases like CH₄, C₂H₂, and C₂H₄, in which some equilibrium data are available, do represent in condensed and usable form such probable thermodynamic properties as are known. If a free-energy equation is consistent with such experimental work as has been done, it is a very concise and convenient representation of the known facts.

However, even when one has reliable thermodynamic data, the story is but incompletely told. Although the thermodynamic facts cannot be violated, after all, the rate of reaction is ultimately the determining factor for practical purposes. For example, Francis³ thinks that the chance of forming benzene from water gas, although thermodynamically quite possible, is small in comparison with that of forming the more stable hydrocarbons and alcohols. However, in spite of the fact that benzene is highly unstable thermodynamically with respect to decomposition into its elements, it is nevertheless a major product from high-temperature distillation processes. Again, although thermodynamically

more stable at lower temperature with respect to such decomposition, benzene does not appear in low-temperature coal tar. In the Fischer process for synthesis of hydrocarbons from water gas, it has been shown⁴ that ethylene is produced in quantities quite comparable to those of ethane, which is far more stable with respect to decomposition into carbon and hydrogen at the temperatures at which this process is carried out. In these cases we see that the rate of reaction is an important factor. Thus the fact that a certain hydrocarbon is far less stable with respect to decomposition into its elements than is another does not necessarily prevent its predominance when formed from other than its elements, for example, from carbon monoxide and hydrogen, as in this case. Although the writer is not recommending that anyone attempt to produce benzene from water gas, such a process does not seem impossible. As far as requiring six carbon atoms (at least 6CO) for its synthesis from water gas, it is known that higher hydrocarbons (containing twenty or more carbon atoms per molecule), which have a great thermodynamic tendency to decompose into their elements or into lower hydrocarbons, are readily formed from water gas. The thermodynamic tendency to form a given hydrocarbon from carbon monoxide and hydrogen is in general quite different from that to form the hydrocarbon from its elements. If the rate of forming the hydrocarbon from water gas is rapid compared to the rate at which it decomposes into its elements under the same conditions, its formation in this way is quite feasible, irrespective of any considerations as to the inherent instability of the product.

The thermodynamic tendency for a reaction to take place depends in part upon the prevailing conditions of concentration. There is perhaps room for a choice of the conditions to be taken as a standard for comparison. The writer prefers, however, to refer to the conditions that have

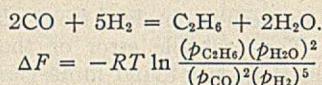
¹ Received April 30, 1928. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

² IND. ENG. CHEM., 19, 801 (1927).

³ *Ibid.*, 20, 277, 283 (1928).

⁴ Smith, Davis, and Reynolds, IND. ENG. CHEM., 20, 462 (1928).

been fairly generally accepted as standard—that is, where all substances involved are at the standard pressure (more strictly, fugacity) of 1 atmosphere. To take a particular case, consider the reaction



represents the maximum work obtainable (free-energy increase) in the reversible formation of 1 mol of C_2H_6 at a pressure of 1 atmosphere when each of the substances involved is maintained at the beginning and throughout the process at a constant pressure of 1 atmosphere. This free-energy increase is then a measure of the tendency for this reaction to take place. It is true that in practice a process such as this in which the pressures of all the substances involved are 1 atmosphere at the beginning and throughout the process would never be encountered. But this, nevertheless, is the process the writer has chosen to consider as a standard for comparison, and this is the general practice in thermodynamic considerations. Thus, when the value of the constant of the reaction, K , is larger, the thermodynamic tendency for the reaction to take place is greater. And, although in forming a mol of one hydrocarbon the molal proportions of reactants and resultants required are different from those required for another hydrocarbon, all the free-energy quantities that have been compared refer to the formation of 1 mol of hydrocarbon from the same reactants and resultants at the same partial pressure. The actual processes corresponding to given free-energy changes are set forth especially clearly by Noyes and Sherrill.⁵

The statement in the first conclusion of the writer's paper² concerning the relative tendencies for different hydrocarbons to form from water gas, of course, refers to the temperature

⁵ "Chemical Principles," The Macmillan Co., New York, 1922.

range considered (0° to 400° C.). Table I in that paper clearly shows that the temperature coefficients of the different reactions are different. A relation between the equilibrium constants of the different reactions, which holds for one temperature range, may not hold for another.

In conclusion, a few minor errors in Francis' paper³ should be pointed out. It is inconsistent to use the present writer's value for the free energy of ethane, which was derived from his value for methane, unless the latter value is accepted. This, however, makes an error of but about 500 calories, which, in comparison with the reliability of some of the other data used, is perhaps not important.

Francis³ erroneously compares his value for methane (gas, 1 atmosphere) with Parks and Kelley's value for methane (liquid, 1 atmosphere) which was derived from Lewis and Randall's⁶ value for methane (gas, 1 atmosphere). The vapor pressure of (hypothetical) liquid methane at 25° C. and 1 atmosphere would, of course, not be 1 atmosphere. Francis' statement that "practical pressures will not usually overcome an unfavorable free-energy change of more than 5000 calories" is rather loose. The effect of pressure depends upon the magnitude of the decrease in volume accompanying the reaction. As a matter of fact, the synthesis of methanol from carbon monoxide and hydrogen is carried on at temperatures where the free energy increase at standard pressure is over 9000 calories.⁷ It must be admitted—and this is a criticism that applies to certain of the writer's own calculations as well as to those of Francis—that, as has been shown frequently in the past and as will be shown again in a paper soon to appear from this laboratory, free-energy values calculated on the basis of rough approximations to and extrapolations of thermal data are often quite erroneous.

⁶ "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

⁷ Lewis and Frolich, *IND. ENG. CHEM.*, **20**, 285 (1928).

Use of Buffers in the Determination of Color by Means of Titanium Trichloride¹

I—Amaranth, Ponceau 3R, and Orange I

O. L. Evenson and D. T. McCutchen

COLOR CERTIFICATION LABORATORY, FOOD, DRUG, AND INSECTICIDE ADMINISTRATION, DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

THE original method for the evaluation of color in azo dyes by means of titanium trichloride was formulated by Knecht and Hibbert.² The hot-water solution of the dye was reduced in the presence of hydrochloric acid, Rochelle salts, or sodium bitartrate, in an atmosphere of carbon dioxide.

For some time this laboratory has carried out the titration of Amaranth (Colour Index 184) in the presence of hydrochloric acid. This method was found objectionable, however, for three reasons: (1) The end point is not sharp; (2) results tend to be slightly low, owing, in small part at least, to fading of the dye in acid solution; (3) it does not permit accurate or convenient evaluation of total color in mixtures of Amaranth with other dyes which cannot, or can only with difficulty, be titrated in acid solution. In an attempt to obviate the necessity of using acid, the titration of Amaranth in the presence of various buffers (or catalyst-buffers) was

investigated. On obtaining good results in these determinations, the experiments were extended to other dyes.

Materials

Commercial samples of dye of certified grade were used, the analysis being made according to the methods prescribed for color certification.³

The following salts were tried as buffers: Rochelle salt, sodium bitartrate, calcium carbonate, sodium acetate, sodium tartrate, sodium citrate, potassium antimony tartrate, and sodium bicarbonate. These were of commercial c. p. grade as obtained from several sources.

The 0.1 *N* titanium trichloride used was standardized with a ferric sulfate solution made from pure ingot iron.³ This result was checked by standardization against sodium oxalate.³ The titanium solution was 1.4 *N* with respect to the hydrochloric acid present.

Procedure

The buffer salt, in the quantity to be used, was dissolved in water by heating to boiling in a wide-mouth Erlenmeyer

¹ Presented before the Division of Dye Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., New York, 1918.

³ U. S. Dept. Agr., *Bull.* **1390**, revised (1928).

flask. The dye solution was then added and the contents of the flask again brought to boiling. The total volume in the flask was in all cases 100 cc. when titration was begun. While the titration mixture was kept in an atmosphere of carbon dioxide, the reducing solution was introduced at such speed as it reacted with the dye until near the end, then drop by drop to end point. During the addition of the titanium trichloride the flask was continuously shaken.

Results

Before any value can be placed on the results of a volumetric determination for color, they must be consistent for varying concentrations of dye in the flask and for different quantities of buffer; they must also agree closely with the "color by difference" wherever complete analysis can be made.

The titration values for Amaranth when determined in the presence of Rochelle salts, sodium bitartrate, or sodium tartrate were very erratic. (Table I) The results obtained using calcium carbonate or sodium acetate as the buffer were not consistent for the two dye concentrations. The results using sodium citrate, potassium antimony tartrate, or sodium bicarbonate were consistent and accurate for any dye concentration used in flask. The end point in each case is very sharp.

Table I—TiCl₃ Consumption of Amaranth when Different Buffers Are Used

BUFFER	BUF-FER DYE		TiCl ₃ CONSUMED				
			No. 1	No. 2	No. 3	No. 4	No. 5
	G.	G.	Cc.	Cc.	Cc.	Cc.	Cc.
Rochelle salt	5	0.1	5.98	5.93	...	6.1	5.95
	10	0.3	17.05	17.08	17.2	16.85	17.15
Sodium bitartrate	5	0.3	16.75	16.95	16.45	16.9	16.5
	10	0.3	16.4	16.6	16.6	17.1	17.0
Sodium tartrate	5	0.3	17.1	17.28	17.0	16.8	...
	10	0.3	17.70	17.50	17.6	17.5	...
Calcium carbonate	5	0.1	6.08	6.08	6.2	6.2	6.3
	10	0.3	17.8	17.83	17.75	17.75	17.75
Sodium acetate	5	0.1	5.95	6.05	6.1	6.1	6.2
	10	0.3	17.8	17.9	17.9	17.95	17.85
Sodium bicarbonate	5	0.1	5.99	6.04	5.95
	10	0.3	17.80	17.65	17.77
Sodium citrate	5	0.1	5.98	5.92	5.92	5.92	5.98
	10	0.3	17.73	17.75	17.78	17.73	17.73
Potassium antimony tartrate	5	0.1	5.93	5.93	5.88	5.93	5.88
	10	0.3	17.73	17.7	17.73	17.7	17.75

The values obtained for Ponceau 3R (Colour Index 80) when titration was carried out in the presence of sodium tartrate, Rochelle salts, or sodium bitartrate were very erratic. When potassium antimony tartrate was used, a sharp end point was not obtained. In the presence of sodium citrate

or sodium bicarbonate the results of titration checked closely the theoretical and were consistent under varying conditions.

Titration of Orange I (Colour Index 150) gave good results in the presence of all the buffers tried, except potassium antimony tartrate, calcium carbonate, and sodium acetate.

The complete analyses of samples of these dyes are shown in Table II. The "color by difference" agrees very closely with that obtained by titration in the presence of the buffer salts indicated.

Crocein Orange (C. I. 26), Orange G (C. I. 27), Ponceau 2G (C. I. 28), Scarlet GR (C. I. 78), and Ponceau 2R (C. I. 79) gave low results with sodium bitartrate. New coccin (C. I. 185), which is isomeric with Amaranth, does not give low results with this buffer, it being possible to titrate this dye accurately in the presence of sodium bitartrate.

Determination of Possible Errors

To determine the necessity for making a correction for titanous chloride consumed by the buffer, sodium citrate or sodium bicarbonate in different quantities was added to a standard solution of ferric sulfate.⁴ No increase in the quantity of reducing solutions required was detected. In another series of determinations 1 mg. of Orange I was titrated with 0.01 N titanium trichloride, using different quantities of a salt. The results thus obtained for sodium citrate are given in Table III. One milligram of Orange I theoretically requires for reduction 1.14 cc. of 0.01 N titanium trichloride. When the volume of solution in the flask was 100 cc., however, the quantity used averaged 0.43 cc. higher. This error is attributed to the dilution and would be negligible when 0.1 N reducing solution is used.

Table III—Tests for Blank on Sodium Citrate

SODIUM CITRATE	TiCl ₃ (0.01 N) PER 1 MG. ORANGE I					CONCD. HCl PER 20 cc. 0.1 N Fe ₂ (SO ₄) ₃	TiCl ₃ PER 20 cc. 0.1 N Fe ₂ (SO ₄) ₃
	No. 1	No. 2	No. 3	No. 4	No. 5		
G./100 cc.	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.
2	1.35	1.30	1.65	1.80	1.80	..	20.15
10	1.55	1.95	1.50	1.35	1.40	10	20.12
20	1.55	1.55	1.75	1.80	2.10	20	20.15
..	1	20.15

Conclusion

The color content of Amaranth may be determined by titration with titanium trichloride in the presence of sodium citrate, sodium bicarbonate, or potassium antimony tartrate. That of Ponceau 3R may be determined by titration with titanium trichloride in the presence of sodium citrate or sodium bicarbonate. Orange I may be titrated in the presence of sodium citrate, sodium bicarbonate, or the tartrates, except potassium antimony tartrate. The correct buffer salt must be determined for each dye.

The results reported here and those of other investigations (unpublished) warrant the conclusion that, for the correct evaluation of the color content of any dye, the buffer used

⁴ Kolthoff and Robinson, *Rec. trav. chim.*, 45, 169 (1926).

Table II—Complete Analysis of Amaranth, Ponceau 3R, and Orange I

DYE	MOISTURE	SODIUM CHLORIDE	SODIUM SULFATE	WATER-INSOLUBLE	ETHER EXTRACT	COLOR BY DIFFERENCE	COLOR BY TITRATION IN PRESENCE OF:				
							Sodium citrate	Sodium bicarbonate	Potassium antimony tartrate	Sodium bitartrate	
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Amaranth	7.90	2.40	..	0.08	0.05	89.57	89.20	89.30	89.10
	9.00	2.42	0.27	0.50	0.20	87.61	86.60	86.70	86.40
	9.55	3.34	..	0.07	0.11	86.93	86.90	86.76
Ponceau 3R	8.45	4.14	0.35	0.25	0.12	86.69	85.40	85.50
	5.72	4.70	0.31	0.12	0.20	88.95	87.87	87.75
Orange I	7.30	3.86	..	0.14	0.07	88.63	87.50	87.30	87.28
	3.20	1.74	..	0.16	0.07	94.83	93.68	93.47	93.68

must be tried thoroughly under a great variety of conditions before any reliance can be placed upon them. This may be due to the nature of the dye, but no attempt has been made

by the writers to determine it. However, if the correct salt to use is known, the dye content can be accurately determined.

Coal Conductivity Cell¹

Eric Sinkinson

LEHIGH UNIVERSITY, BETHLEHEM, PA.

The ohmic resistance of powdered coal can be measured with a fair degree of accuracy by using the specially designed cell described herein, in circuit with an ordinary Wheatstone bridge combination. The cell containing the coal is operated simultaneously with a standard cell, into which is placed coal, graphite, or charcoal, according to the type of measurement to be made in the test cell. By this means comparative measurements of resistance can be made with any series of coals properly prepared, provided they are conductors of electricity.

A critical examination of the cell and method of using it has been conducted to determine its usefulness under varying conditions. It was found that concordant results can be obtained on the same sample, having regard to the

character of the substance and the limits of accuracy of the method. The method may be used in the process of sampling and the comparison of samples, before any other work has been done on them.

Measurement of the resistance of a coal before and after boiling with concentrated hydrochloric acid to remove the soluble portion of the ash shows that this treatment lowers the resistance of the coal from 12,730 ohms to 9360 ohms, by the removal of 1.40 per cent of its ash.

The resistance of Pennsylvanian and Scotch coals has been compared.

Finally, the method has been used to clear up an anomaly, previously found, that the adsorption of carbon dioxide by a bituminous coal is greater than by the fusain taken from it.

THE purpose of this investigation was to devise a method of measuring the electrical conductivity of powdered coal and, by applying it, to study the physical effect of mineral matter and free carbon on coal substance.

If a lump of anthracite is ground to a centimeter cube, polished, and the electrical conductivity measured across opposite faces, it will not have the same ohmic resistances along the bedding planes and transverse to them. A test showed an ohmic resistance of 789 across one pair of faces, and 4509 transverse, while in a second sample one pair of faces gave an ohmic resistance of 992 and another 5090. Therefore, before measuring the electrical resistance of coal it must be pulverized to make the mass homogeneous. Even then, the manipulation becomes complicated unless special precautions are observed in packing the coal powder suitably before measuring the resistance. This difficulty is overcome by constructing a resistance or conductivity cell as follows.

Description and Use of Cell

The conductivity cell consists of two stout glass tubes, *A* and *B* (Figure 1) of uniform bore, 9 cm. long and 1 cm. internal diameter, clamped axially in a vertical position. The units are closed by brass plungers, *C*, *D*, *E*, which also serve as electrodes to make contact with the powdered coal in the cells. The central plunger, *D*, is common to the cells *A* and *B*, and forms an electrical contact between them. The plunger *E* is fixed to the base frame of a stout metal clamp by an insulator *J*, through which runs a connecting wire. A similar plunger *C* held by an insulator, *H*, is fixed to the top bar, *F*, of the frame. Plunger *C* has also a connecting wire fitted through its respective insulator, *H*. The top bar, *F*, of the clamp slides on two vertical rods, *M M*, on which are screwed wing nuts, *K K*. These press down bar *F* and plunger *C* and lower it into top cell *A*. Thus, when coal is placed in cells *A* and *B*, the thrust of *F* is transmitted uniformly through their contents.

When in use the cell is coupled to a Leeds & Northrup bridge assembly for 60-cycle current. The working range

is from 1 to 600,000 ohms, and settings can be made to 0.1 per cent.

OPERATION—In the lower cell *B*, place 1 gram of 48-mesh beechwood charcoal, then the central plunger *D*, the glass sleeve of cell *A*, into this 1 gram of 48-mesh coal on which the test is to be made. The top plunger closes the test cell. Screw down clamp *F* until both upper and lower plungers simultaneously compress the charcoal standard and the coal. The pressure is thus evenly distributed through cells *A* and *B*. Connect the lower cell to the bridge (not shown in figure) by a two-way switch, *L*. Measure the resistance and in subsequent measurements set the initial resistance at this figure. Turn the two-way switch to connect the upper cell to the bridge and measure the resistance of the coal. To compare coal resistances, change the coal in the upper cell, *A*, connect the bridge to the lower cell, *B*, and bring its resistance to the original value. Now switch over to the upper cell, *A*, and measure the resistance of the coal as before. By keeping the resistance of *B* constant, the coal in *A* will be subjected to the same conditions and give comparative measurements. The quantities of any size coal used can be determined by weight or specific volume—i. e., the ratio of the weight to the specific gravity.

Critical Examination of Method

One gram of 48-mesh Jeddo coal was placed in cell *B* and the same quantity in *A*. The resistance on the dials of the bridge was set at 4000 ohms and cell *B* connected in circuit. The galvanometer needle was brought to the zero position by regulation of the wing nuts. The upper cell then showed a resistance of 4240 ohms, thereby giving a relative resistance ratio of 1.06. The process was repeated with a resistance of 3000 ohms in the lower cell, when the upper showed 3090 ohms, giving a relative resistance ratio of 1.03. The contents of the lower cell were then replaced by those from the upper, and vice versa. The resistance of the lower cell was set at 3000 ohms, which caused the upper cell to register 2900 ohms, with a relative resistance ratio of 1.03. The relative resistance ratio is therefore constant under the two conditions of operation.

¹ Received March 31, 1928.

Constancy of Relative Resistance Ratio over a Given Pressure Range

One gram of Ceylon graphite, 48-mesh, was placed in each cell and the pressure applied to the electrodes by adding weights to the pan attached to the top electrode, instead of using the winged nuts, in order to measure the pressure actually applied to the graphite in the cells.

The electrodes and pan were first weighed. The electrode *D* weighs 111 grams, *C* 22 grams, and the pan 10 grams. The total weight applied to the lower cell is therefore 143 grams—and that to the upper cell 32 grams. Under these conditions the upper cell had a resistance of 1.21 grams and the lower, 1.27 grams; a relative resistance ratio of 1.05. Weights were then added to the pan and the corresponding resistances measured. The results are shown in Table I.

Table I—Relative Resistance Ratios for Various Pressures

WEIGHT APPLIED	RESISTANCE TOP CELL	RESISTANCE BOTTOM CELL	RELATIVE RESISTANCE RATIO
Grams	Ohm	Ohm	
7000	0.156	0.164	1.05
5000	0.164	0.207	1.26
2500	0.200	0.264	1.32
2000	0.212	0.282	1.33
1500	0.264	0.360	1.36
1000	0.280	0.410	1.46
500	0.380	0.537	1.41
400	0.447	0.610	1.36
200	0.472	0.657	1.39

From these figures a relative resistance ratio-pressure curve was plotted. (Figure 2) It can be seen that the relative resistance ratio becomes unity at an applied pressure of 7050 grams, and that measurements of resistance in the cell should be made at pressures around 7000 grams. This pressure is easily attained by screwing down the wing nuts and without strain. In practice it did not seem possible to bring the relative resistance ratio to unity, for on screwing down the clamps until the resistance in the cells was reduced as low as 0.093 ohm the resistance ratio was still 1.16. This discrepancy may be due in part to uneven distribution of pressure throughout the contents of the cells. For any particular standard resistance with which to compare the relative resistances of samples, a pressure equivalent of approximately 7000 grams was employed. If the standard cell is made to show a resistance appropriate to this pressure for every test made, there will be no need to measure the actual pressure every time.

Most Suitable Mesh of Coal

A standard mesh of 80 was chosen at random; and charcoal, because of its low resistance compared with coal and its extreme sensitivity to pressure change, made a very suitable standard. The quantity of charcoal placed in the lower cell when subjected to an equivalent pressure of 7 kg. gave a resistance measurement of 1.18 ohms. This is well within the range of constancy determined from Figure 2. One-gram samples of coal of different mesh from the Mammoth Vein of Morris Ridge Stripping near Mt. Carmel were employed and their resistances measured and tabulated. (Table II)

Table II—Comparative Resistances of Coal of Various Screen Sizes

(Standard resistance, 1.18 ohms)			
SCREEN	RESISTANCE ^a	SCREEN	RESISTANCE ^a
Mesh	Ohms	Mesh	Ohms
20	2500	65	1461
28	2033	100	2110
35	1900	150	5160
48	1157	200	6468

^a These figures are not corrected for contact resistance, coal to brass, because, by presenting four brass contact surfaces to the coal, instead of two, there is a greater liability to error.

The most uniform results were from screen 35 to 65, with 48 as an average. The higher resistances of the smaller screen sizes are probably due to binding of the coal, and the lateral pressure in the mass transmitted to the walls of the

cell. Vaseline the cell walls will rectify this. For example, a 200-mesh coal showed a resistance of 6468 ohms, but after vaselining the cell walls the resistance fell to 4000 ohms.

With graphite these discrepancies are not apparent. This trouble can also be avoided by using samples of coal not larger than 0.5 to 1 gram.

Effect of Increasing Number of Contact Surfaces

Grinding coal increases the number of contact surfaces and this has a marked effect on the resistance. Experiments with different screened samples of an adsorbite charcoal and beechwood charcoal gave the results shown in Table III.

Table III—Effect of Grinding Coal on Resistance

ADSORBITE CHARCOAL		BEECHWOOD CHARCOAL	
Screen	Resistance	Screen	Resistance
Mesh	Ohms	Mesh	Ohms
6-14	0.62	6-14	1.08
14-24	0.90	14-24	1.93
24-48	1.92	24-48	1.97
48-80	7.02	48-80	3.90
80-finer ^a	59.10	80-100	8.70
		100-finer ^a	49.30

^a Contains a large proportion of much finer material.

Algebraical Representation of Observations

Measured resistances of different weight increments of 48-mesh graphite, against a standard of 7.76 ohms, are tabulated in Table IV.

Table IV—Resistances of Various Weights of Graphite
(Standard resistance, 7.76 ohms)

WEIGHT RESISTANCE		WEIGHT RESISTANCE		WEIGHT RESISTANCE	
Gram	Ohm	Grams	Ohm	Grams	Ohm
0.10	0.058	0.75	0.073	1.50	0.092
0.20	0.061	0.90	0.075	1.75	0.101
0.50	0.064	1.00	0.078	2.00	0.113
0.60	0.066	1.25	0.084		

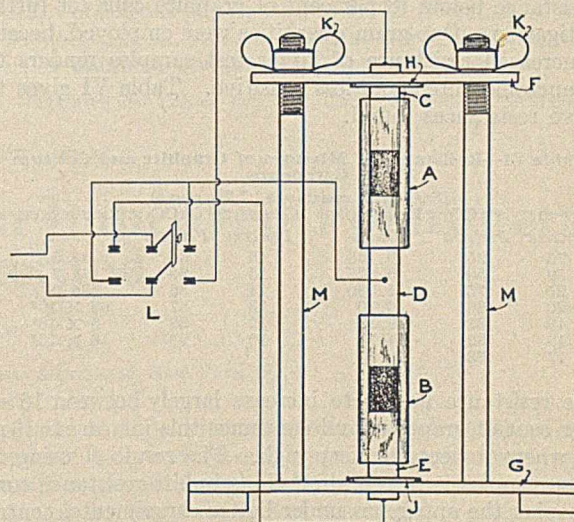


Figure 1—Coal Conductivity Cell

A graph plotted on semi-logarithm paper, using the weights of graphite as abscissas and the logarithms of the resistances as ordinates, proved to be a straight line. Therefore, the connection between the two quantities, *g* and *r*, the weight and the resistance of the graphite, respectively, can be represented by an equation of the form:

$$g - k \log r = s$$

in which *k* and *s* are constants to be determined. Substituting in this equation the values of *g*, and *log r* for the eleven observations listed in the Table IV, gives the equations

$$\begin{aligned} 0.10 - 1.23657 k &= s & 1.00 - 1.10791 k &= s \\ 0.20 - 1.21467 k &= s & 1.25 - 1.07572 k &= s \\ 0.50 - 1.19382 k &= s & 1.50 - 1.03621 k &= s \\ 0.60 - 1.18046 k &= s & 1.75 - 0.99568 k &= s \\ 0.75 - 1.13668 k &= s & 2.00 - 0.94692 k &= s \\ 0.90 - 1.12494 k &= s & & \end{aligned}$$

From the best values of k and s as determined by the method of least squares are found the normal equations:

$$11.179888 - 13.727157 k = 12.24958 s$$

$$13.9075 - 11.17988 k = 10.55 s$$

The solution of these equations gives

$$k = -6.6576 g \text{ and } s = 8.37343$$

so that for a theoretical relation one finds

$$g - 6.65769 \log r = 8.37343$$

$$\text{or } r^{6.65769} = 10^{g-8.37343}$$

From the form

$$\log_{10} r = 0.150202 g - 1.25771$$

The closeness of agreement between the observed and calculated values is evident in Table V.

Table V—Calculated and Observed Values of Resistance of Graphite Samples

g	0.152020 g	$\log_{10} r$	r (calcd.)	r (obsd.)	Diff.
0.10	0.0152020	8.757492-10	0.0572	0.058	+0.0008
0.20	0.0304040	8.772694-10	0.0593	0.061	+0.0017
0.50	0.0760101	8.813300-10	0.0658	0.064	-0.0018
0.60	0.0912121	8.833502-10	0.0682	0.066	-0.0022
0.75	0.1140152	8.856305-10	0.0718	0.073	+0.0012
0.90	0.1308182	8.879108-10	0.0757	0.075	-0.0007
1.00	0.1520202	8.894310-10	0.0784	0.078	-0.0004
1.25	0.1900253	8.932315-10	0.0856	0.084	-0.0016
1.50	0.2280303	8.970320-10	0.0934	0.092	-0.0014
1.75	0.2660354	9.008323-10	0.1019	0.101	-0.0009
2.00	0.3040400	9.046330-10	0.1113	0.113	+0.0017

Mixtures of Graphite with Non-Conducting Powder

Intimate mixtures of graphite and calcium carbonate, 48 mesh, were made up and the resistances of 0.5-gram quantities measured to find at what point such a mixture becomes a non-conductor. The mixture containing 18 per cent of graphite was found to be a conductor, while that containing 17 per cent was a non-conductor. This very large increase in resistance below 18 per cent of graphite calls for further investigation. One-gram quantities were employed, because the increased resistance of larger test samples renders the resistance measurements less sensitive. Table VI gives the relative resistances found.

Table VI—Resistance of Mixtures of Graphite and Calcium Carbonate

GRAPHITE		CaCO ₃		RESISTANCE	
Per cent	Per cent	Ohms	Per cent	Per cent	Ohms
75	25	0.155	16	84	42.5
50	50	0.225	15	85	141.7
25	75	1.880	14	86	326.0
20	80	6.90	13	87	68 × 10 ⁸
19	81	9.15	12	88	5 × 10 ⁸
18	82	14.7	10	90	6 × 10 ⁸
17	83	18.4			

The resistance begins to increase largely between 16 and 15 per cent of graphite, and continues this increase to 13 per cent, where it becomes very high. The result of using the 1-gram samples is to round off the graphite-resistance curve by keeping the apparatus under better experimental control.

In order to determine whether coal would behave like graphite under the same conditions, mixtures of fusain from a Morris Ridge coal with calcium carbonate in the same proportions as the graphite mixture were tested. The results are given in Table VII.

Table VII—Resistance of Mixtures of Fusain and Calcium Carbonate

FUSAIN		CaCO ₃		RESISTANCE	
Per cent	Per cent	Ohms	Per cent	Per cent	Ohms
75	25	127	18	82	17200
50	50	228	17	83	35200
25	75	2770	16	84	70000
20	80	11400	15	85	2 × 10 ⁸
19	81	16300	10	90	8 × 10 ⁸

Comparison of the results of Tables VI and VII shows that, whereas the chief bend in the graphite-resistance curve comes at 13 per cent graphite, the fusain resistance curve bends sharply at 15 per cent. This may be due to the different character of the carbon in the two series of mixtures.

Resistance of Coal at Electrode Surface

The contact resistance between coal and electrode was obtained by inserting a brass cylinder of the same cross-sectional area as the electrodes between two layers of coal in the cell, thus producing four contact resistances.

One gram of Jeddo coal, 48-mesh, had a resistance of 2225 ohms. After the cylinder was inserted as described, the resistance became 2245 ohms—an increase of 20 ohms. The actual resistance of the coal was therefore 2205 ohms.

One gram of Ceylon graphite tested in the same way was found to have a resistance of 0.080 ohm before insertion of cylinder, and 0.089 ohm after—an increase of 0.009 ohm. The actual resistance of the graphite would therefore be 0.071 ohm. Concordant results were obtained on repetition.

Use of Method to Examine Coal

A Primrose Oak Hill coal was dried, and a sample showed on analysis the following figures: volatile matter 6.39, fixed carbon 77.95, ash 15.68 per cent. A sample was ground to pass a 48-mesh screen and the resistance of a 0.5-gram quantity was measured and found to be 12,730 ohms. The powdered coal was boiled in concentrated hydrochloric acid for 8 hours to remove the soluble portion of the ash. After washing with distilled water, it was boiled a further 8 hours with distilled water, washed, dried, and the resistance of a 0.5-gram sample measured. The resistance was 7600

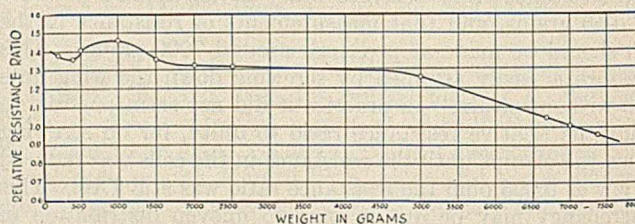


Figure 2

ohms. The ash content had decreased from 15.68 per cent to 14.30 per cent—a difference of 1.40 per cent. To insure that all the soluble chlorides had been washed out, the sample was boiled for 8 hours longer in water, and dried. The resistance was now found to have increased to 9630. This resistance was maintained within the limits of experimental error after subsequent boilings with water.

Influence of Ash on Coal Resistances

The following coals with their ash contents were analyzed and their relative resistances measured:

- Short Mountain, Lykens Valley Basin
- Lee, No. 7, Nanticoke, Wyoming Basin
- Cameron, Shamokin Basin
- Scott Colliery, Mt. Carmel, Shamokin Basin
- Wm. Penn, Mahony Basin

Table VIII—Analysis and Resistances of Several Coals (Standard resistance, 7.76 ohms)

COAL	VOLATILE MATTER	FIXED CARBON	ASH	RESISTANCE
	Per cent	Per cent	Per cent	Ohms
(a)	8.32	83.95	7.73	5 × 10 ⁸
(b)	7.55	89.35	3.10	7.5 × 10 ⁸
(c)	7.02	84.45	8.53	4 × 10 ⁸
(d)	5.75	89.66	4.59	1.5 × 10 ⁸
(e)	3.47	90.02	6.51	1533

Table IX—Analyses of Coal Ashes

COAL	(a)	(b)	(c)	(d)	(e)
	Per cent	Per cent	Per cent	Per cent	Per cent
Silica	38.80	42.90	42.07	42.94	41.55
Alumina	33.24	31.97	36.56	25.04	36.58
Calcium oxide	2.80	2.13	4.76	11.08	5.00
Manganese oxide	Trace	0.81	Trace	1.28	1.00
Sulfur (as SO ₂)	2.75	2.61	3.21	4.61	3.76
Ferric oxide	21.95	0.35	1.70	0.41	0.31
Undetermined	0.45	12.23	12.70	14.56	11.80

It is evident from Table VIII that coals (a) to (d) are practically non-conductors, whereas coal (e), with 90 per cent of carbon and 6.51 per cent of ash, is conducting. In order to be assured that the conducting quality does not lie in the character of the ash, the ashes of the coals were analyzed. (Table IX)

Iron compounds other than pyrites have little influence on the conductivity. Coal (a), with an ash content of 7.73 per cent, of which 21.95 per cent is iron estimated as ferric oxide, is practically non-conducting. It is evident that increase in resistance is not determined by ash content alone, for it is clearly shown that there is a big difference in resistance of actual coal substance for different anthracites.

Conductivity of Scotch Anthracites

Two Scotch anthracites were chosen because of their similarity of composition, and wide difference of conductivity (Table X):

- (a) Hassockrigg Colliery, Virtuewell Seam, Lanarkshire
(b) Polmaise, Main Coal Seam, Stirlingshire

Table X—Conductivity of Scotch Anthracites
(Dry coal. Standard resistance, 7.76 ohms)

COAL	VOLATILE	FIXED	ASH	RESISTANCE
	MATTER	CARBON		
	Per cent	Per cent	Per cent	Ohms
(a)	9.66	87.36	2.98	6×10^6
(b)	7.51	87.40	5.09	75

Coal (a) is similar to the Pennsylvanian coal except for lower ash content, and the resistances are of the same order. Coal (b), however, has a greater ash content than (a), and very slightly more fixed carbon when calculated on the dry ashless basis—viz., (a) 90.05 and (b) 92.08 per cent; the resistance is, however, only 75 ohms, as compared with a non-conductor.

Comparison of Bituminous Coal and Fusain from Same

Finally, the cell was used to clear up an unexplained anomaly in a previous paper,² in which a description of a Freeport vein coal shows a greater adsorption value towards carbon dioxide than the fusain taken from it. Accordingly, it is proposed to test whether the resistance of the coal and fusain, respectively, follow the order expected for two such substances. The results are summarized in Table XI.

Table XI—Adsorption and Resistance of Freeport Bituminous Coal and of Fusain Prepared from It
(One-gram sample. Standard 7.76 ohms)

	BITUMINOUS COAL	FUSAIN
Volume of CO ₂ adsorbed at N. T. P., cc.	112	45
Resistance, ohms	4×10^6	362

It is evident that the order of resistances is in keeping with what might be anticipated, but the reverse is true for the adsorption figures. The explanation attempted in the previous paper was that the fusain has a lower activity towards carbon dioxide because (1) of infiltrations of bituminous matter into its pores,² of condensation of oxidation products previously adsorbed in gaseous form, and (3) of the possibility of its not being fusain. The order of the resistances indicates that it is fusain.

It can readily be seen that a cell of the nature described can be used to measure the resistance not only of powdered coal but also of any other conducting powders.

Acknowledgment

Acknowledgment is due to Howard Eckfeldt, professor of mining engineering, Lehigh University, for constructing the cell described; to J. B. Reynolds, professor of mathematics in Lehigh University, for advice about the mathematical work in the paper; and to H. M. Secretary of Mines in London, Col. G. R. Lane-Fox, for the Scotch anthracites specially obtained and analyzed for this work.

² Sinkinson and Turner, *IND. ENG. CHEM.*, 18, 602 (1926), Table IV.

A New Soluble Starch and an Improved Polarimetric Lintner Method¹

H. C. Gore

THE FLEISCHMANN LABORATORIES, 158TH ST. AND MOTT AVE., NEW YORK, N. Y.

IN THE polarimetric method proposed by the writer² a 2 per cent solution of Lintner's soluble starch was used, and the range within which fall in polarization followed the Kjeldahl law of proportionality during saccharification was slightly more than 3° V. It was obvious that the accuracy of the method could be greatly improved if this range could be increased. It has been found possible to do this through the use of a special type of soluble starch.

This new soluble starch is prepared by treating starch with a 13 per cent hydrochloric acid solution. When its 6 per cent solution is allowed to cool and stand at room temperature, it separates into a mixture of coagulum and a solution of starch which can be separated by filtration, while with other soluble starch the 6 per cent solution cannot be filtered clear. A clear, permanent water-soluble solution of starch of about 5 per cent concentration can thus readily be prepared. With this comparatively strong starch solution the polarization fall with which Kjeldahl's law is followed was found to be at least 11.3° V.

Details of a polarimetric method retaining the Lintner scale have been worked out, which, while approximately as accurate as the methods based on the estimation of reduced copper, is far less tedious and exacting.

Preparation of Soluble Starch Solution

One part of potato starch is mixed at room temperature with 1.5 parts of hydrochloric acid of approximately 13 per cent concentration, prepared by mixing 1 part of strong hydrochloric acid by volume with 2 parts of water, and allowed to stand for 6 days. The starch is then washed with distilled water, suspended in water, and the last traces of acid, which cling persistently to the starch, neutralized with ammonia. The starch is then washed several times by decantation, passed through a fine sieve with water to remove any coarse impurities, collected in a Büchner funnel, and washed in the funnel until the washings are free from chlorides. The starch is then dried in a gentle current of warm air. The yield is about 75 per cent of the starch taken.

A 6 per cent solution of the special starch is made up by adding the calculated weight, mixed with a little water, to

¹ Presented before the Division of Sugar Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² *J. Assocn. Official Agr. Chem.*, 7, 364 (1924).

hot water, heating to boiling, cooling, and making up to volume. The solution is allowed to cool and stand overnight or longer. It is then filtered on a folded filter, returning the first turbid runnings to the filter. Filtration is slow, and several hours or overnight is necessary.

The starch solution thus prepared, preserved by shaking with a little toluene and keeping in a closed flask, keeps indefinitely substantially unchanged. It sometimes becomes slightly turbid, but this turbidity may be readily removed by filtration.

Method

In determining the diastatic activity of an infusion of malt, the pH of the starch solution is adjusted to 4.8 by adding Walpole's acetate buffer (8 cc. of 1 *N* acetic acid and 12 cc. of 1 *N* sodium acetate made up to 100 cc. with water) at the rate of 2 cc. of buffer to each 100 cc. of starch solution. The malt infusion is so prepared that each cubic centimeter represents 50 mg. or a known multiple of 50 mg.

The initial polarization is made by mixing 50 cc. of the buffered starch solution with 1 cc. of strong ammonia and 5 cc. of the malt infusion, mixed in a dry flask in the order named. The solution is then filtered if necessary and polarized.

Five cubic centimeters of malt infusion at 21° C. are placed in a dry flask and 50 cc. of the buffered starch solution, also at 21° C., added, counting time from the moment when the first of the starch solution reaches the malt infusion. The mixture is then allowed to stand in a water bath at 21° C. for a time within which the polarization should not decrease more than 11.3° V. (where a 4-dc. tube is used in polarizing). One cubic centimeter of strong ammonia is then added, the

solution filtered, if necessary, and polarized. In filtering, the precautions described by Zerban,³ consisting of rejecting the first runnings of the filtrates and keeping the funnels covered with watch glasses, should be observed.

The two solutions should be polarized at the same temperature to avoid errors due to the marked effect of temperature on the polarizations.

The diastatic power is calculated from the formula,

$$L = \frac{100 D}{t \times l \times c}$$

where *L* is degrees Lintner, *D* is the fall in polarization observed due to 250 mg. of sample, *t* is the time in hours, *l* is the length of tube in decimeters, and *c* is a constant determined experimentally. *c* = 4.6.

Notes on Method

The clear starch solution, prepared as described above from the soluble starch containing 13.25 per cent of moisture, contained 4.706 grams per 100 cc. It polarized at 105.3° V. at 20° C. in a 4-dc. tube, and a 25-cc. portion reduced 66.6 mg. of cuprous oxide when treated by the Munson and Walker method. Thus the specific rotation was 194 and the reducing power expressed as per cent of dextrose was 2.43.

The factor *c* was determined by the use of an infusion of malt, the diastatic activity of which was determined by the gravimetric Lintner method. The soluble starch used in this determination was of Kahlbaum's make, carefully rewashed and redried. The 2 per cent starch solution contained the Walpole 4.8 acetate buffer at the rate of 2 cc. per 100 cc. of starch solution.

³ Hardin and Zerban, *IND. ENG. CHEM.*, 16, 1175 (1926).

Electrochemical Polarization Process for Prevention of Corrosion in Locomotive Boilers^{1,2}

L. O. Gunderson³

THE CHICAGO AND ALTON RAILROAD COMPANY, BLOOMINGTON, ILL.

THE normal life of a locomotive fire box and boiler shell used in a soft or treated non-corrosive water district may be indefinite, while the flues, by successive piece-welding and cutting down to fit shorter boilers, will last upwards of ten years or until worn thin from the fire side. Under these conditions general overhauling of the boiler is made necessary only by federal requirement in interest of safety once in four years, unless an official extension is granted. This overhauling consists of removing and re-applying the flues, examining and renewing a few stay bolts, and other minor repairs, and generally costs only a few hundred dollars.

In a corrosive-water district we may find that fire boxes will last only a comparatively few years, in some localities only two or three years, representing a loss of from \$2000 to \$3000 depending on the size of the locomotive. During this period the locomotive in such corrosive-water district will have had two sets of flues destroyed by pitting and

grooving, representing an approximate loss of \$1200 to \$3200 for the two sets of steel flues, in addition to the loss of a few hundred dollars due to scrapping flue sheets and stay bolts that would be destroyed by corrosion.

Recently the writer had a close check made of the cost of renewing the belly of a Pacific type passenger locomotive, made necessary because of corrosion in form of grooves and pits after only four years' service. The cost of labor and material was \$2150, which included stripping the boiler and removing it from the frame, all made necessary by corrosion, although the actual cost of the corroded material was less than a hundred dollars. These figures demonstrate the involved character of corrosion in locomotive boilers, where the actual loss is only fractionally represented by the cost of the material. It has been estimated that the railroads of the United States spend 12 to 15 million dollars annually to repair boiler material destroyed by corrosion.

To make a correct diagnosis of cases of corrosion in locomotive boilers is no simple matter, especially on road engines that use a large variety of feed waters on a division. This and other variables make locomotive boiler corrosion a problem much more involved than corrosion in stationary power-plant boilers.

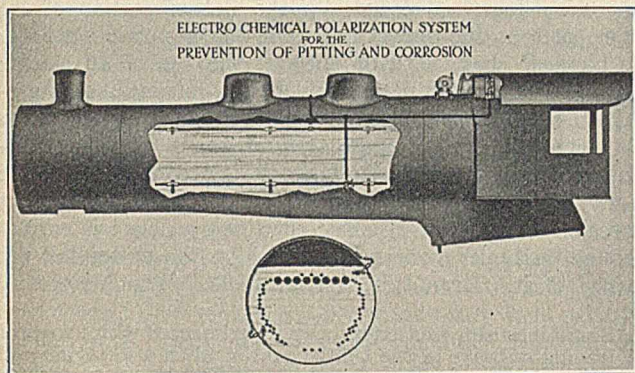
In the same water district some boilers will pit and groove primarily at the forward end, where feed water is injected with more or less oxygen content, and the fire-box end will

¹ Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

² Some details of this process have been noted by the author, *Ry. Rev.*, September 24, 1926; *Proc. Pittsburgh Ry. Club*, April 28, 1927; *Am. Ry. Eng. Assoc. Bull.*, 29, 135 (1927); *Proc. Western Ry. Club*, March 19, 1928; and by Carrick, *J. Am. Water Works Assoc.*, 19, 704 (1928).

³ Present position, chemical engineer, Electro-Chemical Engineering Corporation, Chicago, Ill.

not be affected, while other boilers using the same water in identical service will show severe corrosion in the fire-box end. The variations seem to be due to differences in rate of circulation and temperature of the injected water. Injected water at abnormally low temperatures will retain oxygen longer in solution and thus contribute to fire-box and rear-end corrosion by permitting oxygen to be carried back by the circulation.



On the writer's road severe corrosion resulting in flue failure from pitting in less than a year's time has taken place in locomotive boilers using feed waters treated to excess caustic alkalinity (10.5 pH). To account for this rapid corrosion it may be assumed either that the hydrogen-ion concentration is increased under boiler conditions of pressure and temperature or that this water supply and many others on the road must possess pronounced film-destroying powers effective in caustic boiler water.

Thermal-Generated Electric Currents in a Locomotive Boiler

The possibilities of thermal-generated electric currents in a locomotive boiler and their effect on pitting and corrosion have been overlooked almost entirely in recent corrosion literature. The destruction wrought by stray-current electrolysis on pipe lines adjacent to street railways that have not well-bonded returns is generally appreciated. Is it then consistent to disregard consideration of possible destructive electrolysis currents in a locomotive boiler? The pioneer work of Burgess⁴ is well worth reviewing. He demonstrated very satisfactorily that heating the boiler metal made it electropositive to the unheated metal, the potential difference increasing somewhat proportionately with the increase in temperature. In a 17-inch experimental boiler under 85 pounds steam pressure he found a potential difference of 3.9 millivolts between the hot inner tube and the cooler outer shell and recorded a current flow of 19.2 milliamperes through the boiler-water electrolyte, and he found that this current in a few hours caused pitting apparent to the naked eye. The magnitude of these values in a locomotive under 200 pounds steam pressure (387° F.) is surprising.

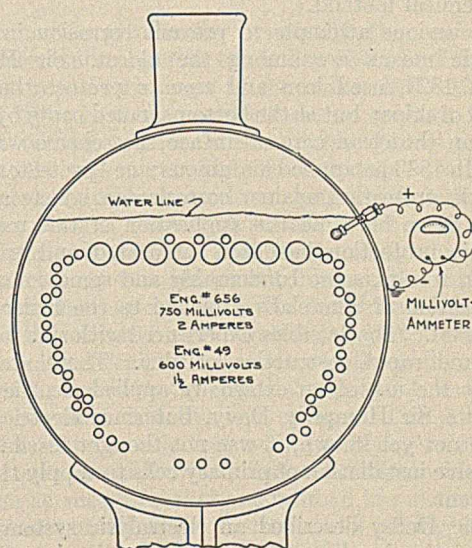
The writer has not completed the test with a boiler tube, owing to the difficulty of maintaining insulation under the high pressure and excessively hot combustion gases in the fire box, which burn off even metal projections protruding from the back flue sheet. However, he used one of the 1-inch wrought-iron pipe anodes (18 feet long) of the electrochemical system to be subsequently described, which pipe is located near the top of the boiler, submerged in the boiler water, and perfectly insulated from metallic contact with the boiler. It extends nearly the length of the boiler flues.

When the boiler was filled with cold boiler water, the potential difference between the pipe and the boiler shell, as

determined by a millivolt-milliammeter, was 2.0 millivolts, the boiler shell being electropositive, evidently because the pipe was covered with ferric oxide formed while serving as an anode in the protection system. As the boiler was fired up, the potential difference was reversed, the pipe becoming electropositive, and with increasing temperature and pressure the potential difference increased proportionately until a value of 1.5 volts was obtained, which gave a flash amperage of 3 amperes across the boiler-water electrolyte. A pronounced electric spark was obtained by making and breaking the circuit. Upon continued shorting of the pipe and the boiler shell the above values rapidly diminished to 25 millivolts and less. These figures refer to the boiler standing still with no steam used nor water injected. The writer attributes this rapid reduction to the polarization by hydrogen deposited on the boiler shell, causing the potential of the two surfaces to approach equilibrium. Breaking the circuit for a few minutes permitted the electromotive force to be rebuilt approaching the original values. Moving the engine caused an immediate marked increase of the lower values.

Readings taken on a Pacific type passenger locomotive over a 127-mile division showed mean value of 750 millivolts and a constant flow of 2 to 2.5 amperes from pipe to boiler shell. These values were maintained throughout the trip. Constant sparks could be obtained by alternately making and breaking the circuit.

On a switch engine in Bloomington, Ill., yards using very corrosive boiler feed water, a fairly constant value of 600 millivolts and a maintained current from the pipe to boiler shell of approximately 1.5 amperes was recorded over a period of 30 minutes. When the locomotive stood still and used no steam, these values rapidly decreased, indicating increased polarization. Running the headlight generator had no effect on these values.



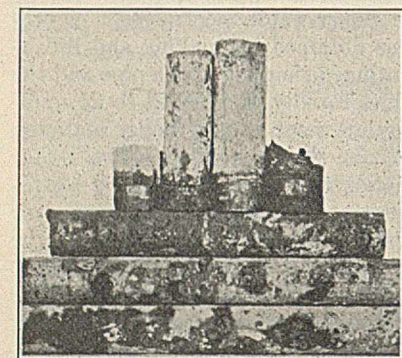
Method of Determining Thermal-Electric Currents Generated in a Locomotive Boiler

The comparatively high amperage across several inches of boiler-water electrolyte seems out of proportion to the voltage; wherefore the writer advances the opinion that some of this current was picked up from the hotter flues beneath, the pipe being the shortest route of less resistance for this current.

When a temperature difference of less than 140° F. between the flue (387° F.) and the boiler shell (250° F. estimate) can create such electromotive force values and magnitude of current as here recorded, the writer can anticipate what he might find when he insulates a flue conveying hot gases

⁴ *Trans. Am. Electrochem. Soc.*, 13, 17 (1908).

of approximately 1000° to 1500° F. The only reason that such electromotive force represented by potential differences between hot and cooler portions of the boiler is not utterly destructive to the hot portions is that the metal-to-metal electrical contact at both ends of the flues permits the current to be released through the circuit—flues to front flue sheet, to cooler boiler shell, to lower fire-box portions and back



Pitting, Grooving, and General Corrosion
Contemporary power equipped with electrochemical polarization system perfectly protected against this destruction

flue sheet, returning to the back end of flues. No one will deny that these thermal generated electric currents are potential and kinetic factors in the corrosion of locomotive boilers. On the assumption that the 2-ampere constant flow of current, recorded on the passenger locomotive, operated according to Faraday's law in dissolving the iron of the pipe, then 50 grams of iron would be corroded away in 24 hours and, since this corrosion is never uniform but in pits, the rate of penetrating the pipe will be proportionately rapid.

Previous Electrolytic Methods of Corrosion Prevention

The foremost methods of trying to reduce or prevent pitting and grooving in locomotive boilers are: overtreatment of feed water to high excess caustic alkalinity, partial de-aeration of feed water by open-type heater, and the electrochemical method.

Of the various attempts to prevent corrosion in boilers, electrolytic means are among the oldest. Sir Humphry Davy, in 1823, used iron and zinc to protect the copper sheathing of ships; but as the bottoms fouled badly by marine growths on the clean copper surface the scheme was abandoned. In 1833 he applied his famous zinc "protectors" as an electrolytic protection against corrosion in boilers and condensers. Since his time the application of this method of electrolytic protection has been advocated and tried with conflicting results, some condemning and some commending the application of zinc slabs attached to the boiler or condenser metal. The troubles experienced with zinc were poor contact and rapid destruction of zinc. There are indications that the use of an externally applied electric current occurred to Sir Humphry Davy, but since electric generators were not yet known, it was not thought feasible to use an expensive installation of primary cells to supply the necessary current.

In 1889⁵ Dolby described an electrolytic system applied to boilers, using insulated electrodes extending into the water of the boiler, and an alternating current supplied by a magneto. The claims were that the alternate plating out of oxygen and hydrogen would cause these elements to recombine to form a thin film of water, which would prevent scale formation. A few years later Wurtz⁶ described a method of protecting mine equipment, boilers, etc., by electrolytic means. An electric current from direct-current dynamo was passed through the electrolyte from anodes inserted therein, making the materials to be protected the cathode in the corroding solution.

Since that time many patents have been issued on electro-

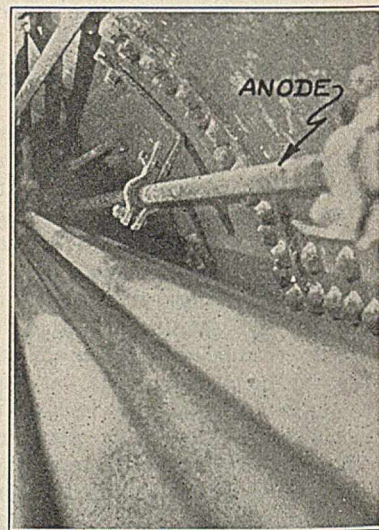
lytic methods and installations and on various types of electrodes used for insulating the anodes from the boiler shell, but practically the only generally known and tried system was that of Elliott Cumberland as described in United States and British patents of 1908 to 1912.⁷

Another type of so-called electrolytic system for the alleged prevention of scale and corrosion in boilers is represented by numerous patents in late years in this country and Europe, and consists essentially of a few wires and contacting points connecting together electrically the hotter portion of the boiler, such as the dome, and some colder portion, such as the blow-off cock, with or without the use of an electric current of very small magnitude (only a few millivolts) generally derived from a thermocouple located at a hot portion of the boiler. One of these systems has a vibrator or interrupter in series with the tiny electric current. If there is any plausible scientific explanation for the alleged effect on scale and corrosion of short-circuiting an electric current through the boiler metal between points, the writer has not learned of it. Even this system is old. Wood⁸ writes:

An acid-incrustor was extensively experimented with by one of the leading railways of the United States, when a few wires and metallic points and connections made to the dome and other parts of the boiler were expected to gather the frictional electricity generated by a boiler under steam, and in connection with the galvanic action excited by the use of impure water, threw down the impurities, one and all, ready to be blown off. The use of zinc plates to help out was then resorted to, and finally zinc plates alone were used, and this electrolytic system disappeared.

Just as the use of zinc plates had its advocates and denouncers, so the electrolytic system with an applied electric current supplied to insulated anodes has had a varied reception in the engineering field, the recorded failures of the system about balancing its satisfactory performances. Its early promoters seem to have been as much concerned about scale prevention as corrosion prevention. Its successes in corrosion prevention appear to be confined to condensers, and its failures are outstanding in boiler installations, where we know the corrosion problem to be most complicated.

The breaking down of the insulation has been suggested as the cause of the failure of the system to protect boilers from corrosion, especially in forms of destructive pitting. However, upon close analysis there is no more reason why pitting should cease when the boiler metal is made a cathode in an electric circuit than that local galvanic action should cease on the zinc plate of a primary cell in service, which battery men early recognized as a serious problem and which they solved by amalgamating the plate. The reason for the protection that amalgamation afforded the zinc plate from cor-



Interior View of Boiler of Engine No. 49, Equipped with Electrochemical System, after 21 Months' Service in Very Corrosive Water Territory. Note Good Condition of Anode

⁷ U. S. Patents 948,968 and 1,020,480; British Patents 8422 (1908), 8068 (1909), 19,637 (1911), and 4251 (1912).

⁸ *Trans. Am. Soc. Mech. Eng.*, **15**, 1069 (1894).

⁵ *Proc. Inst. Civil Eng. (London)*, **99**, 88 (1889).

⁶ *Eng. Mag.*, **7**, 297 (1894).

rosion by acids is that the discharge potential of hydrogen on mercury exceeds the potential of zinc⁹ and thus the voltaic couple becomes polarized.

Use of Arsenic to Cause Polarization

Likewise, to prevent local action or pitting in a boiler surface acting as cathode of an electric current, it becomes necessary to destroy or render ineffective the local voltaic couples as was done by amalgamating the plate in the primary cell. To bring about the polarization of this local action, the writer conceived the idea of plating out on the boiler heating surfaces a metal below iron in the electromotive series which has a high discharge potential of hydrogen, or a high hydrogen overvoltage. Arsenic is the ideal metal, for it alone possesses the necessary characteristics for this purpose.

It has been demonstrated experimentally in the laboratory¹⁰ and by experience in practical engineering application that the fact that a metallic substance acts as a whole as a cathode in an electric current does not necessarily stop local galvanic couples from functioning at various points on its surface. This experiment may be duplicated by anyone by simply connecting a strip of copper and a strip of iron and partly immersing this couple in a dilute acid solution or corrosive water, noting the rapid corrosion of the iron. When this iron-copper couple is made to act as a cathode in an electric circuit by connecting it to the negative pole of a dry cell and a carbon or other insoluble anode is immersed in the same solution connected to the positive pole of the cell, with the passage of this applied electric current the corrosion will continue at only a slightly reduced rate. If a few crystals of sodium arsenate are added to the corrosive solution, all corrosion and local galvanic action will cease at once owing to polarization. On shutting off the electric current and causing air or oxygen gas to bubble through the solution around the copper strip, the iron again starts to corrode, because the oxygen destroys the polarization on the arsenic-plated copper by combining chemically with the oxygen to form water. Likewise galvanic corrosion will continue in a boiler in spite of the arsenic plating owing to the dissolved oxygen in the feed water. With the gas still bubbling through the solution, on passing the electric current as before, corrosion of the iron will be entirely prevented. This complete protection is due to the fact that an excess of nascent hydrogen is constantly being plated out, and which will chemically reduce any oxygen adjacent to the metal surface before it can impair the protective hydrogen polarizing film. This is the theoretical explanation of the success of the electrochemical polarization process of corrosion prevention in acids or other corrosive waters containing oxygen or other oxidizing agents.

It is well known that arsenic as an impurity in sulfuric acid destroys the pickling qualities of the acid by its polarizing action. Dissolved oxygen or other oxidizing agents will destroy the protection by removing the hydrogen film. The writer finds only one reference to a successful application of arsenic alone as a protection against corrosion in an industrial boiler.¹¹ In this case the acid corrosion caused by absorption of sulfur dioxide from flue gases in the cooling tower was stopped by the addition of a soluble arsenic salt, the protection apparently being due to the elimination of oxygen from the boiler make-up water by being used up in oxidizing the sulfur dioxide to sulfurous acid.

Arsenic alone added to a boiler water will afford no pro-

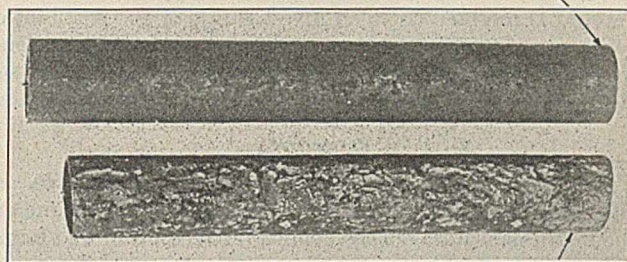
tection against corrosion, because the dissolved oxygen will continually destroy the protective polarizing film of hydrogen. However, by continually passing a small electric current from insulated anodes to the interior boiler surfaces as cathode and plating out constantly an excess of nascent hydrogen, the polarization by the arsenic will be perpetuated by virtue of the fact that the excess hydrogen will combine with any oxygen which diffuses through to the metal surface, thus preventing impairment of the protective polarizing film of hydrogen, identically as in the laboratory experiment cited above.

Application to Locomotive Practice

In present locomotive practice the so-called electrochemical polarization system of corrosion prevention as installed and successfully operated on four railroads is described essentially as follows:

Two completely insulated electrodes are inserted in the boiler shell, one in the upper part of the boiler and one diagonally opposite in the lower part. The conducting members of these electrodes are rigidly connected to iron anodes

Engine 49, 21 months' service, electrochemical protection—



Engine 49, 18 months' service, no protection—

which extend longitudinally practically the entire length of the boiler, submerged in the boiler water and rigidly attached by insulating clamps to the boiler shell. Conduited insulated wires connect the electrodes to a shunt from the headlight turbo-generator, with suitable control apparatus located in the cab to provide approximately 2 volts with 2 or 3 amperes to each electrode, making about 0.002 ampere per square foot of protected surface. The negative pole of the generator is grounded to the boiler shell, which permits the current to travel in the circuit from anodes through the boiler-water electrolyte to the boiler metal, through which it completes the circuit to the negative bus bar of the generator. A soluble arsenic salt is added to the boiler water at the rate of 2 pounds for the initial charge and 1 pound every 2 weeks while the locomotive is in service. This permits the plating out of the arsenic "secondary cathode," which is the one important essential of the polarization effect which makes the system so successful that one railroad has made it standard equipment on all its locomotives. All pitting, grooving, or other forms of corrosion have been prevented for nearly four years in locomotive boilers equipped with this system, while contemporary unprotected boilers are severely attacked, some failing from pitting in less than a year.

Besides preventing the local action or pitting due to potential differences between the elements of the pits, the system described prevents electrolysis by the thermal-generated electric currents described earlier in this paper. To prevent corrosion in a locomotive boiler no method is complete until it overcomes the action of the flow of electric currents generated within the boiler as a result of thermal differences. The electromotive force may be sufficient to plate out hydrogen as a gas, thus corroding the boiler metal in the absence of oxygen, even in alkaline waters.

⁹ Watts, *Trans. Am. Electrochem. Soc.*, **32**, 279 (1917).

¹⁰ Gunderson, *Ry. Rev.*, **79**, No. 10, 335 (1926).

¹¹ Cushman and Gardner, "Corrosion and Preservation of Iron and Steel," p. 297.

The Dipping Refractometer for Determining the Concentration of Dilute Glue Liquors¹

A. C. Hart

ARMOUR GLUE WORKS, CHICAGO, ILL.

GLUE manufacturers have long needed a simple, rapid, yet fairly accurate method for determining the percentage of glue in dilute liquors. At present the "Glueometer," which is merely a specially calibrated specific gravity spindle, probably is the most commonly used instrument for this purpose. At best its accuracy is about ± 0.5 per cent. As the temperature correction increases this figure increases accordingly. The pycnometer offers a more accurate method, but one that requires considerable time and very good technic. Since a variation of 1 per cent in the concentration of a glue liquor changes the specific gravity only about 0.0030, the accuracy of this method is limited to about ± 0.10 per cent and for hurried routine work this percentage is probably doubled. This error is not too great for most practical work, but the need for a more rapid method led to an investigation of the possibilities of the dipping refractometer. A careful review of the literature revealed that surprisingly little work has been done on this subject² considering its possible wide application.

Procedure

The Zeiss dipping refractometer, chosen for its accuracy and ease of operation, was used throughout the experiments. The instrument was checked against distilled water and found to be properly adjusted.

All readings were checked by two or more individuals, and it was found that they always agreed within ± 0.2 of one scale division, which is the equivalent of ± 0.00008 in terms of refractive index or ± 0.05 per cent as glue. In routine work various factors, such as inadequate temperature control, cloudiness of samples, etc., would probably limit the accuracy to ± 0.10 per cent which is still entirely satisfactory for any routine work. Best results were obtained when the samples were clear, the instrument absolutely clean, and a daylight, microscopic lamp used for illumination. Even very cloudy samples were read with little difficulty if the light was properly adjusted.

Samples were prepared by accurately weighing the glue on an analytical balance, adding the requisite amount of water, cold, and allowing to soak for one hour. The glue was then put into solution in the regular way by warming to 60° C. All glue percentages given refer to the commercial product containing 12 per cent moisture, correction for same being made when necessary. All readings were taken at 20° C.

Data

Table I—Refractometer Readings

KIND OF GLUE	SCALE	REFRACTIVE	GLUE	ASH
	READING	INDEX		
			Per cent	Per cent
Ashless gelatin (Eastman Kodak Co.)	15.5	1.33339	0.25	0.00
	16.7	1.33385	0.50	
	19.1	1.33478	1.00	
	23.6	1.33651	2.00	
	27.7	1.33798	3.00	
Edible gelatin	32.0	1.33972	4.00	0.70
	35.9	1.34121	5.00	
	15.5	1.33339	0.25	
	16.5	1.33378	0.50	
	18.6	1.33458	1.00	

Table I—Refractometer Readings—Continued

KIND OF GLUE	SCALE	REFRACTIVE	GLUE	ASH
	READING	INDEX		
			Per cent	Per cent
Edible gelatin (cont'd)	23.1	1.33632	2.00	
	27.2	1.33789	3.00	
	31.6	1.33956	4.00	
	35.6	1.34090	5.00	
High-grade hide	15.5	1.33339	0.25	2.89
	16.5	1.33378	0.50	
	18.8	1.33466	1.00	
	20.5	1.33532	1.50	
	24.7	1.33694	2.50	
	28.7	1.33847	3.50	
Medium-grade hide	33.1	1.34014	4.50	
	15.3	1.33332	0.25	2.43
	16.4	1.33375	0.50	
	18.8	1.33466	1.00	
	20.1	1.33517	1.50	
	24.7	1.33694	2.50	
	28.7	1.33847	3.50	
High-grade bone	32.9	1.34006	4.50	
	18.6	1.33458	1.00	2.44
	23.0	1.33628	2.00	
	26.6	1.33766	3.00	
	30.7	1.33923	4.00	
Medium-grade bone	34.5	1.34067	5.00	
	18.6	1.33458	1.00	3.73
	23.0	1.33628	2.00	
	26.4	1.33758	3.00	
	30.6	1.33919	4.00	
	34.3	1.34059	5.00	

The specific refractivity of glue may be computed from the formula:

$$n - n_1 = a \times c$$

$$\text{or } a = \frac{n - n_1}{c}$$

where n = refractive index of solution
 n_1 = refractive index of solvent (water)
 c = per cent of glue in solution
 a = specific refractivity of glue or gelatin

Taking the refractive index of water at 20° C. as 1.33298 and using values given in Table I, we obtain the results in Table II.

Table II—Specific Refractivities of Glue Liquors

KIND OF GLUE	GLUE	$n - n_1$	a
	Per cent		
Ashless gelatin (Eastman Kodak Co.)	1.00	0.00180	0.00180
	2.00	0.00353	0.00177
	3.00	0.00500	0.00167
	4.00	0.00674	0.00169
	5.00	0.00823	0.00165
		Av.	0.00172
Edible gelatin	1.00	0.00160	0.00160
	2.00	0.00334	0.00167
	3.00	0.00491	0.00164
	4.00	0.00658	0.00165
	5.00	0.00792	0.00158
		Av.	0.00163
High-grade hide	1.00	0.00168	0.00168
	1.50	0.00234	0.00156
	2.50	0.00396	0.00158
	3.50	0.00549	0.00157
	4.50	0.00716	0.00159
		Av.	0.00160
Medium-grade hide	1.00	0.00168	0.00168
	1.50	0.00219	0.00146
	2.50	0.00396	0.00158
	3.50	0.00549	0.00159
	4.50	0.00708	0.00157
		Av.	0.00158
High-grade bone	1.00	0.00160	0.00160
	2.00	0.00330	0.00165
	3.00	0.00468	0.00156
	4.00	0.00625	0.00156
	5.00	0.00769	0.00154
		Av.	0.00158
Medium-grade bone	1.00	0.00160	0.00160
	2.00	0.00330	0.00165
	3.00	0.00460	0.00153
	4.00	0.00621	0.00153
	5.00	0.00761	0.00152
		Av.	0.00157
		Grand average	0.00161

¹ Received March 12, 1928.² Walpole, *Kolloid-Z.*, 13, 241 (1918-19); Robertson, "The Physical Chemistry of the Proteins," pp. 60 and 359; Bogue, "Chemistry and Technology of Gelatin and Glue," p. 119.

Converting this grand average of specific refractivity for all commercial glues studied to a 100 per cent dry glue basis

$$\frac{0.00161 \times 100}{88} = 0.00183$$

we find that this work agrees very well with that of Walpole.

Discussion

These experiments are too few to permit one to draw absolute conclusions, but they do present a number of very interesting possibilities from both practical and theoretical standpoints.

The point that first attracted attention was the fact that the specific refractivities of the glues examined were not equal. The variation was too great to be attributed to experimental error alone, so other possible factors were considered in order that the variation might be either eliminated or corrected.

To find out if variation in ash content was causing these differences an ash determination was made on each sample, with results as noted in Table I. The extreme range was found to be 3.73 per cent. When we consider that only dilute solutions (none over 5 per cent) were studied, the possible effect due to ash becomes almost negligible. For example, if two glues differing in ash content by 2 per cent are made up to a 5 per cent solution, the resulting difference in ash would be only 0.10 per cent. The difference between the specific refractivity of this ash and that of the correspond-

ing amount of glue is so slight that 0.10 per cent could not be detected.

Furthermore, the ash variation did not correlate with specific refractivity. For example, the difference in ash between the high-grade hide and the edible gelatin is more than four times that between edible gelatin and ashless gelatin, yet the difference in specific refractivity is only approximately half as great.

It is a well-established fact that in a homologous series, the power of refractivity is dependent upon the size of the molecule. The protein molecule in gelatin is exceedingly large, but breaks down readily into molecules of diminishing size until finally the simple amino acids are reached. Naturally, the specific refractivity of any of these hydrolytic products is less than the original. The grade of any glue is dependent upon this same decomposition. Consequently, we might reasonably expect a high-grade glue or gelatin to have greater refractive powers than a low-grade glue when made up in equal concentrations—which is in perfect accord with data given above.

As a result the approximate grade of any glue upon which readings are taken should be known before expressing results in terms of percentages, if extreme accuracy is essential.

Acknowledgment

The writer wishes to acknowledge the cooperation of Mr. R. S. Chalfont of Carl Zeiss, Inc., Chicago, Ill.

A Continuous-Extraction Apparatus¹

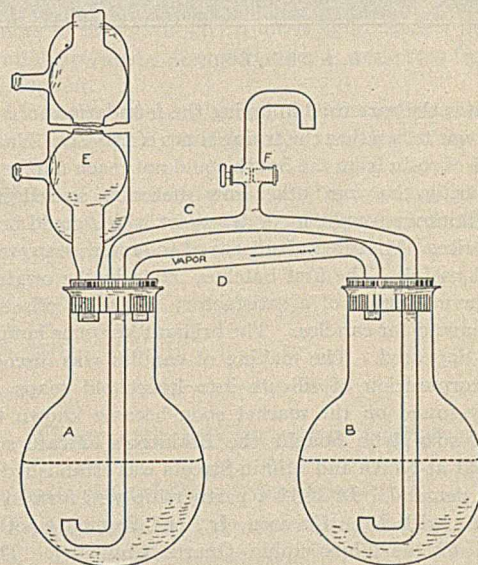
H. L. Maxwell

SCHOOL OF CHEMICAL ENGINEERING, PURDUE UNIVERSITY, LAFAYETTE, IND.

IN ORDER to make a rapid and accurate determination of oil in several varieties of kernels, from which the oil proved to be only sparingly soluble in the solvent, it was found advisable to construct a continuous-extraction apparatus in which the oil-laden solvent was continuously drawn off and the hot, clean solvent continuously returned to the extraction flask. The first extractor of this type² designed by the writer was one in which two flasks were connected by a siphon to transfer the oil-laden solvent and also a short glass tube to return the purified solvent as vapor. Although the apparatus has been used extensively, it had at least two disadvantages—the difficulty in filling the siphon at the beginning of the extraction, and the tendency of bubbles to collect in the upper part of the siphon during extraction.

Recently an improved design, as shown in the accompanying diagram, has overcome the two difficulties with the siphon. The material to be extracted is placed in flask A. Both flasks are than half filled with solvent, ether, alcohol, or water, as the case may be. The siphon C is filled by applying suction through stopcock F. The flasks with condenser and attachments are placed in a water bath or on a sand bath if the solvent used is water. When heated, the vapor produced in flask B forces its way through the short tube D into flask A, where it is condensed by the condenser E. The vapor from flask A condenses in the same way, returning to the same flask. These processes lower the level of the liquid in flask B and raise the level in flask A, thus starting siphon which carries the oil-laden solvent from flask A to B. The solvent vaporizes, leaving its burden of oil in flask B and returning in the form of vapor through D to flask A to be condensed and begin anew its cycle of extraction, trans-

porting and depositing another portion of oil. The tips of the siphon are bent up to prevent the admission of bubbles. If a few bubbles do by chance get into the siphon, they will be caught in the vertical tube immediately before stopcock F and will not interfere with the operation of the siphon.



This continuous extractor has been tested by placing a solution of alcohol and iodine in flask A and pure alcohol in flask B and noting the time necessary to transport all the iodine to flask B. The instrument is economical in both time and solvent.

The advantages in this improved type of extractor are:

(1) The material being extracted is treated with clean, hot solvent. (2) Siphon C is readily filled by applying suction through stopcock F. (3) Small amounts of air accidentally getting into the siphon will be entrapped below F and will not interfere with the operation of the siphon.

¹ Received April 27, 1928.

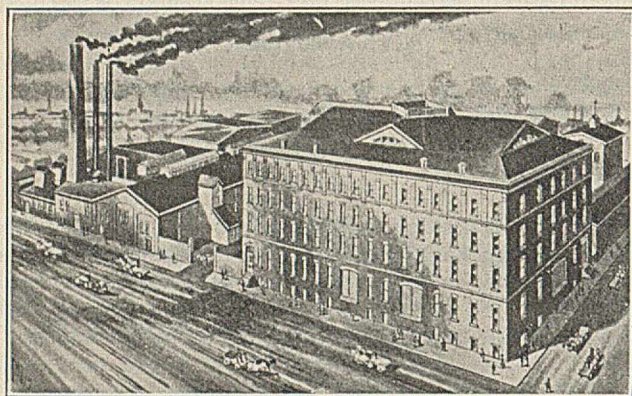
² *Chem. News*, 116, 122 (1918).

AMERICAN CHEMICAL INDUSTRIES

Philadelphia Quartz Company

ANDREW JACKSON had been in the White House for three years, the first issue of the *Liberator* had been published, railway carriages still presented the form and dimensions of the horse-drawn stagecoach, when a quiet and earnest Quaker of Philadelphia, Joseph Elkinton by name, prayerfully decided to embark upon the manufacture of soap and candles. Though trained as a silversmith, he had for fifteen years previously taught school at the Quaker Indian Mission at Tunessassa, N. Y.

In the summer of 1831 his little shop was opened at 783 South Second Street. Industry and thrift caused such a degree of prosperity that by the end of '34 the books showed a net gain of \$1320.98³/₄. The missing quarter cent remains a mystery,



Jos. S. & Thos. Elkinton Factory

but indicates the care used in laying the foundations of an enterprise that was to weather the trying times of the Civil War period.

Supplies of rosin from the South could not reach northern soap-makers during the war, other raw materials soared in price, and the Elkintons sought for a detergent which could be offered at a low price. Mixtures of silicate of soda and soap were tried and found useful. The first batches, made in the original soap factory, gave promise of a satisfactory means of offsetting the waning demand for candles. The brilliant kerosene lamp had by this time appeared. The making of candles was discontinued.

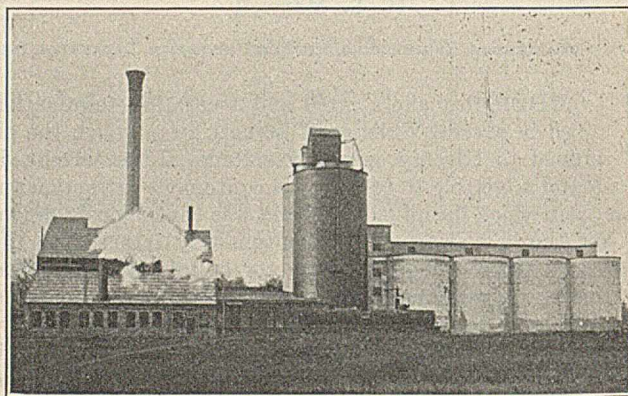
The incorporation of silicate into household soaps and the favor they found on the market soon became known to other makers of soap who bought the Elkinton's silicate solutions. A new plant at Ninth and Mifflin Streets was established to meet the rising demand. In 1864 a partnership was formed for this undertaking with John Greacen, Jr., and Samuel Booth, under the name of the Philadelphia Quartz Company. This continued until '68, when the Elkintons purchased the interests of Greacen and Booth. They sold their silicate product under the trade name of Philadelphia Quartz Company, while the soap business was operated under the firm name of Joseph S. and Thomas Elkinton. The new chemical business seems to have developed slowly, as evidenced by this report to Joseph S. Elkinton, November, 1866. "We have sent away twelve barrels of silicate this week which does not speak very well for revival of trade. I am sorry, but I have not doubted for a moment but what something will turn up that will give you business, even if this dies out entirely." But gradual progress was made.

In the centennial year Charles W. Goudy, a soap-maker in

Marshalltown, Iowa, who had been buying unusual quantities of silicate to put into his soap, was engaged as a salesman. His method of selling silicate for soap-making was unique. He used to take a miniature soap factory from his grip and make a small batch of silicated soap. If necessary, he would repeat the demonstration in the prospect's plant with regular equipment. Skeptical manufacturers were shown that silicate had detergent value when Charles Goudy washed his hands with it. He also gave his customers advice on how to market their soap.

This was the beginning of the company's pioneer efforts to prove the value of silicates of soda not only in washing but in many other industrial processes. The Elkintons thus made it a policy to sell more than just silicate of soda. They tried to incorporate satisfaction into their products. The sales of silicate increased steadily until it was necessary to provide additional manufacturing facilities to serve the patrons of the company. A plant was built at Anderson, Ind., in 1889.

The manufacture of soap was discontinued in 1904, when the firm devoted its entire energies to the production of silicates of soda. At this time the business was incorporated as the Philadelphia Quartz Company. In 1905 a new silicate plant was opened at Chester, Pa., which was to replace shortly the Philadelphia Works.



Rahway Works, Showing Stock Tanks

For about forty years after the Civil War the principal use of silicate of soda was as an ingredient for laundry soaps. Although the adhesive value of silicate was discovered early, the appearance of the corrugated box as a shipping container during the nineties created a new outlet which, together with solid laminated fiber for shipping cases and wall board, was destined to overshadow detergent uses. The phenomenal growth of the use of fiber cases for the transportation of all kinds of products, of course, required silicate of soda in increasing quantities. All that goes to make a dinner, from soup to nuts, even including fresh fish, poultry, and lettuce, is shipped in fiber containers made with silicate of soda.

Other useful applications for silicate of soda were discovered when it was found that the proportions of the ingredients could be varied to produce widely different properties. For example, in consistency the solutions vary from thin, highly fluid liquids to those that are so thick that they will hardly flow. These differences are due not only to concentration but to differences in the ratio between Na_2O and SiO_2 , which is arbitrarily set at

points between 1:1 and 1:4. Special apparatus and treatment are necessary to dissolve any but the most alkaline silicates. These are not so useful as the more siliceous ones, so for convenience silicates are sold mostly in solution. They are, however, shipped in as concentrated a form as is consistent with easy handling. Thus a liquid silicate in which the ratio is $\text{Na}_2\text{O}:2\text{SiO}_2$ will flow somewhat like molasses when it contains 54 per cent solids. At this concentration a solution of $\text{Na}_2\text{O}:3.25\text{SiO}_2$ ratio will be a glassy solid. It will pour freely at a concentration of 38 per cent. In order to save freight on shipping large quantities of water, new factories sprang up closer to the consuming markets. In addition to those at Anderson and Chester, plants have been established at Buffalo, N. Y.; Kansas City, Kans.; Rahway, N. J.; and St. Louis, Mo. Recently the silicate plant of the Central Commercial Company at Utica, Ill., was acquired. In 1917 the Philadelphia Quartz Company of California was formed, establishing a plant at Berkeley, Calif.

Many other uses for silicates have been found. Most of these depend on the colloidal properties. The Philadelphia Quartz Company maintains engineering and chemical staffs, who not only work on manufacturing problems but who are available for consultation and, when desirable, for coöperative work to help the consumers secure the full advantages of silicate.

The general headquarters of the Philadelphia Quartz Company are at 121 South Third St., Philadelphia, Pa. A Chicago office was recently opened at 205 West Wacker Drive.

Among the executives are: President, William T. Elkinton, vice president, Alfred C. Elkinton, both grandsons of the founder, Joseph Elkinton; vice president, Thomas W. Elkinton; secretary and chemical director, James G. Vail; treasurer, F. Algernon Evans; general representative, George W. Goudy; sales director, J. Passmore Elkinton; manager of Purchasing and Traffic Departments, William Martin; chief engineer and production manager, Lloyd B. Edgerton.

NOTES AND CORRESPONDENCE

Number of Plates in Fractionating Columns

Editor of Industrial and Engineering Chemistry:

In the article on the "Design of Fractionating Columns" by Keyes, Soukup, and Nichols, in the May, 1928, issue of *INDUSTRIAL AND ENGINEERING CHEMISTRY*, it is shown that if one chooses a reflux ratio of 5 mols of reflux per mol of product, there results a more or less constant proportionality between (a) the number of plates computed from an operating line having a slope $O/V = 0.833$ and (b) the number of plates figured from the diagonal which has the slope $O/V = 1$, and that this assumption leads to a slight simplification of the McCabe and Thiele¹ method of determining rectifying column heights.

It should be definitely pointed out that if a very small reflux ratio is chosen the above proportionality fails, and the simplified method will give results that are too low.

Reflux ratios that are considerably less than 5 are of practical significance. As the reflux ratio is increased, it is true that the height of the column does decrease, but per unit of product both the volume of vapor and the necessary cross section increase. The following table shows the effect of changing the reflux ratio upon the relative dimensions of the column. It is based on the continuous separation of an equimolar mixture of benzene and toluene, to give a distillate containing 99.9 mol per cent benzene and bottoms containing 0.1 mol per cent benzene.

REFLUX RATIO O/V	REFLUX RATIO O/P	VAPOR V/P	NO. OF PERFECT PLATES N	RELATIVE VOLUME OF COLUMN V_{xn}/P
0.582	1.39	2.39	41	98
0.636	1.75	2.75	31	84
0.667	2.00	3.00	28	84
0.767	3.29	4.29	24	101
0.833	5.00	6.00	21	126
1.000	Infinite	Infinite	15	Infinite

By interpolation from the table, one finds that the minimum volume of the column, 83 relative units of volume, corresponds to a reflux ratio $O/P = 1.8$. For this case the minimum reflux ratio, corresponding to an infinite number of plates, is 1.34. Even with heat costing nothing, one would always here use a reflux ratio greater than 1.34 but less than 1.8. Considering the cost of heat by making an economic balance, the optimum reflux ratio would be even less for this case.

¹ *IND. ENG. CHEM.*, **19**, 907 (1927).

The modified method suggested by Keyes, Soukup, and Nichols, then, should be applied very cautiously if the optimum reflux is much less than 5.

W. L. McCABE

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICH.
June 24, 1928

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Editor of Industrial and Engineering Chemistry:

In reply to a criticism of our recent article, I quite agree with Doctor McCabe when he states that our system of determining the number of plates will give a lower figure than if his very low reflux ratios are used. The difference is not great from a practical standpoint.

The desirability of using very low reflux ratios and designing the column accordingly is debatable and should not be argued here.

It may be of interest to point out that our method of determining the number of plates in a fractionating column has been used ten years and we have yet to find any serious defect in it.

D. B. KEYES

UNIVERSITY OF ILLINOIS
URBANA, ILL.
June 25, 1928

Corrected Nitrogen Figures

Editor of Industrial and Engineering Chemistry:

In the article entitled "Present Status of Coal By-Product Nitrogen," by Mildred S. Sherman, *IND. ENG. CHEM.*, **20**, 80 (1928), exports of nitrogen salts are neglected.

In the last paragraph on page 80 it is stated that the excess of consumption of nitrogen over domestic production is 178,080 tons. From government statistics I note that in 1926, 40,000 tons of nitrogen were exported, mainly in the form of ammonium sulfate. Consequently, the excess of consumption of nitrogen over domestic production in 1926 was nearer 138,080 tons than the quantity calculated by Mrs. Sherman.

CHAPLIN TYLER

LAZOTE, INC.
WILMINGTON, DEL.
May 23, 1928

Melting Point of 2-Chloroanthraquinone

Editor of Industrial and Engineering Chemistry:

In a paper published by the writer in *IND. ENG. CHEM.*, 17, 722 (1925), the melting point of 2-chloroanthraquinone is given as 204° C. An occasion recently arose requiring the preparation of pure 2-chloroanthraquinone, according to the method given in that article, and its melting point was found to be 212.4° C.

(corrected). On examining the original notes on this work, it was discovered that the melting point is correctly recorded there as 212.4° C. (corrected). I regret exceedingly that this typographical error was overlooked.

M. PHILLIPS

BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.
July 3, 1928

BOOK REVIEWS

Petroleum and Its Products. BY W. A. GRUSE. 340 pages. McGraw-Hill Book Company, Inc., New York, 1928. Price, \$4.50.

This book is concerned primarily with the chemistry of petroleum and the refining processes and contains enough information in regard to the processes themselves, from the point of view of the chemist, to make the work intelligible. It covers a field similar to that of the well-known book of Gurwitsch.

The book can be divided into three main sections. The first (97 pages) covers the chemical and physical properties of petroleum and the compounds contained in it, together with a brief résumé of the theories of the origin of petroleum. This section is particularly complete with references to the original literature. An ingenious chart on the classification of crude petroleum is included. The second section (113 pages) discusses the processes of refining and takes up the individual processes of distillation, chemical refining, adsorption, and cracking from the point of view of their underlying theories and of the fundamental changes which they accomplish. In some instances it seems that too much emphasis has been placed on the time-honored obsolescent procedures at the expense of the more modern scientific developments. This is notably true of the discussion of distillation. The third section (130 pages) includes chapters on the main products from petroleum, describing their properties, the requirements set by their uses, and the main scientific facts related to their application. One chapter contains a clear and simple outline of the theoretical side of lubrication. It is to be regretted that the author has chosen to express the simplified Sommerfield criterion other than as the familiar *ZN/P* function which has come into such general use as symbolizing it.

Portions of the book would be of greater value if the author had discussed more completely, and possibly at the risk of incurring displeasure, certain phases of his subject which are somewhat controversial. For example, the different properties of lubricating oils from various types of crude petroleum are scarcely touched. The differences in carbon residue, volatility, and rate of viscosity change with temperature in oils of the same viscosities from different sources are passed over in a few words, and the fact that the rate of viscosity change with temperature varies with the crude source of the oil is not even mentioned. The comparison of native asphalts with the residuum product is also inadequately discussed.

On the whole, the book is readable and contains a large collection of scientific material related to petroleum which has been carefully coordinated. It is recommended to trained chemists interested in petroleum.—J. BENNETT HILL

Chemical Encyclopædia. An Epitomized Digest of Chemistry and Its Industrial Applications. BY C. T. KINGZETT. 4th edition. 807 pages. D. Van Nostrand Co., Inc., New York, 1928. Price, \$10.00.

According to the preface the subject matters comprise pure, physical, and applied chemistry; description of the elements and their chief compounds (organic and inorganic), as also the methods of their preparation and their characters and uses; brief accounts of ores and other natural products together with their utilization; and the more important chemical terms and theories. The purpose of the work is further illuminated by the statement that it is also intended for members of Parliament, editors, medical practitioners, lawyers, etc. In an effort to increase the value and use of the present edition, many references are given to recent publications, which amplify the brief statements made.

It is obviously impossible to attempt to cover the fields enumerated above in 800 pages, and give more than a fragment

about any of the products listed. This probably accounts for the fact that the statements about the uses of most of them are very general; thus, ammonium tartrate is used in the textile industry but the specific use is not indicated. Many definitions tell little more than that for barium acetate—"a white crystalline compound, soluble in water." The entry under organic chemistry merely states that there are three English books on the subject. However, the fact that author and publisher have been willing to carry such a work through four editions indicates that there must be a demand for it.

The principal use of the work to readers of *INDUSTRIAL AND ENGINEERING CHEMISTRY* would seem to be as a source of information regarding the many trade names which are listed, and which cannot be found readily because they give no clue as to the class of materials to which they refer. In noting the literature citations, the reviewer is struck with the difficulty of conveniently referring to the present British system of abstracts contrasted with our *Chemical Abstracts*.—C. J. WEST

Methods for the Analysis of Cereals and Cereal Products. BY D. A. COLEMAN, F. A. COLLATZ, H. C. FELLOWS, M. D. MIZE, AND C. B. MORISON. 176 pages. Published by American Association of Cereal Chemists, Kansas City, Mo., 1928. Price, to members, \$3.00; to non-members, \$3.50.

The Association of Cereal Chemists deserves great credit, not only for bringing together the methods applicable to the analysis of wheat, flour, bread, alimentary paste, feeding stuffs, etc., but for including so much valuable relevant information, especially definitions of most of the raw materials used in baking, as well as of mill products and other feeds.

The first 85 pages, which constitute Part I, are devoted to the methods of analysis. This is followed by Part II, which consists of 19 pages of definitions and 70 pages of tables.

At the beginning of the book it is stated that "access has been had to the methods of analysis of the Association of Official Agricultural Chemists, acknowledgment of which is hereby made." The force of this acknowledgment is offset by the fact that the methods for ash in flour, and fiber in feeding stuffs are especially credited to the A. O. A. C., leaving one to suppose that the numerous other methods not so credited may be of different origin. As a matter of fact, many of the methods described are taken bodily from the A. O. A. C. Methods of Analysis. In a number of instances, however, the A. O. A. C. methods have been inserted with slight changes in verbiage, which in some cases have not made for clarity. For example, the A. O. A. C. method for fat determination reads as follows: "Extract about 2 g. of the sample dried as directed under * * * with anhydrous ether, etc. The new version reads: "Extract about 2 g. of the dried sample as in Part II * * * with anhydrous ether, etc." This reads as though extraction itself is to be done "as in Part II." Throughout the book reference is made to Part I, Part II, etc., instead of to Chapter I, II, etc., for the methods are all in Part I.

Many of the best-known methods are described in excessive detail, whereas the most recent, and probably the least known, method—viz., that dealing with H-ion concentration—is dismissed with a mere ten lines. None of the main principles underlying the electrometric method has been inserted, not even a description of the indicator or coloration method, which is based upon the electrometric method and which might have been found most useful.

When this loose-leaf and handy volume is revised, the association will no doubt give full credit to each of A. O. A. C. methods used; to the Department of Agriculture's definitions of the various foods; to the Millers' National Federation, and to the

Association of Feed Control Officials, whose published definitions of flour and feeds have been incorporated. All told, it is a worth-while book and contains much helpful information.—
J. A. LE CLERC

Snapshots of Science. By E. E. SLOSSON. 299 pages. Illustrated. Century Company, New York, 1928. Price, \$2.00.

The name of Slosson, director of Science Service, author of "Creative Chemistry" and various other books to humanize science, is so well known to the chemical fraternity that whatever he writes finds a wide circle of readers among chemists and makes a lengthy review unnecessary. Doctor Slosson explains that "snapshots are the only kind of pictures that can be taken of rapidly moving objects, and science is moving so rapidly nowadays that it makes the on-looker's head swim to watch it."

The book contains seventy-nine such snapshots, being short articles three or four pages in length that give information about or explanation of some of the late developments in the various sciences. The book is much wider than chemistry and the author has dipped into all the fields of natural science in choosing examples to show how things are moving forward. It is not often that one finds between a single pair of covers stories touching astronomy and archeology, physics and chemistry, psychology and mathematics. Most of the snapshots concern the application to daily life of the discoveries of science. It is the kind of book that one can take up at odd moments and begin to read with interest wherever the book chances to open. It is written in the well-known style of Doctor Slosson and is both interesting and instructive.

Cements, Limes and Plasters. Their Materials, Manufacture and Properties. By EDWIN C. ECKEL. 3rd edition. 699 pages. John Wiley and Sons, Inc., New York, 1928. Price, \$7.00.

This book through its two previous editions has been the standard reference volume for fundamental information concerning manufacture and properties of cements, limes, and plasters, and it is a disappointment to find that the text of the third edition does not include revisions to bring it up to date. A new section has been added which briefly (45 pages), but yet most comprehensively, discusses the alumina and high-strength portlands, and this may be considered as equivalent to a revision of the old text on cements.

To assume that there have been no developments or improvements in the last six years that are worth mentioning in the lime and gypsum industries certainly is not justified. The latest reference cited in the bibliography on hydrated lime is dated 1904 and in the text no mention is made of new products or of improvements in burning and hydrating practice which have resulted from the recent published work of Azbe, Haslam, Withrow, Porter, Mathers, and others. Cost data given on lime are also largely obsolete.

It is hoped that a revised edition will not long be delayed, but until such revision does appear the present volume will remain a valuable reference on cements and on the basic operations in the other structural material industries covered.—G. J. FINK

Safety and Production. An Engineering and Statistical Study of the Comparative Relationships between Industrial Safety and Production. A Report by the AMERICAN ENGINEERING COUNCIL. 414 pages. Harper & Brothers, New York, 1928. Price, \$5.00.

This is a report upon work undertaken at the instance of the National Bureau of Casualty and Surety Underwriters. The problem rested basically upon the following conditions:

(a) An insurance experience since the war of increasing industrial accidents and, in particular, increasing accidents costs.

(b) A substantial increase during the past decade in the productivity of the American industrial worker.

(c) A generally accepted, but unproved, thesis that "the safe factory in general is the efficient factory, and the efficient factory in turn is the safe factory."

(d) A further development of this thesis (also, hitherto unproved) that safety in the factory and efficiency of production are both aspects of good executive control, and that a right organization in industry will, with proper managerial effort, bring about both efficient and safe production, and, further, that neither can be satisfactorily achieved by itself alone.

The method of investigation was to gather the experience records of a large number of industrial plants from which both

accident and production rates could be determined. The data sought were the average number of employees per year, number of man-hours worked per year, annual production, number of lost-time accidents per year, and number of days lost due to lost-time accidents per year. The committee, after correlating the results of its investigations, records ten findings as follows:

1—Industrial accidents can be controlled under modern conditions of highly efficient productivity.

2—The rate of change in production per man-hour for the industrial groups studied is greater than the rate of change in accident frequency per man-hour or the rate of change in accident severity per man-hour. Quantitatively, the production rate was 14.4 per cent higher in 1925 than in 1922, the accident-frequency rate 10.4 per cent lower in 1925 than in 1922, and the accident-severity rate 2.5 per cent higher in 1925 than in 1922.

3—The experience of a large group of companies shows that material reductions in accident rates can be obtained simultaneously with an increase in production rate.

4—Major industrial executives have as much responsibility to initiate accident prevention as to initiate improvement in productivity.

5—Efforts to improve safety performance do not interfere with production.

6—Maximum productivity is ordinarily secured only when the accident performance tends toward the irreducible minimum.

7—The production and accident performances of the best plants in each industry studied clearly show that tremendous improvements can be achieved by the majority of plants in each industry.

8—The incidental or accompanying cost of industrial accidents is a loss in industrial operation which should not be neglected.

9—Organized safety work is being carried on in a relatively small percentage of industrial plants.

10—A large number of industrial establishments keep no accident records and make no attempt to analyze their experience as the first step in decreasing accidents.

A number of recommendations were also made which, if adopted, it is believed would bring about a new safety movement in industry which would far eclipse the old. The outstanding recommendation is to have American industrialists adopt the same executive policy toward safety which they have fully developed toward production.

It is interesting to note that in the chemical industry, where the data are based upon findings and experience of thirty-five chemical companies, there has been marked increase in the rate of production during the last five years, attended with a reduction in the accident frequency rate, which declined faster than the production rate increased.

The first part of the volume states the problem in detail and gives the findings and recommendations of the committee and a digest of the report. Part II deals with levels of performance, increased productivity and reduction of accidents, accidents in terms of production, and discussions of individual accidents. Part III deals with sixteen specific industries with a chapter on miscellaneous industries and an introduction. There are three appendixes. Throughout the volume are many statistics and a large number of graphs which present in attractive and easily understood form many of the data supplied by the cooperating industries. Manufacturers and others particularly interested in maximum production with maximum safety will find much to guide them in this engineering and statistical study.

Elements of Machine Design. By JAMES D. HOFFMAN AND LYNN A. SCIPIO. 327 pages. Ginn and Company, Boston, 1928. Price, \$3.80.

This book is a well-written presentation of the subjects ordinarily included in elementary machine design. There are two main divisions to the book, one on the elements and the other on the applications.

The first division consists of nine chapters on: Materials Used in Machine Construction; Static Forces; Shafting, Keys, and Couplings; Flywheels and Pulleys; Belt Drives and Rope Drives; Friction Gearing; Spur and Bevel Gearing; Screw Gearing; Bearings; Flat Plates, Pipes, and Cylinders; Joints and Fastenings. The material is well prepared but brief. Definite references to sources of information are given in the text, while a list of general references and a very liberal collection of problems at the end of each chapter add to the value of the book.

The second division consists of seven chapters and appendix, and contains illustrative designs worked out for a toggle joint press, a jib crane, a belt-driven punch, an overhead traveling crane, and a Scotch marine boiler. Chapter XVIII covers some studies in kinematics. As stated in the preface, "it has been the aims of the authors to illustrate, by the use of typical examples of design, methods of attack whereby the student may get the greatest amount of information in the least possible time."

This practical purpose appears to be well accomplished. A general statement is made in regard to each machine, followed by a specification and analysis of the design as a whole and of each part. Methods of calculation, illustrations, and definite references are freely given. This section on illustrative designs should be very helpful to the student and for reference. It is so complete as to be ideal for self instruction.

The appendix contains very little information. The authors might do well to consider the latest "American standards" for bolt heads and units, fine and coarse screw threads, shafting, keyways, and other new data.

The book has many possibilities for usefulness. While intended for students of mechanical engineering, it will prove of value for reference by engineers who have occasional design problems. It can be used profitably for a beginning course in either classroom or laboratory.—CARL LARS SVENSEN

History of Alpha Chi Sigma Fraternity. BY HARRY A. CURTIS. 200 pages, 50 illustrations. May be purchased from John R. Kuebler, National Secretary, 5503 East Washington St., Indianapolis, Ind. Price, \$3.00, cloth bound.

When one reads this history it quickly becomes evident why Alpha Chi Sigma, the oldest and largest chemical organization of a fraternal nature, has had such a tremendous influence on both science and its membership in the United States. From its very inception, in 1902, this chemical professional group has continuously stressed its responsibility to chemistry and chemists, and this spirit of constructive service has been admirably reflected in this volume.

The history includes the complete story of the national organization and of the negotiations and official proceedings which led to the founding of each of the subsidiary chapters, including the forty-first collegiate chapter, which was installed November, 1927. Since this work has been in part or as a whole reviewed by almost every former grand officer who was for any period of years active in executive position, it is a monument of painstaking accuracy. And yet Curtis has written into the text in an inimitable style also that spirit of the organization which will serve as a wonderful stimulus to every member reader. To those chemists who are not members of the fraternity and who care to know the inside story of the workings and the purposes of this order, the book can be most cordially commended. Especially is it suggested for the perusal of any faculty man whose relations with the subsidiary groups of Alpha Chi Sigma leave in his mind any doubt as to the worthwhileness of the real spirit of professional service that permeates this organization.—R. S. MCBRIDE

The Elements of Industrial Engineering. BY GEORGE HUGH SHEPARD. 541 pages. Ginn and Company, Boston, 1928. Price, \$4.80.

As the author states in his preface, this volume is an attempt, first "to reduce industrial engineering to a few definite and comprehensive principles, by which the engineer can analyze any situation in management and synthesize the procedure; secondly, to bring students immediately into contact with these principles; and thirdly, to cause them to learn the principles practically by using them in their daily lives."

The importance, which the author places on the student's own campus activities as a basis for the acquisition of the necessary experience and skill in the analysis and synthesis essential in the principles of management, is shown by his including its discussion in the first chapters of the book.

The subject matter of the text is an elaboration of thirteen principles of management somewhat modified from the "Twelve Principles of Efficiency" of Harrington Emerson. Three of these principles have been selected as primary, since they seem to include all the rest. These are ideals, personnel, and organization. Ideals include, as secondary principles, adaptation of conditions and work to each other, correct methods, and instruction. Personnel includes fair deal and discipline. Organization includes planning and despatching, records, standards, and efficiency reward. The thirteenth is the all-inclusive principle, higher common sense, which is the application of all the other principles. Every one of these principles applies to every management problem, no matter how varied may be the specific cases. However, the author forewarns the student not to expect to find management some cut-and-dried routine system which can be applied mechanically. He points out that there is "no universal system," "management situations are infinite in number and variety and a manager can deal with them only by doing his own thinking on the basis of a thorough knowledge of fundamental principles."

The book should be in the hands of every college student and

particularly those of engineering colleges. If its preliminary study were seriously made early in the sophomore year, it could not fail to benefit the rest of the student's course. A more detailed study again in the senior year would be of the greatest possible advantage to every young engineer about to enter upon his professional career.—W. L. JENNINGS

Jod—Ein Überblick über seine Biologische und Pharmakologische Bedeutung. 46 pages. Published by the Komitee für Chilesalpeter in Berlin, Uhland-Strasse 188, Berlin-Charlottenburg, Germany, 1927.

While the pharmacological usefulness of iodine has long been appreciated although imperfectly understood, it is only within recent years that the importance of its biochemical functions has won recognition. This has been due chiefly to the discovery and isolation of the thyroid hormone, thyroxin. The vital role played by thyroxin in the biochemistry of the human chemical system and its profound influence on the principal physiological functions of the body have caused attention to be centered on the thyroid gland. Accordingly any contribution to the knowledge of the subject is welcome and a short, popular-style presentation as is the present brochure should meet with approval.

This little paper-bound book presents its thesis in an introduction and six chapters as follows: (1) General Considerations Concerning Iodine; (2) Iodine as a Bio-Element; (3) The Iodine-Containing Hormone of the Thyroid Gland; (4) The Relation of Iodine Intake to the Goiter Problem; (5) The Pharmacology of Iodine; and (6) Clinical Use of Iodine and Iodine Preparations. Chapter 6 presents a list of available iodine preparations with their proprietary names, composition, characteristics, and manufacturers.

While the trade significance of this publication is apparent from its source, its value must be determined by its substance rather than its purpose. Its purpose being what it is, it is natural that it should be illogical in pointing the way to a pharmacological solution of a purely dietary problem, the goiter problem; but there is no lack of logic in citing the names of manufacturers of iodine preparations, since they are likewise the purchasers of iodine. At least it may be said that this publication is no more illogical than those issued by the same propaganda bureau seeking to connect the German goiter problem with the discontinuation of the use of Chile nitrates in German agriculture and recommending that goiter be combated by a return to that use. There is no question of the importance of the biochemical role played by iodine, but from Chile nitrates to the thyroid gland is a far cry.—J. W. TURRENTINE

Destillieren und Rektifizieren. BY KURT THORMANN. 112 pages. Verlag von Otto Spamer, Leipzig, 1928. Price, bound, 14 marks; paper, 12 marks.

In his preface the author very properly states that Hausbrand, the standard German reference work on distillation, is not always reliable and that there is need for a more accurate and up-to-date volume on this subject.

The author has prepared a concise volume of 112 pages including 65 cuts showing diagrammatic sketches of distilling apparatus and graphical presentation of data. The following subjects are discussed: properties of liquid mixtures; batch or discontinuous distillation; continuous distillation; separation of mixtures having more than two components (ternary and quaternary); packed columns; and equipment for alcohol distillation.

The treatment is from the mathematical viewpoint based on Gibbs' phase rule and the laws of Raoult, Dalton, and Trouton. At best the equations are complicated and care must be exercised in their application. For ready use in design work there is still room for simplification. The method of determining the number of plates required, as described by Keyes and collaborators in the May issue of INDUSTRIAL AND ENGINEERING CHEMISTRY, is a step in this direction.

The book will be of considerable interest to technologists working on distillation problems.—A. A. BACKHAUS

Die Verflüssigung der Kohle nach Fr. Bergius. BY WALTER FRIEDMANN. 60 pages. Allgemeiner Industrie-Verlag G. m. b. H., Berlin, 1928.

This booklet is a technologic and economic review of the Bergius process for liquefying coal by hydrogenation under pressure. The author introduces the subject with a chapter on the form value of fuels—solid, liquid, and gaseous—and the conversion from one form to another. He then reviews historically the developments in physical chemistry, coal chemistry, and studies

on the origin of coal which antedated the work of Bergius and furnished the foundation for his discovery.

The development of the Bergius process is then traced from the early theoretical work up to the establishment of a large-scale hydrogenation plant at Manheim. This is told in an interesting narrative style with comments by the author on the chemical and economic relationships between the production of motor fuel, fuel oil, and lubricating oils. The last two chapters contain cost estimates for the production of oil from coal and comparisons with the price of and duty on imported petroleum.

The booklet does not contain detailed information on the technology of the process, chemical composition of the products, or the yields obtained from various types of coal; but it does give an excellent general description of the process, its present status in Germany, and the economic relationships involved.—A. C. FIELDNER

Das Essener Heft. Report of the Convention of the Association for Water, Earth, and Air Hygiene held in Essen in June, 1927. 518 pages, 288 illustrations and tables. Published by and obtainable through the Landesanstalt für Wasser-, Boden- und Lufthygiene, Berlin-Dahlem, Eherenbergstr. 38-42. Price, 12 marks.

This volume contains the proceedings of the twenty-fifth annual convention of the Association for Water, Earth, and Air Hygiene held in Essen in June, 1927, the first convention outside the city of Berlin.

At the same time as the convention an exposition (Achema) of chemical apparatus was held in Essen under the auspices of the Division for Water Chemistry of the Association of German Chemists (Vereins deutscher Chemiker). Part 9, pages 439-94, of the volume is given over to a description, profusely illustrated, of the apparatus exhibited at this exposition.

The papers covered the entire field of sanitary science from the engineering phases of water supply and waste treatment, the effects of air pollution on human population and vegetation, to the disinfection of clothing and the control of vermin. The subjects are all clearly and authoritatively treated, and profusely illustrated. The volume furnishes an exceedingly valuable summary of current practice in the field of sanitation. The questions are naturally discussed from the standpoint of applications to German conditions, but references are frequently made to recent progress in other countries. Of the 350 delegates to this convention a considerable number came from foreign countries.—A. M. BUSWELL

Die elektrolytischen Metallniederschläge. Lehrbuch der Galvanotechnik. BY W. PFANHAUSER. 7th edition. xiv + 912 pages. 383 figures. 16.5 × 24 cm. Verlag von Julius Springer, Berlin, 1928. Price, bound, 40 marks.

This is by far the most comprehensive treatise published on electroplating and electroforming and related topics. About one-sixth is devoted to a "theoretical part," and the rest consists of specific information, usually in considerable detail, upon both major and minor applications of electroplating. Purely as an encyclopedia of processes and equipment, the book is certain to be of value to anyone engaged in research or development work in this field.

The explanation of principles of electrodeposition in language that is scientifically sound, and at the same time intelligible and useful to the practical plater, is an extremely difficult task, which no author has yet fully accomplished. Throughout this text accuracy is sacrificed for simplicity in expressing the resistivity of the plating solutions in ohms instead of ohm-cm. or ohm-dm. This error is the more confusing because the author (page 14) computes the values in ohm-dm. instead of in ohm-cm., the unit employed in most scientific work. The assumption (pages 118 and 119) that the adhesion of electrodeposits is a simple function of the relative melting points on the absolute scale and of the "absolute hardness" of the respective metals is an unproved hypothesis that would be more appropriately presented in a scientific symposium than in an elementary textbook.

One weakness of this text, encountered in many other books devoted largely to practical methods, and especially in revisions of such books, is the failure to coordinate new matter and to apply in the rest of the text the principles explained in the theoretical part. Thus on page 106 a detailed description is given of the principles and methods of measuring throwing power recently published by Blum and Haring, but this is preceded, without critical comment, by a different and inconsistent explanation advanced by Pfanhauser many years ago. On page 224 the

principles of pH are explained clearly, but in the chapter on nickel deposition only incidental references to pH control are made; and empirical directions to make the bath "weakly acid" are still given.

The inclusion of numerous formulas with so little critical discussion of their relative value makes the book more useful as an encyclopedia than as a working guide. One very commendable feature, however, is the inclusion with each formula of such data as bath voltage, current density, temperature, density and resistivity of the solution, cathode efficiency, and thickness of deposit produced in one hour.

The chapter on nickel includes operating data for proprietary salts made by the company with which the author is connected, such as "Britannia," "Germania," "Neptun," "Mars," etc., without indicating their composition. Whatever justification there may be for the sale or use of such proprietary products, there is no excuse for including them in a textbook of this scope. Their place is in a trade catalog.

By far the best chapter is that on chromium, which is the most complete treatment of all phases of this subject that has ever been published. No attempt has been made to include an exhaustive bibliography or a critical discussion of theories. Sufficient references are given, however, to present a very good perspective of the present status of the process and its applications, especially in Germany. One unfortunate error occurred in translating the column headings in a table (page 584) derived from Bureau of Standards Technologic Paper 346, by Haring and Barrows. The data of these authors for "Ratio of limiting current densities" and for "Optimum average current density" are given by Pfanhauser in columns designated as the "lower" and "upper" limits of current density, respectively. If uncorrected, this table may be very misleading to the readers.

On the whole the book is more valuable for the vast array of facts which it contains than for its presentation or explanation of principles.—W. BLUM

Den Analytiske Paavisning af Blegning af Hvedemel. (The Analytical Detection of the Bleaching of Wheat Flour.) With a summary in English. BY HOLGER JORGENSEN. 70 pages. L. Levinson, junr., Akts., Copenhagen, 1928.

This paper-covered booklet consists of some 40 pages of Danish text and a 22-page summary in English. Five tables of analyses accompany the Danish and 4 the English section.

The discussion includes the natural color of flour; the four chief agents commonly used in bleaching: nitrogen peroxide, chlorine, nitrogen trichloride, and benzoyl peroxide; the action of these agents upon the carotin or coloring matter of flour; the attitude of officials of various governments toward bleaching; the laws that have already been enacted in this regard; a statement of the objects of the research—viz., to solve the problem of analytically determining whether a flour has been bleached and the nature of the bleaching agent.

No method has as yet been evolved to determine with certainty the nature of each of these bleaching agents, especially benzoyl peroxide. As only 13 grams of this bleaching agent (containing 16 per cent benzoyl peroxide) are used to bleach 100 kg. flour, the amount of benzoic acid present in flour cannot exceed 1 part per 50,000, the detection of which has thus far baffled all efforts.

The nitrogen peroxide is detected by the well-known Griess-Ilosvay method; chlorine by the presence of chlorine in the fat, though in the case of flour bleached with nitrogen trichloride it is a most difficult matter to establish that fact unless the flour has been heavily treated. The quantitative determination of both nitrogen peroxide and chlorine is carried on in accordance with methods essentially the same as those approved by the Association of Official Agricultural Chemists.

The methods used to determine moisture, ash, and fat differ widely from those used here. No American chemist would choose to determine moisture in flour by drying 8 grams in a partial vacuum at 80-85° C. for 16 hours; nor would he burn 20 to 50 grams of flour to estimate the ash, nor extract 40 grams with gasoline to obtain the fat.

The real contribution consists in the emphasis placed upon the gasoline value and conclusion that any flour with a gasoline value of 90 or less has been bleached. Winton's method, with slight modifications, has been used.

A flour containing as much as 15 mg. chlorine or 40 times 10⁻⁵ grams nitrogen peroxide per kilogram may be declared to have been bleached. It is well known that flour will occasionally absorb more nitrogen peroxide than the standard above given. American flours, unbleached, have likewise been noted to have a lesser gasoline value than 90.

Altogether this is an interesting and important contribution to the subject.—J. A. LE CLERC

GOVERNMENT PUBLICATIONS

Notice—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.

Bureau of Fisheries

Nature and Extent of Fouling of Ships' Bottoms. J. PAUL VISSCHER. Document 1031. 252 pp. Price, 35 cents.

Bureau of Foreign and Domestic Commerce

The International Cartel Movement. LOUIS DOMERATZKY. *Trade Information Bulletin* 556. 61 pp.

Trade in Iodine. Compiled by O. P. HARTLEY from reports by representatives of Departments of Commerce and State and other sources. *Trade Information Bulletin* 561. 35 pp. Paper, 10 cents.

Bureau of Mines

Active List of Permissible Explosives Approved Prior to June 30, 1928. *Reports of Investigations* 2879. 8 pp.

Consumption of Explosives in May, 1928. *Consumption of Explosives* 75. 9 pp.

Copper Milling Research in Michigan. A. W. FAHRENWALD. *Reports of Investigations* 2878. 5 pp.

Electric-Furnace Cast Iron. C. E. WILLIAMS AND C. E. SIMS. *Technical Paper* 418. 48 pp. Paper, 10 cents.

Fires and Fire Prevention in Lake Superior Mines. F. C. GREGORY. *Circular* 6073. 17 pp.

Flotation of Fluorspar Ores for Acid Spar. W. H. COGHILL AND O. W. GREEMAN. *Reports of Investigations* 2877. 3 pp.

Petroleum, Petroleum Products, and Natural-Gas Gasoline, May, 1928. *Monthly Petroleum Statement* 38. 8 pp.

Rock Strata Gases in the Cripple Creek District and Their Effect on Mining. E. H. DENNY, K. L. MARSHALL, AND A. C. FIELDNER. *Reports of Investigations* 2865A. 4 pp.

Russian Papers on Measurements of Terrestrial Radioactivity. L. N. BOGOLAVLENSKY, A. A. LOMAKIN, AND A. CHEREPENIKOV. With a Supplementary Chapter on Radioactive Substances and Methods for Locating Them. F. W. LEE. *Circular* 6072. 27 pp.

Use of the Acetylene Tetrachloride Method of Porosity Determination in Petroleum Engineering Field Studies. CHASE E. SUTTON. *Reports of Investigations* 2876. 10 pp.

Bureau of Standards

Bureau of Standards Soil-Corrosion Studies. I—Soils, Materials, and Results of Early Observations. K. H. LOGAN, S. P. EWING, AND C. D. YROMANS. *Technologic Paper* 368. 107 pp. Paper, 50 cents.

Bureau of the Census

Record Book of Business Statistics. A Supplement to the Survey of Current Business. Part II—Metals and Machinery. 59 pp. Paper, 10 cents.

Department of Agriculture

A Study of the Apparent Viscosity of Milk as Influenced by Some Physical Factors. G. M. BATEMAN AND P. F. SHARP. *Journal of Agricultural Research*, 36 (April 1, 1928), 647-74.

Good Proportions in the Diet. CAROLINE L. HUNT. *Farmers' Bulletin* 1313. Reprinted with slight changes. 22 pp.

Review of United States Patents Relating to Pest Control. R. C. ROARK. Volume 1, No. 4. 15 pp.

The Growth of Rhode Island Reds and the Effect of Feeding Skim Milk on the Constants of Their Growth Curves. H. W. TITUS AND M. A. JULL. *Journal of Agricultural Research*, 36 (March 15, 1928), 515-40.

Geological Survey

Contributions to Economic Geology (Short Papers and Preliminary Reports) 1927. Part I—Metals and Nonmetals except Fuels. G. F. LOUGHLIN AND G. R. MANSFIELD. *Bulletin* 795. 221 pp. Paper, 50 cents.

Sedimentary Rocks of the San Rafael Swell and Some Adjacent Areas in Eastern Utah. JAMES GILLULY AND J. B. REESIDE, JR. *Professional Paper* 150D. Pp. 61-110.

Surface Water Supply of the United States 1923. Part XI—Pacific Slope Basins in California. N. C. GROVER, H. D. MCGLASHAN, AND F. F. HENSHAW. Prepared in cooperation with the States of California and Oregon. *Water-Supply Paper* 571. 431 pp. Paper, 50 cents.

Surface Water Supply of the United States 1924. Part II—South Atlantic Slope and Eastern Gulf of Mexico Basins. N. C. GROVER, A. H. HORTON, W. E. HALL, AND W. R. KING. Prepared in cooperation with the State of North Carolina. *Water-Supply Paper* 582. 66 pp. Paper, 10 cents.

The Pocono Fauna of the Broad Top Coal Field, Pennsylvania. G. H. GIRTY. *Professional Paper* 150-E. Pp. 111-27.

Labor Statistics Bureau

New Test for Industrial Lead Poisoning. Presence of Basophilic Red Cells in Lead Poisoning and Lead Absorption. CAREY P. MCCORD. Industrial Accidents and Hygiene Series, *Bulletin* 460. 33 pp. Paper, 10 cents.

National Museum

Zeolites from Ritter Hot Spring, Grant County, Oregon. D. F. HEWETT, E. V. SHANNON, AND F. A. GONYER. *Proceedings*, 73, Art. 16, No. 2737, 18 pp.

Public Health Service

A 10-Year Record of Absences from Work on Account of Sickness and Accidents. Experience of Employees of the Edison Electric Illuminating Co. of Boston, 1915 to 1924, Inclusive. D. K. BRUNDAGE. *Reprint* 1142 from *Public Health Reports*. 22 pp. Paper, 5 cents.

Effect of Certain Trade Waste on Sludge Digestion. WILLEM RUDOLFS. *Reprint* 1223 from *Public Health Reports*. 8 pp. Paper, 5 cents.

Effect of Salt on Sludge Digestion. WILLEM RUDOLFS. *Reprint* 1221 from *Public Health Reports*. 8 pp. Paper, 5 cents.

Metallographic Study of the Path of Fatigue Failure in Copper. HERBERT F. MOORE AND FRANK C. HOWARD. *Bulletin* 176, Engineering Experiment Station, University of Illinois, Urbana, Ill. 31 pp. Price, 20 cents.

Report of the Committee on Sanitary Control in the Development of Ground-Water Supplies. *Reprint* 1126 from *Public Health Reports*. 13 pp. Paper, 5 cents.

Sewage-Polluted Surface Waters as a Source of Water Supply. H. W. STREETER. *Public Health Reports*, 43 (June 15, 1928), 1498-1522.

Studies on Oxidation-Reduction. XI—Potentiometric and Spectrophotometric Studies of Bindschedler's Green and Toluylene Blue. MAX PHILLIPS, W. MANSFIELD CLARK, AND BARNETT COHEN. *Supplement* 61 to *Public Health Reports*. 36 pp. Paper, 10 cents.

Same. XII—A Note on the Scharfing Reaction (in Reply to Kodama). W. MANSFIELD CLARK, BARNETT COHEN, AND M. X. SULLIVAN. *Supplement* 66 to *Public Health Reports*. 10 pp. Paper, 5 cents.

The Health of Workers in Dusty Trades. *Public Health Reports*, 43 (June 15, 1928), 1497-8.

New Books

Causes of Failure of Wrought Iron Chains. H. J. GOUGH AND A. J. MURPHY. Engineering Research Special Report No. 3. Department of Scientific and Industrial Research. 167 pp. Illustrated. H. M. Stationery Office, London. Price, 7 s. 6 d. net.

Embrittlement of Boiler Plate. S. W. PARR AND F. G. STRAUB. *Bulletin* 177. 71 pp. Engineering Experiment Station, University of Illinois, Urbana. Price, 40 cents.

Fabrikation der Alkaloide. JULIUS SCHWYZER. 123 pp. Illustrated. Julius Springer, Berlin.

First Report of the Committee on Photochemistry. H. S. TAYLOR, *Chairman*. Reprint and Circular Series of the National Research Council, No. 81. Reprinted from *Journal of Physical Chemistry*. 95 pp. National Research Council, Washington, D. C. Price, \$1.00.

Foreign Commerce and Navigation of the United States. Calendar Year 1926. Vol. II—Bureau of Foreign and Domestic Commerce. 627 pp. Government Printing Office, Washington, D. C. Price, \$1.75.

Report of Test by the Director of Fuel Research on the Crozier Retort Installed by Mineral Oils Extraction, Limited, at Wembley. Department of Scientific and Industrial Research. 21 pp. H. M. Stationery Office, London. Price, 9 d., net.

Tariff on Animal and Vegetable Oils. PHILIP G. WRIGHT. 347 pp. The Macmillan Co., New York. Price, \$2.50.

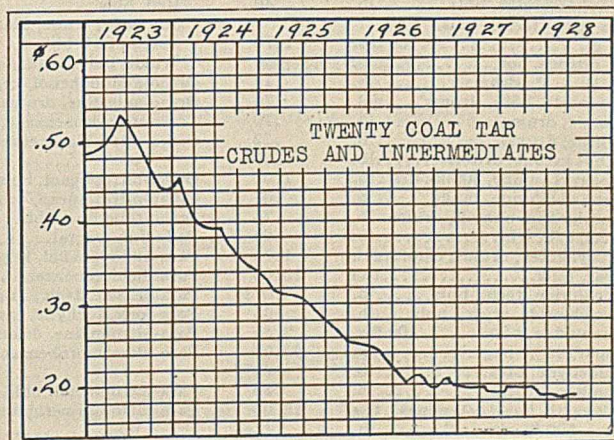
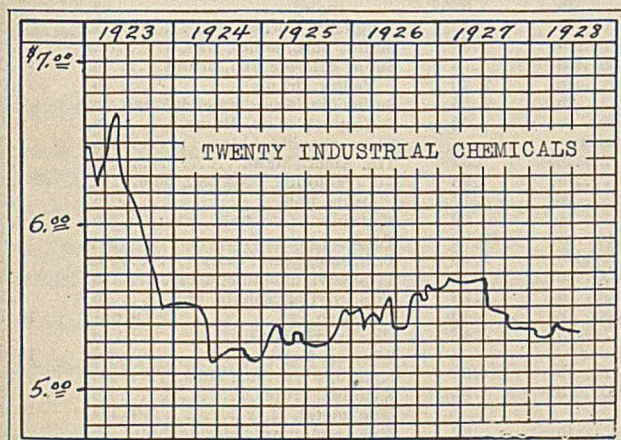
Textilchemische Erfindungen. Berichte über Neuere Deutsche Reichspatents aus dem Gebiete der Färberei, Bleicherei, Appretur, Mercerisation, Wascherei usw., der Chemischen Gewinnung der Gespinnstfasern, des Karbonisierens sowie der Teerfarbstoffe. ADOLF LEHNE. Lieferung II (July-December, 1927). 74 pp. A. Ziemsen Verlag, Wittenberg. Price, 6 marks.

Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege. J. FORMÁMEK AND J. KNOP. 2nd edition. Illustrated. Vol. II. Pp. 575-774. Julius Springer, Berlin. Price, 39 marks.

MARKET REPORT—JULY, 1928

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON JULY 15

Acetanilide, U. S. P., bbls.....lb.	36	Sulfuric, 66°, c/l. cbys., wks.		Sulfate, bulk, wks.....100 lbs.	2.20
Acetic anhydride, 92-95%, cbys. lb.	29100 lbs.	1.60	Thiocyanate, tech., kegs.....lb.	.40
Acetone, C. P., drums, wks.....lb.	.15	66°, tanks, wks.....ton	15.00	Amyl acetate, tech., drums.....gal.	1.90
Acetophenetidine, bbls.....lb.	1.40	60°, tanks, wks.....ton	10.50	Aniline oil, drums.....lb.	.15½
Acid, acetic, 28%, c/l. bbls. 100 lbs.	3.38	Oleum, 20%, tanks, wks.. ton	18.00	Anthracene, 80-85%, casks, wks.lb.	.60
56%, c/l. bbls.....100 lbs.	6.34	40%, tanks, wks.....ton	42.00	Anthraquinone, subl., bbls.....lb.	.90
Glacial, c/l. bbls.....100 lbs.	11.92	Sulfurous, U. S. P., 6%, cbys. lb.	.05	Antimony, metal.....lb.	.09½
Acetylsalicylic, bbls.....lb.	.85	Tannic, tech., bbls.....lb.	.30	Antimony chloride, anhyd.,	
Anthranilic, 99-100%, drums..lb.	.98	Tartaric, U. S. P., cryst.,		drugs.....lb.	.17
Benzoic, tech., bbls.....lb.	.57	bbls.....lb.	.38	Oxide, bbls.....lb.	.10½
Boric, bags.....lb.	.06½	Tungstic, kegs.....lb.	1.00	Salt, dom., bbls.....lb.	.18
Butyric, 80%, pure, 5-lb. bot..lb.	.55	Valeric, C. P., 10-lb. bot.....lb.	2.50	Sulfide, crimson, bbls.....lb.	.25
Chloroacetic, mono-, bbls.,		Alcohol, U. S. P., 190 proof,		Golden, bbls.....lb.	.16
wks.....lb.	.25	bbls.....gal.	2.66½	Vermilion, bbls.....lb.	.38
Di-, cbys.....lb.	1.00	Amyl, 10%, Imp. drums.....gal.	1.40	Tartrolactate, bbls.....lb.	.45
Tri-, bbls.....lb.	2.50	Butyl, drums, c/l., wks.....lb.	.18½	Argols, red powder, bbls.....lb.	.08
Chlorosulfonic, drums, wks....lb.	.15	Cologne spirit, bbls.....gal.	2.67	Arsenic, metal, kegs.....lb.	.45
Chromic, pure, 98%, drums....lb.	.25	Denatured, No. 5, comp. de-		Red, kegs, cases.....lb.	.10½
Cinnamic, 5-lb. cans.....lb.	3.25	nat., c/l. drs.....gal.	.43	White, c/l. kegs.....lb.	.03¾
Citric, U. S. P., kegs, bbls....lb.	.46	No. 1, comp. denat., drs.....gal.	.45	Asbestine, bulk, c/l.....ton	14.75
Cresylic, pale, drums.....gal.	.73	Isoamyl, drums.....gal.	2.50	Barium carbonate, bbls., bags,	
Formic, 85%, cbys., N. Y.....lb.	.11	Isobutyl, ref., drums.....lb.	...	wks.....ton	57.00
Gallic, U. S. P., bbls.....lb.	.74	Isopropyl, ref., drums.....gal.	1.00	Chloride, bags, wks.....ton	56.00
Glycerophosphoric, 25%, 1-		Propyl, ref., drums.....lb.	1.00	Dioxide, bbls, wks.....lb.	.13
lb. bot.....lb.	1.40	Wood, see Methanol		Hydroxide, bbls.....lb.	.04¾
H, bbls., wks.....lb.	.57	Alpha-naphthol, bbls.....lb.	.65	Nitrate, casks.....lb.	.07½
Hydriodic, 10%, U. S. P., 5-		Alpha-naphthylamine, bbls.....lb.	.35	Barium sulfocyanate, 400-lb.	
lb. bot.....lb.	.67	Alum, ammonia, lump, bbls.,		bbls.....lb.	.27
Hydrobromic, 48%, cbys., wks.lb.	.45	wks.....100 lbs.	3.25	Barytes, floated, 350-lb. bbls.,	
Hydrochloric, 20°, tanks,		Chrome, casks, wks.....100 lbs.	5.25	wks.....ton	23.00
wks.....100 lbs.	1.70	Potash, lump, bbls., wks..100 lbs.	3.10	Benzaldehyde, tech., drums.....lb.	.85
Hydrofluoric, 30%, bbls., wks.lb.	.06	Soda, bbls., wks.....100 lbs.	3.75	F. F. C., cbys.....lb.	1.40
60%, bbls., wks.....lb.	.13	Aluminum, metal, N. Y.....lb.	.243	U. S. P., cbys.....lb.	1.15
Hydrofluosilicic, 35%, bbls.,		Aluminum chloride, anhyd.,		Benzene, pure, tanks, mills....gal.	.22
wks.....lb.	.11	drugs.....lb.	.35	Benzidine base, bbls.....lb.	.70
Hypophosphorus, 30%, U.		Aluminum stearate, 100-lb. bbl..lb.	.23	Benzoyl chloride, carboys.....lb.	1.00
S. P., 5-gal. demis.....lb.	.85	Aluminum sulfate, comm'l,		Benzyl acetate, cbys.....lb.	1.30
Lactic, 22%, dark, bbls.....lb.	.04¾	bags, wks.....100 lbs.	1.40	Alcohol, 5-liter bot.....lb.	1.40
66%, light, bbls., wks.....lb.	.26	Iron-free, bags, wks.....100 lbs.	1.75	Chloride, tech., drums.....lb.	.25
Mixed, tanks, wks.....N unit	.07¾	Aminoazobenzene, 110-lb. kegs..lb.	1.15	Beta-naphthol, bbls.....lb.	.24
S unit	.01	Ammonia, anhydrous, cyl., wks..lb.	.14	Beta-naphthylamine, bbls.....lb.	.63
Molybdic, 85%, kegs.....lb.	1.25	Ammonia water, 26°, drums,		Bismuth, metal, cases.....lb.	1.70
Naphthionic, tech., bbls.....lb.	.55	wks.....lb.	.03	Bismuth, nitrate, 25-lb. jars.....lb.	1.80
Nitric, C. P., cbys.....lb.	.12	Ammonium acetate, kegs.....lb.	.34	Oxychloride, boxes.....lb.	3.10
Nitric, 38°, c/l. cbys., wks.		Bifluoride, bbls.....lb.	.21	Subnitrate, U. S. P., 25-lb.	
.....100 lbs.	5.00	Bromide, 50-lb. boxes.....lb.	.48	jars.....lb.	2.05
Oxalic, bbls., wks.....lb.	.10¾	Carbonate, tech., casks.....lb.	.08¾	Blanc fixe, dry, bbls.....ton	80.00
Phosphate, bulk.....ton	9.00	Chloride, gray, bbls.....100 lbs.	5.40100 lbs.	2.00
Phosphoric, 50%, cbys.....lb.	.08	Lump, casks.....lb.	.11	Bone ash, kegs.....lb.	.06
Picramic, bbls.....lb.	.50	Iodide, 25-lb. jars.....lb.	5.20	Bone black, bbls.....lb.	.08¾
Picric, bbls., c/l.....lb.	.40	Nitrate, tech., cryst., bbls.....lb.	.06	Borax, powd., bbls.....lb.	.02½
Pyrogallic, tech., bbls.....lb.	.86	Oxalate, kegs.....lb.	.35	Bordeaux mixture, bbls.....lb.	.11
Salicylic, tech., bbls.....lb.	.27	Persulfate, cases.....lb.	.27½	British gum, com., c/l.....100 lbs.	4.37
Stearic, d. p., bbls., c/l.....lb.	.11¾	Phosphate, dibasic, tech.,		Bromine, bot.....lb.	.45
Sulfanilic, 250-lb. bbls.....lb.	.15	bbls.....lb.	.18	Bromobenzene, drums.....lb.	.50



Bromoform, 5-lb. bot. lb.	1.65	Hexamethylenetetramine, tech., drums. lb.	.62	Phenol, drums. lb.	.13
Butyl acetate, 100-gal. drums. gal.	1.38	Hydrogen peroxide, 25 vol., bbls. lb.	.06½	Phenolphthalein, drums. lb.	1.10
Cadmium bromide, 50-lb. jars. lb.	1.20	Hydroquinone, kegs. lb.	1.25	Phenylethyl alcohol, 1-lb. bot. lb.	7.00
Cadmium, metal, boxes. lb.	.65	Indigo, 20%, paste, bbls. lb.	2.80	Phosphorus, red, cases. lb.	.60
Cadmium sulfide, cs. lb.	1.35	Iodine, crude, 200-lb. kgs. lb.	4.20	Phosphorus trichloride, cyl. lb.	.45
Caffeine, U. S. P., 5-lb. cans. lb.	2.80	Iodine, resub., jars. lb.	4.65	Phthalic anhydride, bbls. lb.	.18
Calcium acetate, bags. 100 lbs.	3.50	Iodoform, bot. lb.	6.00	Platinum, metal. oz.	76.00
Arsenate, bbls. lb.	.07	Iridium, metal. oz.	280.00	Potash, caustic, drums. lb.	.07½
Carbide, drums. lb.	.05	Kieselguhr, bags. ton	60.00	Potassium acetate, kegs. lb.	.29
Chloride, drums, wks. ton	20.00	Lead, metal. 100 lbs.	6.20	Bicarbonate, casks. lb.	.09
Cyanide, 100-lb. drums. lb.	.30	Lead acetate, bbls., white. lb.	.13	Bichromate, casks. lb.	.09
Lactate, tech., bbls. lb.	.35	Arsenate, bbls. lb.	.13	Binodate, bbls. lb.	.16
Nitrate, bbls. ton	52.00	Oxide, litharge, bbls. lb.	.08½	Bromate, cs. lb.	.35
Phosphate, monobas., bbls. lb.	.07	Red, bbls. lb.	.09½	Carbonate, 80-85%, calc., casks. lb.	.05½
Tribas., bbls. lb.	.11	Peroxide, drums. lb.	.25	Chlorate, kegs. lb.	.08
Calcium carbonate, tech., bgs. 100 lbs.	1.00	White, basic carb., bbls. lb.	.09	Chloride. ton	34.55
U. S. P., precip., 175-lb. bbl. lb.	.06½	Sulfate, bbls. lb.	.08½	Cyanide, cases. lb.	.55
Camphor, Amer., bbls. lb.	.70½	Lime, hydrated, bbls. 100 lbs.	.85	Meta-bisulfite, bbls. lb.	.11½
Jap., cases. lb.	.62	Lime, live, chemical, bbls., wks. 100 lbs.	1.05	Permanganate, drums. lb.	.14½
Camphor, monobrom., cs. lb.	1.85	Limestone, ground, bags, wks. ton	4.50	Prussiate, red, casks. lb.	.37
Caramel, bbls. gal.	.63	Lithium carbonate, 100-lb. kgs. lb.	1.45	Yellow, casks. lb.	.18
Carbazole, bbls. lb.	.15	Lithopone, bbls. lb.	.06½	Titanium oxalate, bbls. lb.	.25
Carbon, activated, drums. lb.	.05	Magnesium, crude. ton	36.00	Pyridine, drums. gal.	1.50
Carbon bisulfide, drums. lb.	.05½	Calcined, 500-lb. bbls., wks. ton	48.00	Quinine bisulfate, 100 oz. oz.	.40
Carbon black, cases. lb.	.12	Magnesium, metal sticks, wks. lb.	.85	Sulfate, 100-oz. cans. oz.	.40
Carbon dioxide, liq., cyl. lb.	.06	Magnesium carbonate, bags. lb.	.06	Resorcinol, tech., kegs. lb.	1.30
Carbon tetrachloride, drums. lb.	.07	Chloride, drums. ton	37.00	Rochelle salt, bbls., U. S. P. lb.	.23
Casein, stand. gr., bbls. lb.	.16	Fluosilicate, cryst., bbls. lb.	.10	R salt, bbls. lb.	.45
Cellulose acetate, kegs. lb.	1.40	Oxide, U. S. P., light, bbls. lb.	.42	Saccharin, cans. lb.	1.75
Cerium oxalate, kegs. lb.	.32	Manganese chloride, casks. lb.	.08	Salt cake, bulk. ton	19.00
Charcoal, willow, powd., bbls. lb.	.06	Dioxide 80%, bbls. ton	80.00	Salt peter, gran., bbls. lb.	.06½
China clay, imp., bags. 100 lbs.	15.00	Sulfate, casks. lb.	.07	Silica, ref., bags. ton	22.00
Chloral hydrate, drums. lb.	.70	Mercury bichloride, cryst., 25 lbs. lb.	1.58	Silver nitrate, 16-oz. bot. oz.	.42
Chloramine, U. S. P., 5-lb. bot. lb.	1.75	Mercury, flasks, 75 lbs. flask	121.00	Soda ash, 58%, light, bags, contract, wks. 100 lbs.	1.40
Chlorine, liq., c/l, cyl. lb.	.03½	Meta-nitroaniline, bbls. lb.	.72	Soda, caustic, 76%, solid, drums, contract, wks. 100 lbs.	3.00
Chlorobenzene, mono., drums. lb.	.07	Meta-phenylenediamine, bbls. lb.	.90	Sodium acetate, bbls. lb.	.04½
Chloroform, tech., drums. lb.	.20	Meta-toluylenediamine, bbls. lb.	.72	Benzoate, bbls. lb.	.50
Chromium acetate, 20° sol., bbls. lb.	.05½	Methanol, pure, tanks. gal.	.44	Bicarbonate, bbls. 100 lbs.	2.41
Coal tar, tanks, bbls., wks. gal.	.07	Denaturing grade, tanks. gal.	.45	Bichromate, casks. lb.	.07½
Cobalt, metal, kegs. lb.	2.50	Methyl acetone, drums. gal.	.68	Bisulfite, bbls. lb.	.04
Cobalt oxide, bbls. lb.	2.10	Salicylate, cases. lb.	.42	Bromide, bbls. lb.	.42
Cod-liver oil, bbls. bbl.	44.50	Methyl chloride, cylinders. lb.	.55	Carbonate, sal soda, bbls., 100 lbs.	1.30
Collodion, drums. lb.	.23	Michler's ketone, bbls. lb.	3.00	Chlorate, kegs. lb.	.05½
Copperas, c/l, bulk. ton	13.00	Monoethylamine, drums. lb.	1.05	Chloride, bags. ton	12.00
Copper, metal, elec. 100 lbs.	14.75	Naphtha, solvent, tanks. gal.	.35	Cyanide, cases. lb.	.20
Copper carbonate, bbls. lb.	.16½	Naphthalene, fake, bbls. lb.	.05	Fluoride, bbls. lb.	.08½
Chloride, bbls. lb.	.28	Nickel, metal. lb.	.33	Metallic, drums, 12¼-lb. bricks, lb.	.27
Cyanide, drums. lb.	.48	Nickel salt, single, bbls. lb.	.10	Naphthionate, bbls. lb.	.55
Oxide, red, bbls. lb.	.16½	Double, bbls. lb.	.10½	Nitrate, crude, bags, N. Y. 100 lbs.	2.17½
Sulfate, c/l, bbls. 100 lbs.	5.30	Niter cake, bulk. ton	4.50	Nitrite, bbls. lb.	.08
Cotton, soluble, bbls. lb.	.40	Nitrobenzene, drums. lb.	.10½	Perborate, bbls. lb.	.21
Cream tartar, bbls. lb.	.26	Oil, castor, No. 1. lb.	.14	Peroxide, cases. lb.	.27
Cyanamide, bulk, N. Y. Ammon. unit	1.67½	China wood, bbls. lb.	.15	Phosphate, trisodium. lb.	.04
Diaminophenol, kegs. lb.	3.80	Coconut, Ceylon, tanks. lb.	.08½	Picramate, kegs. lb.	.69
Dianisidine, kegs. lb.	2.85	Cod, N. F., tanks. gal.	.62	Prussiate, bbls. lb.	1.12
Dibutylphthalate, drums, wks. lb.	.29½	Corn, crude, tanks, mills. lb.	.09	Silicate, drums, tanks, 40° 100 lbs.	1.20
Diethylaniline, drums. lb.	.55	Cottonseed, crude, tanks. lb.	nom.	Silicofluoride, bbls. lb.	.04½
Diethylene glycol, l. c. l. lots, drums. lb.	.20	Lard, edible, bbls. lb.	.16½	Stannate, drums. lb.	.48½
Carload lots, drums. lb.	.15	Linseed, bbls. lb.	.102	Sulfate, anhyd., bbls. lb.	.02½
Diethylphthalate, drums. lb.	.24	Menhaden, crude, tanks. gal.	nom.	Sulfide, cryst., bbls. lb.	.02½
Diethylsulfate, tech., drums. lb.	.20	Neat's-foot, pure, bbls. lb.	.15½	Solid, 60%. lb.	.03½
Dimethylaniline, drums. lb.	.30	Oleo, No. 1, bbls. lb.	.14	Sulfocyanide, bbls. lb.	.40
Dimethylsulfate, drums. lb.	.45	Olive oil, denat., bbls. gal.	1.18	Thiosulfate, reg., crys., bbls. lb.	.02½
Dinitrobenzene, drums. lb.	.15½	Foots, bbls. lb.	.09%	Tungstate, kegs. lb.	.80
Dinitrochlorobenzene, bbls. lb.	.15	Palm, Lagos, casks. lb.	.07½	Strontium carbonate, bbls. lb.	.07½
Dinitronaphthalene, bbls. lb.	.32	Peanut, crude, tanks. lb.	.12	Nitrate, bbls. lb.	.08½
Dinitrophenol, bbls. lb.	.31	Perilla, bbls. lb.	.13½	Strychnine alkaloid, 100 oz., powd. oz.	.46
Diphenylamine, bbls. lb.	.45	Rapeseed, bbls., English. gal.	.88	Sulfate, powder. oz.	.38
Diphenylguanidine, bbls. lb.	.40	Red, bbls. lb.	.08½	Sulfur, bulk, mines, wks. ton	18.00
Epsom salt, tech., bbls., c/l, N. Y. 100 lbs.	1.70	Soy bean, crude, bbls. lb.	.12½	Sulfur chloride, red, drums. lb.	.05
Ether, nitrous, bot. lb.	.90	Sperm, 38°, bbls. gal.	.84	Yellow, drums. lb.	.03½
Ether, U. S. P., drums. lb.	.16	Whale, bbls., natural, winter. gal.	.76	Sulfur dioxide, commercial, cyl. lb.	.08
Ethyl acetate, 85%, drums. gal.	.76	Ortho-aminophenol, kegs. lb.	2.20	Sulfuryl chloride, drums. lb.	.10
Bromide, drums. lb.	.70	Ortho-anisidine, drums. lb.	2.35	Thiocarbanilid, bbls. lb.	.22
Chloride, drums. lb.	.22	Ortho-dichlorobenzene, drums. lb.	.06	Tin, Amer., stand. lb.	.47½
Methyl ketone, drums. lb.	.30	Ortho-nitrochlorobenzene, drums. lb.	.32	Tin bichloride, 50% sol., bbls. lb.	.15
Ethylbenzyl aniline, 300-lb. drs. lb.	1.05	Ortho-nitrophenol, bbls. lb.	.85	Oxide, bbls. lb.	.56
Ethylene dichloride, tanks. lb.	.07	Ortho-nitrotoluene, drums. lb.	.17	Titanium oxide, bbls., wks. lb.	.40
Chlorohydrin, anhyd., drums. lb.	.75	Ortho-toluidine, bbls. lb.	.29	Toluene, tanks. gal.	.35
Glycol, c/l, wks. lb.	.26	Palladium, metal. oz.	46.80	Tribromophenol, cases. lb.	1.10
Ethyl ether, drums, cars. gal.	1.79	Para-aminophenol, kegs. lb.	1.15	Triphenylguanidine, drums. lb.	.69
Feldspar, bulk. ton	20.00	Para-dichlorobenzene. lb.	.17	Triphenyl phosphate, bbls. lb.	.70
Ferric chloride, tech., bbls. lb.	.07½	Para-dehyde, tech., drums. lb.	.26	Tungsten. WO ₃ unit	10.75
Ferrous chloride, cryst., bbls. lb.	.05	Para-formaldehyde, cases. lb.	.40	Urea, pure, cases. lb.	.18
Ferrous sulfide, bbls. 100 lbs.	2.50	Para-nitroaniline, drums. lb.	.48	Whiting, bags. ton	18.00
Fluorspar, 95%, bags. ton	25.00	Para-nitrochlorobenzene, drums. lb.	.32	Xylene, 5°, drums, mills. gal.	.32
Formaldehyde, bbls. lb.	.08½	Para-nitrophenol, bbls. lb.	.50	Xylidine, drums. lb.	.38
Formaniline, drums. lb.	.38	Para-nitrosodimethylaniline, bbls. lb.	.92	Zinc, metal, N. Y. 100 lbs.	6.45
Fuller's earth, bags, c/l, mines. ton	15.00	Para-nitrotoluene, bbls. lb.	.30	Zinc ammonium chloride, bbls. lb.	.05½
Furfural, 500-lb. drs., c/l. lb.	.17½	Para-phenylenediamine, bbls. lb.	1.15	Chloride, granulated, drums. lb.	.06½
Glauber's salt, bbls. 100 lbs.	.70	Para-toluidine, bbls. lb.	.40	Oxide, Amer., bbls. lb.	.07½
Glucose, 70°, bags, dry. 100 lbs.	3.14	Paris Green, 250-lb. kegs. lb.	.23	Stearate, bbls. lb.	.19
Glycerol, C. P., drums. lb.	.15			Zinc dust, bbls., kegs, c/l. lb.	.09
G salt, bbls. lb.	.50				