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THE LISTENING POST

Overheard about This Issue

President Redman, in an address replete with quotable sentences and filled with economic wisdom, enters a strong plea for stabilized research, which he characterizes as the "heartbeat of modern civilization." This address (page 1198) places the burden of continuing and continuous research upon financiers who have had provided for them all the requirements and the need for it. Such a scholarly treatment of so important a thesis deserves the widest possible reading by people in all walks of life.

Unit Processes as distinct from unit operations are stressed in a series of three articles in a symposium on reaction equipment. This symposium is to continue in future issues and is intended to emphasize the chemical aspects of chemical engineering rather than its purely mechanical phases as typified by the so-called unit operations. The present offering treats of sulfuric acid converters by DuBois and Harney (page 1091), esterification by Keyes (page 1096), and oxidation of hydrocarbons by Marek (page 1103). Although the material presented is not essentially new, its discussion from a different point of view is valuable.

On the Purely Mechanical Side of chemical engineering, Cuno (page 1109) supplies an inclusive discussion of pumps and pumping of special value in these days when layouts are being revised for the utmost economy of operation.

Sulfur has always been of fundamental importance in chemical economy, and hence the fears sometimes expressed, that we may reach a time when sulfur will no longer be plentiful and cheap, require much more than passing attention. A world without sulfuric acid and sulfur is quite as difficult to imagine at the moment as E. C. Franklin's fanciful "ammono" world in which ammonia replaces water. A careful analysis of the facts as we now know them by Taylor (page 1116) indicates that, although fundamental readjustments must in all probability be made as sulfur reserves dwindle to the point of making the cost of the element higher, the possibility of a sulfur famine is too remote to require a revolution in industrial methods within any reasonable time. Especially valuable in connection with this paper is the survey of methods already devised for recovering elementary sulfur from sulfur dioxide in flue gases and fumes.

Ramie may become a more important commercial fiber as a result of further development of a chemical method of preparation described by Carter and Horton (page 1162). Although the work reported is in a preliminary stage of development, it suggests important possibilities as it is carried further.

So Interested are we in our own food that we are likely to forget the important place in our national economy of feed for our beasts and fowls. Maynard and Tunison (page 1168) have given careful study to the characteristics of fish meal forming a large part of the rations of farm animals and here present the results of their investigations of digestibility as related to method of preparation.

Although Rapid Developments of the past decade have often forced new materials into satisfactory commercial use before the limiting conditions for their safe application were fully known, it is certainly the part of wisdom to complete studies of limiting properties before serious consequences compel it. Carlisle and Levine (page 1164) give us the results of their studies of trichloroethylene, already in commercial use as a solvent.

When Advertising Agencies discovered that science and scientists had a public appeal in their promotional campaigns, trouble started for all concerned. Not only has the general public been given a most unfortunately warped impression of the keen interest of chemists, physicians, dentists, physicists, and others, in cigarettes, tooth pastes, toilet papers, and a host of other common commodities, but also the license taken in stating research findings frequently presents a false picture of their real nature. When discussion of this subject is as general as at present, it is refreshing to get the real facts in at least one moot case. Gordon and Shand (page 1148) give us the truth about the surface tension of tooth pastes and in so doing lay one of chemistry's advertising specters by the simplest and most obvious method, stating without the assistance of advertising writers what they found by direct comparison. Such statements go a long way toward revitalizing our faith in our co-workers in chemistry after it has received several telling blows.

Economically the commercial development of a business depends quite as closely on the proper selection and use of a trademark as upon patents, yet in discussions of these subjects for chemical people trade-marks are usually dismissed with trifling attention. Sadtler (page 1194) helps correct this situation by providing a helpful summary of what trade-marks are and how they may be handled. No other commercial property is so likely to be destroyed by careless or thoughtless use as these merchandising essentials, and hence it is particularly needful that all likely to have to do with them be familiar with the law on the subject.

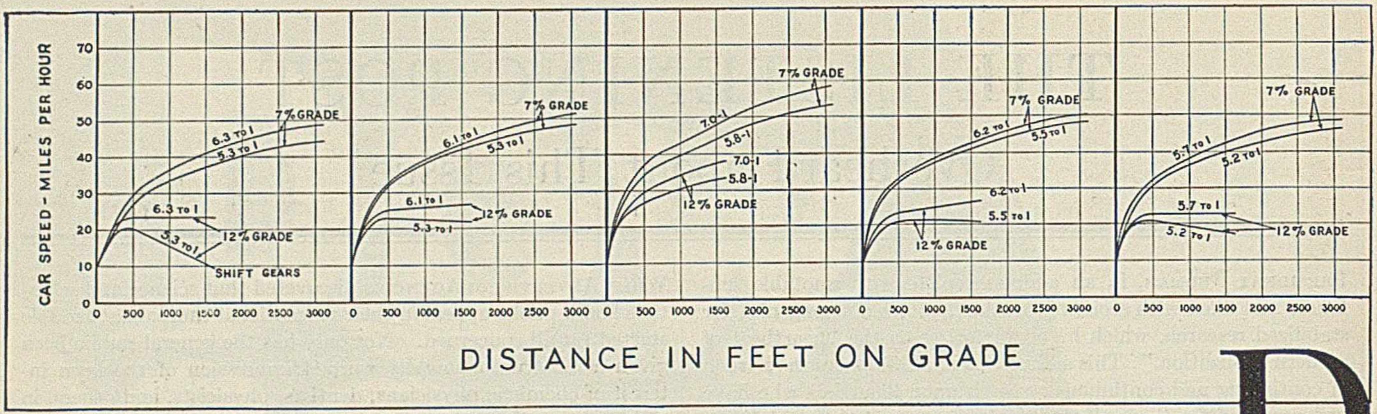
Development of hydrogenation of petroleum into an important branch of industry and the technological advances involved in the process are still new enough to attract attention even from those outside the industry. Already the word "hydrofining" is being introduced into the language by it. Byrne, Gohr, and Haslam (page 1129) bring us up to date on activities in this field.

As Winter Approaches, the problem of prevention of freezing of oleum and mixed acid stored at the plant becomes serious. More findings on the freezing points of nitric-sulfuric mixtures are presented by Coster and O'Callaghan (page 1146) on the basis of which plant managers may lay their plans for avoiding trouble in the coming months.

Nonpoisonous Germicides have been sought diligently and now we have a confirmation of what has been suspected—namely, that irradiated oils produce a distinctly germicidal atmosphere around themselves. Harris, Bunker, and Milas (page 1181) have looked into this phenomenon and conclude that the germicidal properties of such oils result from the evolution of gaseous organic peroxides rather than from re-radiation as others have believed. The confirmation of this property of oils stimulates speculation as to its possible application.

Methods of Decolorizing Oils are reviewed by Thurman (page 1187).

Desulfurization of Coal, already accorded some attention in previous issues, is further treated by Mangelsdorf and Broughton (page 1136) who find their results somewhat different from those of Snow (see August issue).

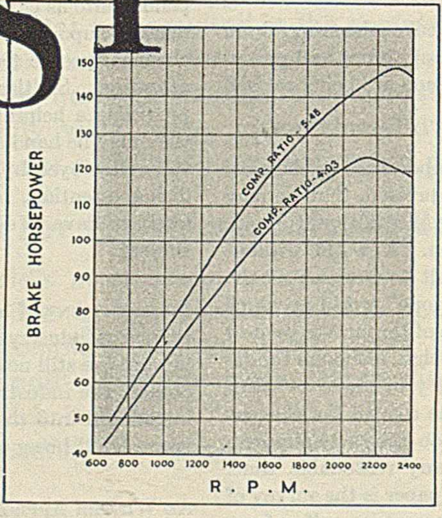


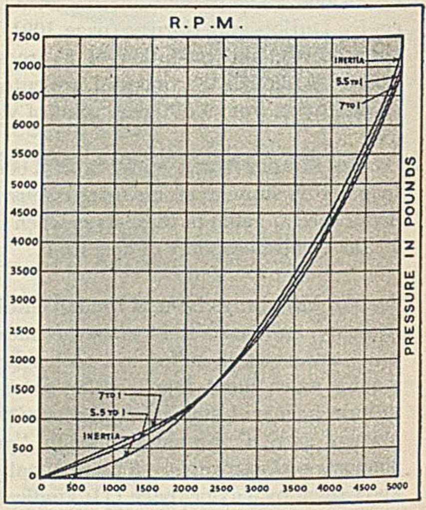
Better hill-climbing ability*—records of hill-climbing tests for five 1932 production cars are plotted above, comparing their performance with low compression ratio to that of high compression ratio. Car speed in miles per hour is shown in vertical scale. Distance up grade is shown in horizontal scale. All tests were made in high gear with cars moving ten miles an hour from a point a few feet preceding start of grade.*

They STEPPED

Other Gains Offered by High Compression Are:

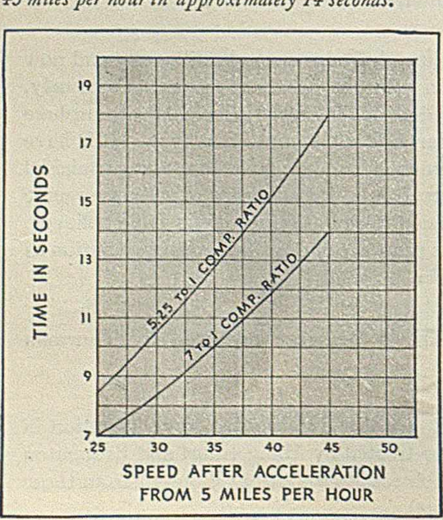
Greater power—(RIGHT). *Many tests with passenger car engines prove that increasing compression ratio from 5-to-1 to 7-to-1 increases power approximately 15% at any given speed and steps up top speed 4 to 6 miles per hour. The chart at the right shows the gain in horsepower effected by increasing compression of a large bore truck engine.*

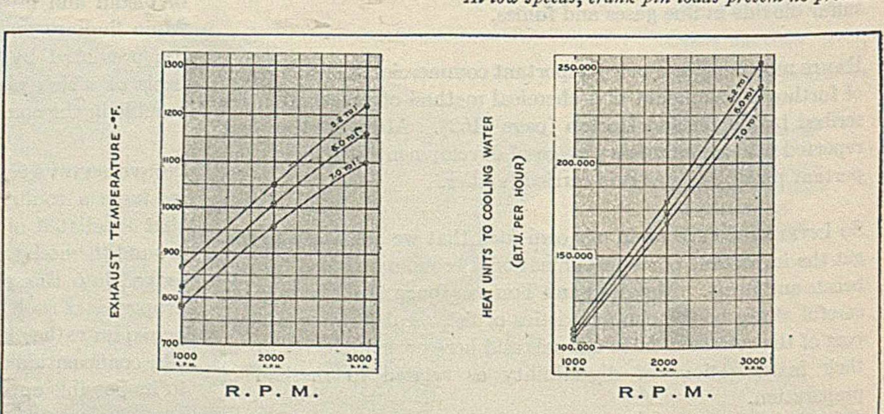




Lower extreme bearing pressures (ABOVE). *At higher speeds, the forces of inertia on crank pin bearings are greater than, and opposed to, the gas pressure in combustion chambers. Increased gas pressure therefore lowers the mean resulting load on crank pin bearings at high speeds. At low speeds, crank pin loads present no problem.*

Faster acceleration—(BELOW). *With 5.25-to-1 compression ratio a given car (not one of those included in above hill-climbing tests) accelerated from 5 miles per hour to 45 m.p.h. in 18 seconds. With 7-to-1 compression ratio the same car reached 45 miles per hour in approximately 14 seconds.*





Less heat to cooling water and exhaust—(ABOVE). *By a more efficient use of the fuel energy, higher compression ratios maintain cooler engine temperatures at any given r.p.m. The lower exhaust gas temperatures impose less heat on exhaust valves and transmit less heat to the driving compartment in hot weather. Less heat transmitted to cooling water by higher compression engines offers relief to overloaded radiators in your new, more powerful models, rather than a further strain.*

UP performance ... at NO increase in manufacturing cost

Improvements resulting from major increases in compression ratio are already being demonstrated by production cars on the road

THERE ARE 1932 cars in all price classes now delivering performance that can be produced only by high compression engines.

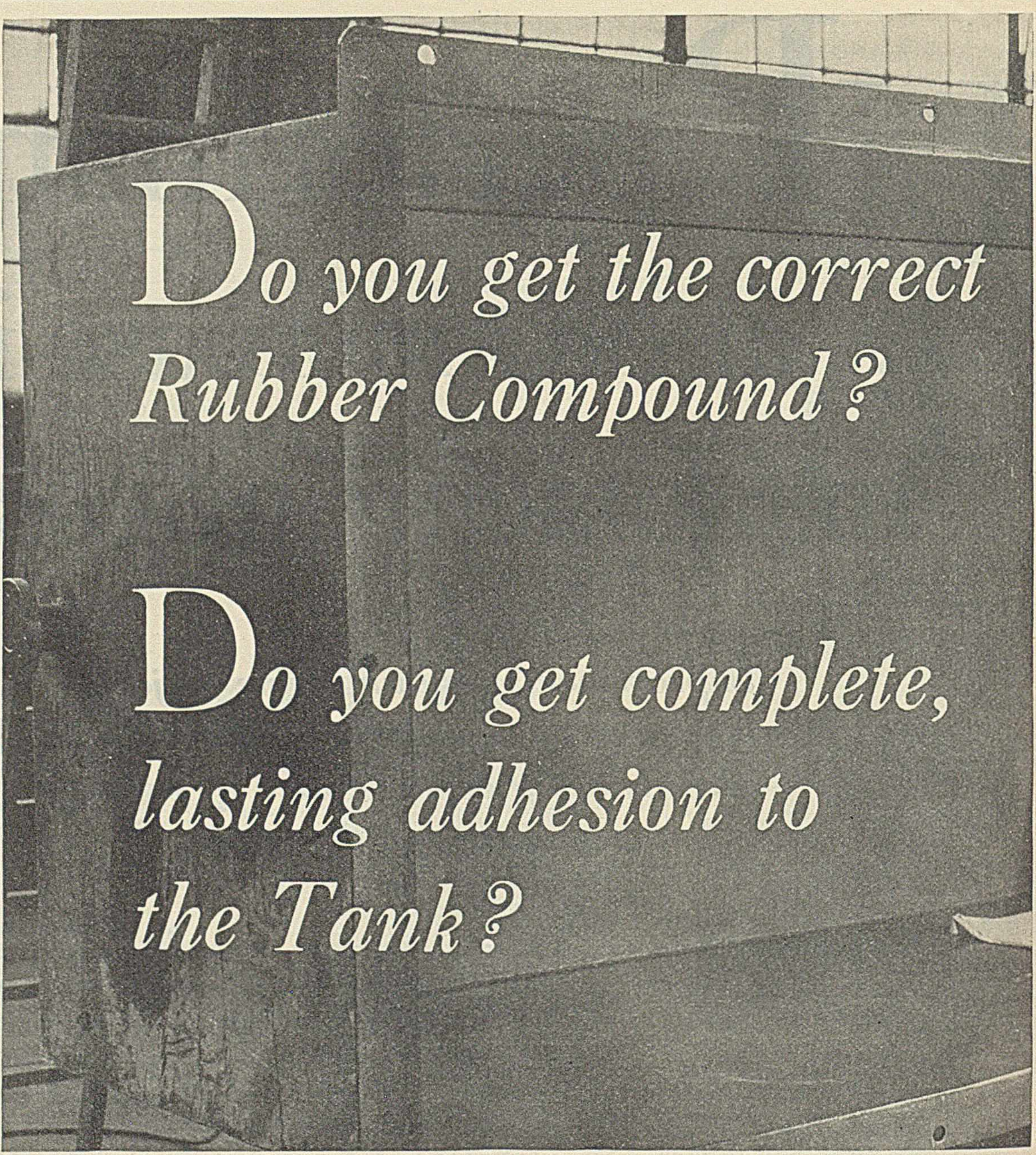
The results of hill-climbing tests on five such cars at high and low compression ratios are shown by the curves at the top of the opposite page. These cars vary widely in price, in permissible compression ratio, and in actual performance figures. In every case the increase in compression ratio provided performance gains that add greatly to the car value.

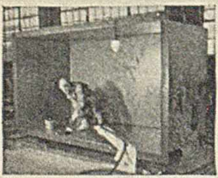
On some of these cars, high compression ratio is standard; on others it is offered at the purchaser's option. Most of the cars having standard high compression also offer an optional lower ratio, although few buyers to whom the high compression car is demonstrated are satisfied with the decreased performance of low compression.

Other benefits of increased compression, higher peak power engine speed, faster car acceleration, less heat to cooling water, lower exhaust gas temperatures, and lower extreme bearing loads, are illustrated by the remaining charts. The fact that realizing these various advantages involves no costly redesigning or retooling is of importance to which attention need hardly be directed.

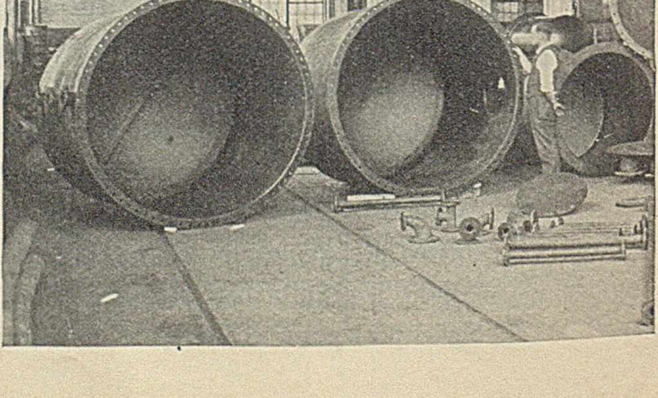
High compression production cars, driven by enthusiastic owners, are now setting the standards of performance by which the car-buying public will judge 1933 cars. Will your 1933 car take advantage of the compression made possible by Ethyl Gasoline to get the kind of performance that will win more sales next year?

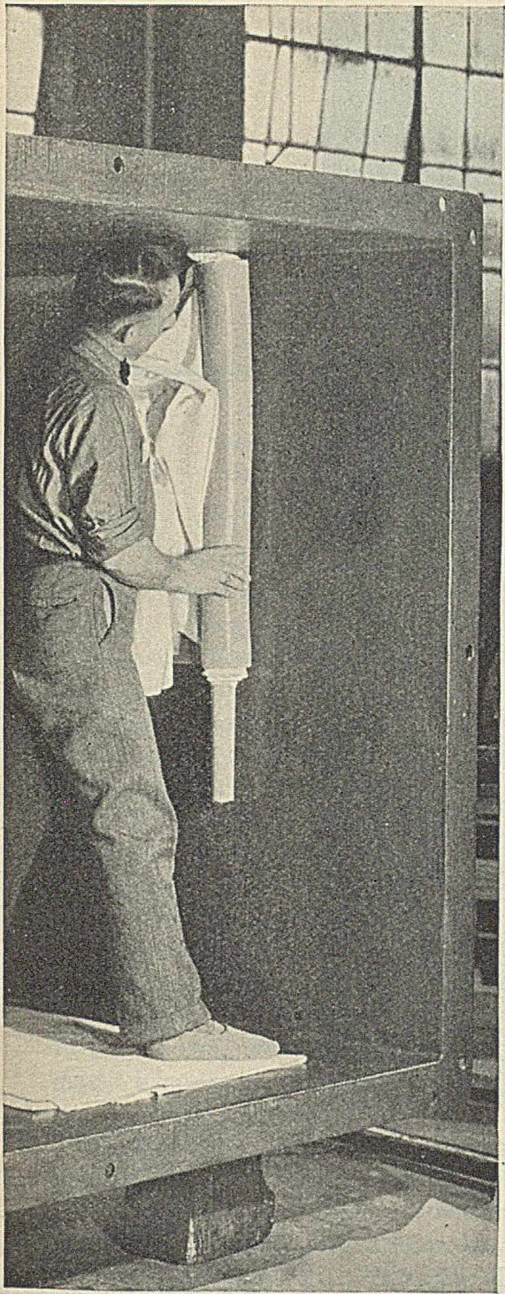
Engineers of the Ethyl Gasoline Corporation have had wide experience with high compression engines. They will be glad to cooperate with you in the development of high compression for your new model. Ethyl Gasoline Corporation, Chrysler Building, New York City, N. Y.





(*Above, left*) **PREPARING A TANK** *for lining by the "Vulcalock" process.* (*right*) *First rubber-lined tanks to handle strong acetic acid successfully. The linings were installed by "Vulcalock" . . . only method that bonds rubber securely to metal with no weakening of the rubber.*





. . . this Goodrich Lining gives you Both

rubber linings to metal surfaces with an adhesion of 500 to 700 pounds per square inch; a practically inseparable union secured with no weakening of the rubber.

For the first time you can have your acid tanks lined with the purest of gum rubber. The yellow, honey-colored rubber stock, admittedly best for most acids, has heretofore refused to adhere to metal surfaces. Now "Vulcalock" fastens it so firmly that for all practical purposes it becomes an integral part of the tank.

Goodrich linings are installed with extreme care. While others were using the wire brush to prepare the surface of the metal for lining, we introduced sand-blasting. And not only do we roughen the receiving surface; we also remove the scale from the steel. Six Goodrich "Acidseal" compounds, "Superflexite," "Triflex" and "Armorite" rubber are all available for tank lining by the "Vulcalock" process.

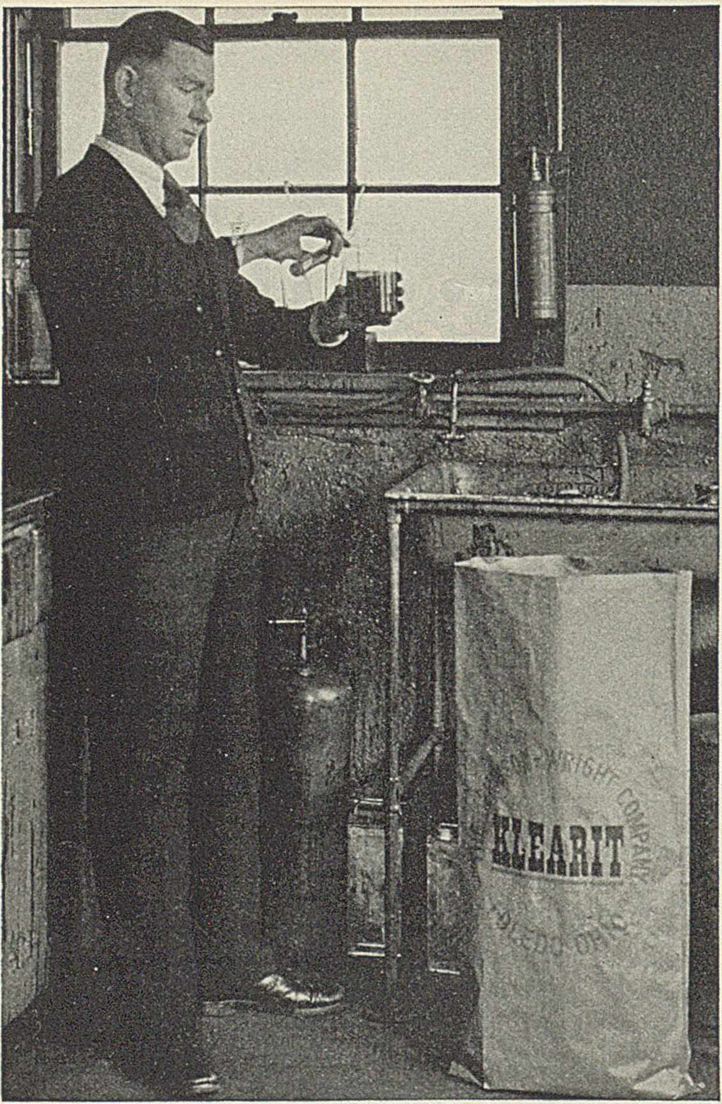
. . .

For individual attention to your rubber-lining problems in the field or in our shops, write to Dr. H. E. Fritz, The B. F. Goodrich Rubber Company, Akron, Ohio. Inquiries carefully considered, without obligation. Prices are based on $1.84 per sq. ft. for lining 3/16 in. thick, our specifications, on plain areas.

B. F. GOODRICH

Vulcalock

PROCESS FOR
BONDING RUBBER TO METAL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Industrial
AND ENGINEERING
Chemistry

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Harrison E. Howe, Editor

The Editor's Point of View

WINTER APPROACHES. Few would wish their lives away, but there are sober-minded men who sincerely wish the approaching winter were past. They realize that business has definitely improved at so many points that the long-awaited turn has probably been made, but they also realize that men and business are alike in that each requires much time for recovery after a prolonged, strength-sapping illness. Very much of that lost strength cannot be regained before winter, scarcely enough to enable the great increase in employment which we all wish. The chemical industry in a large sense is purveyor to other industries, and general recovery must be realized to a large extent before great improvement can be expected in it. In any event winter is liable to be a harsh, unfriendly, and even cruel season for many, even under normal circumstances, not to mention times of depression.

The fact that great efforts have been made privately and publicly through numerous organizations during previous months may make it somewhat more difficult to do what is needed in the immediate future, but the situation must be met. We are concerned with the problem involved in aiding all those in distress, but we are naturally most interested in the men and women with whom we have most in common—the chemists.

The problem has had the concerted thought of several groups and a great deal has already been accomplished. We wish to be advised of the details of any and all successful undertakings, in order that these constructive data may be transmitted to other points where they can be used. Where local funds are being raised, it should be suggested that at least a portion of those coming from the chemical industry be made available especially to help unemployed chemists, providing them where possible with the type of work which they are trained to do.

One of the most needful things is the direct help and advice of the leaders of chemical industry. These executives can do much to encourage and assist committees in industrial centers where they are gravely attacking a problem which is brand new to them. There is a certain obligation to do this, for beneath the chemical industry is the foundation of the science itself, laid by the chemical fraternity. In the better times to come there will be keen competition to be met only with the help of chemists. The demand, the insistent demand as of yore, will make itself heard again. Chemists and more chemists will be wanted. These trained, experienced, and tried chemists now unemployed will be among the first to be wanted, but if in the interval we allow them to lose their morale, even their self-respect, they may become unemployable. The investment made in them by the state and industry may be lost, in which case we shall all be poorer. The industrial leader sees to it that his easily replaceable plant is carefully kept in stand-by serviceable condition. Can he afford to see less done in the case of men, so often replaceable only with the greatest difficulty?

The time immediately before us may be the most difficult of all—the darkness before the dawn. We must not fail in doing our part as circumstances and ability dictate. We should assist those who are devoting their time and efforts to this cause. It is inactivity and lack of effort that condemn one.

⁂

THE CASE OF AMMONIUM SULFATE. There are few, if any, better examples of a compound buffeted by the complex currents of modern industry than ammonium sulfate. The material is of great importance to the fertilizer industry, but that fact only serves to increase the complications which face the manufacturer. True, it is a by-product and, if unprofitable, one might think it could go to waste. But no—has not the public come to appreciate the substantial losses involved in treating coal in the old beehive ovens, and has not the country become nitrogen-conscious, thanks to the Muscle Shoals controversy? Furthermore, no matter how the books may be kept as to costs, whatever is realized from the sale of a by-product has a bearing on the cost of such principal products as gas, pig iron, or steel, and consequently is of indirect interest to ultimate consumers. Nor can the gas companies neglect ammonia and simply allow it to remain in the gas and be burned. This introduces corrosion difficulties, and besides, in many places city ordinances and regulations require the removal of ammonia. In several localities surplus gas from coke ovens is used for domestic supply, thereby reducing costs to householders and factories, and this gas must also be made ammonia-free.

Ammonium sulfate has sustained some important reverses. Formerly the manufacturer could rely on 72 cents per ton of coal carbonized as an income from sulfate to be credited to operations. This was roughly equivalent to 6 cents per thousand cubic feet of all the gas made, or about $1.08 per ton of pig iron. Then came synthetic ammonia, which so reduced prices that one-third of the return was soon lost. The synthetic method makes possible anhydrous ammonia at a cost very little above that for aqua, which is produced by gas works as an alternative to sulfate. The present world overcapacity for producing fixed nitrogen is therefore a major and controlling factor in the whole price structure. Any reasonable regulation of production and distribution with its resulting stabilization of prices is just as important to ammonium sulfate as to Chilean nitrate or synthetic ammonia and its products.

The latest trouble seems to lie in the duty-free status of ammonium sulfate. Regarded as a raw material from the standpoint of the fertilizer industry and of agriculture, it was deprived June 18, 1930, of the protection which had been intended to equalize costs of manufacture. Because of unrestricted importation our producers have been forced to lose another third of their former return per ton of coal from this by-product. While sulfate is a raw material in the eyes of the agriculturalist, it is nevertheless a finished product from the standpoint of those who produce it. In effect, the operators of by-product coke ovens are required to conserve ammonia, but their return on the operation is determined by what European makers will accept for their surplus. If this entails a loss to the American producer, he can pocket it or pass it along to another group of consumers in higher prices for his principal products. In doing this, he runs the risk of increased difficulty of meeting competition.

In such circumstances one thinks first of costs of production and the possibility of lowering them. A medium-sized plant carbonizing 1000 to 1200 tons of coal per day will have fixed charges on investment of 60 to 75 cents per ton of coal. Of this, about 10 per cent will be for equipment required for the recovery of ammonia. Since recovery as sulfate averages from 1.1 to 1.2 per cent of the total, this fixed charge becomes from $5.50 to $6 a ton of sulfate produced. One ton of 60° Baumé acid is required per ton of sulfate, and this acid is quoted around $10 in tank cars at works. We then have from $15.50 to $16 per ton of sulfate, without reckoning costs of operation, maintenance, overhead, and selling. Today our manufacturers are figuratively pinning a $5 bill on each ton of ammonium sulfate which they ship.

It is well known that labor costs favor foreign producers. What of the sulfate radical? Abroad, gypsum and calcium anhydrite are in wide use. The reaction between the calcium sulfate in water suspension, ammonia, and carbon dioxide yields a solution of ammonium sulfate which must be concentrated and the compound crystallized. As a by-product, there is a salable precipitated calcium carbonate. Investigators are of the opinion that the somewhat lower cost possible in some places by this method is altogether insufficient to change materially the price position of sulfate in America.

The result of the removal of tariff protection is evident from these figures, which are for the first six months of each year:

	1930	1931	1932
Export, tons	49,436	54,484	13,672
Import, tons	3,010	33,911	165,441
Price per unit of nitrogen (20 pounds)	$1.92	$1.45	$0.97

While it is true that all forms of fixed nitrogen have declined sharply in price as compared, say, with values in 1919, sulfate of ammonia has shown the greatest recession—to 21 per cent of the 1919 price as compared with calcium cyanamide, 29 per cent, and sodium nitrate, 39 per cent.

In Sweden the question of dumping arose some time ago and the Swedish Bureau of Chemical Industry recommended an import duty, notwithstanding the fact that nitrogen fertilizers in general enter that country free of duty. In our own country the American Iron and Steel Institute more than a year ago alleged the dumping of European sulfate of ammonia. The question has been carefully investigated and was somewhat complicated by the depreciated currency situation in some foreign lands. In due course a report was made by the Bureau of Customs to Treasury Department officials and under date of August 16 findings of dumping against sulfate of ammonia from Germany, Belgium, and Poland were made public. It was held that the American industry was being injured and is likely to be injured by reason of the importation of this compound at less than its fair value. It is understood that dumping penalties are about to be assessed against certain importers. The question of whether or not sulfate is also being dumped by Holland and England is still under consideration.

American producers of ammonium sulfate are well equipped. They employ research and may be expected to take full advantage of advances in technology. What they ask is a fair and reasonably stable price and protection for their labor and capital against dumping. Surely such an attitude is sound.

Symposium on the Design, Construction, and Operation of Reaction Equipment

Presented before the Division of Industrial and Engineering Chemistry at the 84th Meeting of the American Chemical Society, Denver, Colo., August 22 to 26, 1932.

CHEMICAL engineering comprises not only the unit operations but also the chemical unit processes fundamental in chemical industries. Unit operations are almost entirely physical in nature—for example, distillation, filtration, grinding, crystallization, etc. Chemical unit processes, on the other hand, are the common standardized processes used in the chemical industries—for example, oxidation, reduction, halogenation, hydration, nitration, esterification, etc.

Much has been written in recent years about unit operations but very little about unit processes. The design, construction, and operation of equipment in which a common chemical reaction takes place are important in any study of the unit processes of chemical engineering. It is strange that this particular subject which means so much to every chemical engineer should have received scarcely any consideration in our modern chemical literature.

The object of this symposium is to bring before our readers a few selected review papers on the design, construction, and operation of equipment in which certain common chemical reactions take place. No attempt has been made to obtain new and original data, but much of the material has been selected from obscure patent literature and from unpublished plant practice. Although these reviews may present little information to those skilled in the particular process, we believe that they will prove of real interest to the majority who have never had the opportunity of working in the particular field.

We hope that this symposium will result in the presentation and publication of many papers on the design, construction, and operation of chemical equipment. Many times the modern chemical engineer is faced with the problem of purchasing or constructing equipment for a common chemical reaction but one which he has never seen operated on a large scale. His only way of obtaining information at the present time is to consult some other chemical engineer who is familiar with the specific subject. Even the university student specializing in chemical engineering, although extremely interested in this general subject, has little opportunity to learn the facts. The need of this symposium is evident.

D. B. KEYES, *Chairman*

Contact Sulfuric Acid Converters

G. DuBois and T. R. Harney, Monsanto Chemical Works, St. Louis, Mo.

The function of the contact sulfuric acid converter is to provide intimate contact between gas and catalyst and to provide as nearly as possible for optimum equilibrium conditions.

Modern methods leading to the attainment of these ends are represented by all developments in internal heat-exchange converters and by the so-called two-pass converter system in which heat exchangers are interposed between converters.

These modern converter systems are described, and a brief summary of present world practice in converters is given.

IT IS not possible to say correctly that any one piece of equipment is more important to a process than any other piece in the same series. However, it is true that in the contact sulfuric acid plant the converter or catalyst chamber probably offers more opportunity for variation in design than does any other element.

The function of the modern converter is that of providing not only intimate contact but also favorable conversion equilibrium conditions. The oxidation of sulfur dioxide to sulfur trioxide is a strongly exothermic reaction and, therefore, if heat is not removed, low conversions will result. On the other hand, with all present-day catalysts, reaction velocities at normal temperatures are too low for commercial operation, and it is therefore necessary to design equipment which can be maintained at temperatures high enough for a commercially successful reaction velocity, and at the same time low enough to permit conversions of 95 per cent or better. This is the problem before designers of present day converters.

In the early days of contact plant operation, very little consideration appears to have been given to the thermal characteristics of the reaction. Initial heat was provided either by the heating of the converter or by the preheating of the entrance gas in an external furnace. Converters were small, and it is possible that radiation was sufficient to permit fairly good conversions. Curiously enough some of these simple converters are still in use, although modern practice has shown them to be uneconomical in most cases.

SCHROEDER-GRILLO CONVERTER

The earliest well-known type of converter, named for its inventors, is the Schroeder-Grillo; it consists simply of a cast-iron cylinder or, in some cases, of relatively short superimposed cylinders, in which there are from four to five layers of catalyst resting on perforated iron or steel grids. In the original Grillo converter, gas entered at the bottom, passed upward through the layers of catalyst, and left at the top through a line leading to the coolers and absorber. In such converters all heat of reaction was wasted, and it was necessary to preheat incoming gases to the desired ignition temperature in an external furnace heated by extraneous fuel. Later the Grillo was modified to a double shell type which consisted simply of the previous simple cylinder containing its shelves of catalysts, but with an annular space around the shell through which partly preheated gas passed upward to distribute over the top layer of catalyst and thence downward through the successive layers, leaving the converter at the bottom.

This modified Grillo converter had the advantage of utilizing a part of the heat of reaction and the further advantage of downflowing instead of upflowing gas. Such downflow tended to reduce the possibility of excessive gas passage through small areas in catalyst layers, owing to flue action caused by channeling of the catalyst. Better distribution was also aided at times, both in the simple and in the double-shell Grillo converters, by the installation of baffle plates between layers of catalyst.

Until the development of vanadium catalysts within the last few years, Schroeder-Grillo converters without exception operated on platinized magnesium sulfate, which catalyst was covered by the original Schroeder patents.

MANNHEIM SYSTEM

Another early type of converter was that employed in the Mannheim contact systems. This system was based on the use of ferric oxide for the first stages of conversion and of platinum for the completion of the reaction. Most such plants operated with pyrites as a source of sulfur, and the iron oxide converter was simply a shaft into which lump pyrites cinder was dumped at the top and from which partly disintegrated and inactive pyrites cinder was withdrawn from the bottom. The platinum in the Mannheim system was deposited, usually from platinic chloride solution, on asbestos mats which were installed on plates, somewhat similar to filter-press plates, in a cast-iron converter of small diameter.

Since the activity of iron oxide below about 600° C. is slight, it was theoretically possible in the iron oxide converter to obtain only about 60 per cent conversion. As a matter of fact, conversions obtained in practice in the one or two plants built and operated in this country seldom exceeded 50 per cent, thus throwing an unexpected load on the platinum.

To the best of the writers' knowledge not more than three Mannheim plants have ever been built in the United States and none of them is now in operation. There are a number of Schroeder plants running, but in most cases they operate either on metallurgical gas where cost of sulfur is a small item, or under other conditions which their owners do not at present believe warrant the installation of more modern equipment. In general, Schroeder converters are of sizes designed for only 5 to 8 tons daily capacity as 100 per cent sulfuric acid.

INTERNAL HEAT-EXCHANGE CONVERTERS

There are two general types of modern converters now being installed, the principal differences between them being in the method selected for the regulation of temperature and for the utilization of the heat of reaction by its transfer to cold gas or to air. These two types of converters are known as the internal heat-exchange type and the two-pass system. The latter is sometimes named also the Herreshoff system, after its inventor, and perhaps might better be called the multipass system since there have been some recent developments leading to the use of three or more stages instead of the original two.

BADISCHE TYPE. The internal heat-exchange type of converter appears to have been used first by Badische in Germany. The original Badische converter consisted essentially of a piece of equipment similar to a tubular boiler. Catalyst, which was originally platinized asbestos, was installed in the tubes and was supported on a rather large number of small trays, the trays being so constructed that they could be dropped into the tube, each one resting on the one below it. Cold gas entered the converter usually at the bottom, passed upward around the tubes which were provided with baffle plates to distribute cold gas, thence downward through the tubes to leave the converter at the bottom.

As this converter was originally designed, it was necessary to arrange transfer surface for gas of a given strength since all incoming gas was exposed to all heat-exchange surface. Because of the difficulty of being assured of a gas of constant strength, Badische converter developments took the form of various arrangements for the introduction of cold gases at different points in the converter, the idea being that, with stronger gases in which greater heat was developed in given volume, a certain amount of cold gas could be so introduced as not to be exposed to all heat-exchange surface.

Ultimately, gas piping became rather complicated in these attempts to provide for fluctuations in gas strength. Badische has now changed to the use of vanadium catalyst, and it is understood that they have also changed to the two-pass tray type of converter without internal heat exchange.

TENTELEW TYPE. Another type of internal heat-exchange converter was that developed by the Tentelew Company. In its original form this converter consisted of a vessel made up in two diameters. The upper and larger section contained a perforated plate on which there were placed a number of cast-iron truncated cones or pyramids. A relatively deep layer of catalyst was then installed on this plate in such a manner that the cones projected through it and for a short distance into the open space above. The function of the cones was to transmit heat from the catalyst into the open space thus serving to preheat incoming gas. The gas passed downward through the layer of catalyst and into the smaller section of the converter in which there were a number of plates carrying relatively thin layers of catalyst. No heat transfer was attempted in the lower section. Such converters, in the original Tentelew installations, used platinized asbestos as the catalyst and were operated with one external heat exchanger.

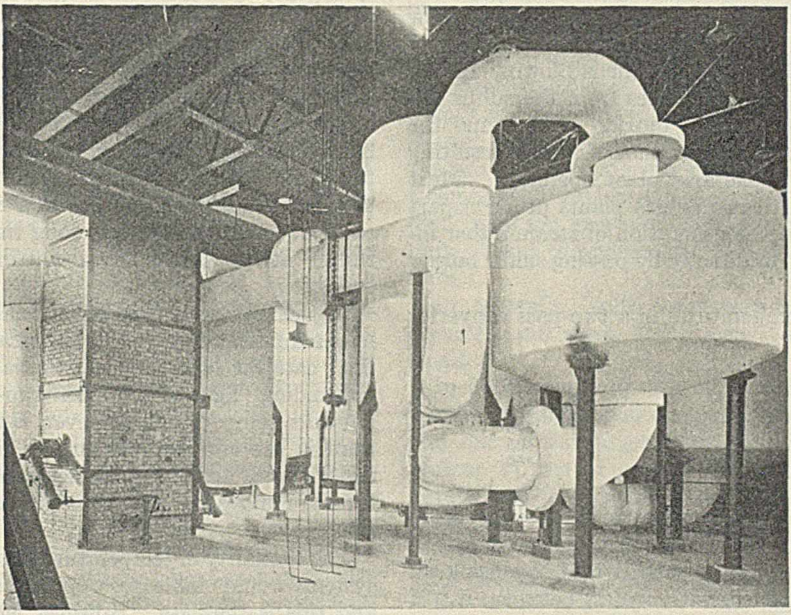
A later development of the Tentelew system led to a converter similar to the Badische type, except that the Tentelew Company held to a relatively large open space above the top of the tubes, and that Tentelew converters always operated with one external heat exchanger.

No more than one or two Tentelew installations have been made in this country.

AMERICAN TYPE. Within the last few years there has been an American development of a converter of the internal heat-exchange type. This converter differs from the Badische and Tentelew systems in that the catalyst is placed outside instead of inside the tubes, as well as in certain other features of design which will be described later. Such placing of the catalyst was made possible by the mechanical strength of vanadium catalysts in connection with which the converter development took place. As mentioned above, previous forms of internal heat-exchange converters have been used principally with platinized asbestos which could be placed only in thin layers and which, therefore, required numerous supporting plates. These plates could be installed only inside of the tubes on account of their regular shape.

In the American form of internal heat-exchange converter there are usually two layers of catalyst, a lower layer containing about 60 to 65 per cent of the total catalyst, and an upper layer containing the remainder. The lower mass is supported by a thin layer of crushed quartz resting upon a perforated plate into which there are rolled a number of relatively large tubes. These tubes project upward into the catalyst and have their upper ends closed. Inside of these larger tubes are smaller tubes open at both ends and rolled into a tube sheet located a small distance below the perforated plate on which the catalyst is supported. Similar construction is employed with tubes extending from above into the upper layer of catalyst and having their lower ends closed.

In operation, partly preheated gas at a temperature of around 300° C. enters the converter below the lower tube sheet, and passes upward through the smaller tubes to the upper or closed end of the larger tubes which are embedded in the lower layer of catalyst. It then flows downward through these larger tubes into the space between the two tube sheets, thence upward through the lower layer of catalyst. Between the two catalyst layers there may or may not be baffle plates for gas-mixing. After passing this open space, the gas continues upward through the upper layer of catalyst and thence out of the converter.



Internal Heat-Exchange System

For operation on metallurgical gases, cold gas enters the converter above the tube sheet into which the upper closed-end tubes are rolled. This sheet is unperforated and the gas passes downward in the large tubes which project into the upper layer of catalyst, thence upward through the small tubes, leaving the converter at the top. From this point it may pass directly to the lower section of the converter and thence through the lower tubes and catalyst, as described above, or it may pass through an external heating furnace before entering the lower section of the converter. The use or nonuse of the external heating furnace depends largely upon the strength of gas being used.

When used in plants employing brimstone as the source of sulfur which in modern installations means the so-called raw gas type of plant, in which it is unnecessary to bring burner gases down to atmospheric temperature for purification, the gas enters the converter in the lower section after being cooled only to about 300° C. In this type of plant, air is usually forced through the upper set of tubes to provide cooling in the final layer of catalyst.

Approximate typical temperatures in such a converter are as follows:

	° C.
Entrance gas under lower tube sheet	300
At entrance to catalyst after passing lower set of tubes	460–480
Maximum in lower layer of catalyst	600
Exit from lower layer of catalyst	465–475
Exit from converter	280

It should be noted that this final temperature does not represent temperature in the upper layer of catalyst, since there is considerable cooling in the space above that layer. Actual temperature at the surface of the upper layer is around 450–460° C., depending on the strength and type of gas being used. At this temperature, equilibrium conversion is of the order of 97.5 to 98.0 per cent.

Multipass Converters

The external heat-exchange type of converter is represented principally in this country by the so-called Herreshoff or multipass converter system. This type of installation consists of a small or first converter containing about 30 per cent of the total catalyst and a large or second converter containing the remainder of the catalyst. There are usually, in connection with the two converters, two heat exchangers known as the small, hot, or primary exchanger, and the large, cold, or secondary exchanger.

In operation, cold burner gas enters the secondary exchanger, which in construction is somewhat similar to a tubular boiler, passes through it (usually outside the tubes), and goes thence to the primary exchanger which is similar in construction but usually smaller in size. Again, sulfur dioxide flow is usually outside the tubes. Upon leaving the primary exchanger, the gas has been brought up to the desired ignition temperature, and it enters the top of the first converter, passes downward through the catalyst, and leaves at the bottom to pass through the tubes of the primary exchanger. In passing these tubes its heat is transferred to the incoming gas, and its temperature is again reduced to the desired entrance temperature in the second converter. Passing downward through the catalyst in the second converter, the gas leaves at the bottom, passes through the tubes of the secondary converter, and is led to the absorbers.

The internal construction of converters of this type is relatively simple. When used with platinized asbestos, the first converter, which is usually a cylindrical cast-iron pot or, in some cases, simply a cast-iron cylinder with flanged top and bottom, may contain from twenty to thirty trays on each of which is evenly spread a thin layer of catalyst. These trays are usually supported on cast-iron supports carried either on the bottom of the converter or on lugs cast into the walls. Trays may be so constructed as to rest on each other or may be separated by short cast-iron columns. To avoid disturbance of the upper layer of catalyst by the gas stream entering the converter, it is customary to cover it with a screen; in most cases before actually entering the catalyst, gas passes downward through a filter of inert material, usually catalyst carrier without platinum on it. The construction of the second converter is similar to that of the first except that it contains from fifty to seventy trays of catalyst.

When used with the modern vanadium catalyst, gas flow is the same, but there are usually only two layers of catalyst in the first converter and three layers in the second. Again, the fact of the greater mechanical strength of vanadium catalyst makes it possible to simplify internal construction by using relatively thick catalyst beds. With vanadium there are always placed baffle plates between the catalyst layers in order to insure good mixing of the gas, and sometimes a spreading plate is placed just beneath the gas inlet in order to get as good a distribution as possible of the gas entering the top layer of catalyst.

In a few installations in this country converters of this type are used with prepared platinum catalysts other than platinized asbestos. Construction is essentially the same as with the vanadium catalyst, except that in some cases four or five or more layers are used, and in other cases, in which the catalyst carrier is in the form of relatively small pellets, broken quartz is used instead of steel screens for catalyst support. The broken quartz is in turn carried on a screen which rests upon cast-iron grids, as do the screens supporting the vanadium catalyst.

In the case of operation on brimstone gases which, as mentioned above, usually means in modern installations the raw gas type of plant, the second heat exchanger becomes merely a sulfur trioxide cooler through which air is blown. In one such modern installation this air passes from the sulfur trioxide cooler through similar sulfur dioxide coolers, and the heat taken up is used for the generation of steam, resulting in an appreciable credit to the acid plant operation. Most or all of the modern American raw gas plants utilize a part of the heat of reaction for the generation of steam either indirectly, as just described, or directly by passing sulfur burner gases through a boiler.

Approximate typical temperatures in a two-pass converter system are as follows:

	° C.
Entering first converter	400
Leaving first converter	575
Entering second converter	405
Leaving second converter	450

Recent developments by one company in this country have tended toward the installation of three or more converters in series. The theory back of this work is that, by using an increased number of converters with coolers between, it will be possible to operate with a stronger gas since the excessive temperatures normally occurring with such gas could be held down by frequent cooling. So far it is understood that this attempt has not been signally successful, since the large amount of power required to force the gas through multiple converters and the theoretically somewhat lower conversion obtainable with the strong gases seem to have equaled, at least, any saving due to lower gas volumes.

Comparison of Internal and External Heat-Exchange Converters

As mentioned above, the internal heat-exchange converter and the external heat-exchange converter, while apparently quite different, actually differ only in the methods adopted by their designers for the proper handling of heat generated in the reaction. Since the oxidation of sulfur trioxide is strongly exothermic, it is obvious that heat must be removed in order to obtain satisfactory conversion. Advocates of internal heat exchange proceed on the theory that this heat should be removed substantially as formed and, therefore, are of the opinion that at no point should catalyst be remote from a cooling surface. This means that converters must be either very small in cross section or must contain a number of tubes or other cooling elements so that, as nearly as possible, there may be flow of heat from all points in the catalyst. The results of this line of reasoning are the various internal heat-exchange converters described.

Advocates of external heat exchange, while recognizing the fact that allowance must be made for favorable thermal equilibrium, are of the opinion that advantage should be taken of another characteristic of the reaction. This is the fact that, with increase in temperature above 400° C., the velocity of the oxidation of sulfur dioxide to sulfur trioxide increases rapidly. For example, while a conversion of only about 80 per cent of the theoretical is possible with an 8 per cent gas from brimstone at a temperature of 585° C., the reaction velocity is such that it is possible to obtain this maximum conversion with a very small amount of catalyst or in a very short time, which means the same thing. In actual practice the 30 per cent of the catalyst which is installed in the first converter is ample for bringing the system to equilibrium at temperatures ranging from 565° to 600° C. Equilibrium having been reached at such temperatures in the two-pass system, gas is withdrawn, cooled to around 400° C., and again exposed to a larger amount of catalyst. Reaction velocities in the second converter are lower, first on account of the lowered sulfur dioxide content of the gases, and secondly on account of temperatures, the latter being due to the relatively small amount of oxidation taking place. This lower temperature results in more favorable conditions for high conversion, and the advocates of the multipass system believe that by their method of handling they have achieved two ends: (1) the utilization of initial high reactions, and (2) the final exposure of the gas to a relatively large amount of catalyst (or for a relatively long time which means the same thing) at temperatures permitting favorable equilibrium conditions.

In the American type of internal heat-exchange converter maximum temperature and temperature of the gas leaving the final catalyst layer are substantially the same as the corresponding figures for the two-pass system. Converter entrance temperature, however, is from 60° to 80° C. higher than in the two-pass system. This greater temperature at the entrance appears to be necessary in order to compensate for the removal of heat through tube walls during the reaction.

The similarity of temperatures in the two types of converter system would indicate approximately equivalent results, and this is the case. However, since the internal heat-exchange type uses about 30 per cent more catalyst, it seems probable that average catalyst temperature in the first converter of the two-pass system is greater than that in the lower catalyst layer of the internal heat-exchange type. This supposition is borne out by cross-sectional checks of temperature and conversion in a two-pass converter. These investigations show a steep temperature gradient for a band 1 to 2 inches wide next to the converter wall. This temperature drop, with its attendant lowering of reaction velocity, is due to heat loss through the wall, and it seems reasonable to suppose that there would be corresponding areas around each tube in the internal heat-exchange converter. Since the percentage of catalyst affected would be much greater in that type of converter, this theory may account for its use of more catalyst.

In actual practice there appears to be no substantial difference in the conversions obtained from the two types of converter, and their relative merits therefore rest upon other considerations.

The internal heat-exchange converter usually occupies less floor space than does the multipass system with its external heat exchangers. On the other hand, while no actual data of construction costs are available, it appears to cost somewhat more on account of its complicated internal construction.

From the point of view of operation, the tubes in the internal heat-exchange type are less accessible for repair. In any equipment handling corrosive gases such as sulfur dioxide and trioxide, a certain amount of repair may be expected over the normal life of the plant; in the case of the internal heat-exchange converter it is necessary to remove all catalyst in order to repair tubes. This means a complete plant shutdown, and loss of time in cooling the converter, in removing and reinstalling the catalyst, and in getting the plant into operation. On the other hand, tube repairs have been made in internal heat exchangers in such a short length of time that preheat was not lost. That is, it was possible to go again into operation without the use of a fuel-fired preheater on account of the large amount of heat held in the catalyst chamber.

This possible advantage of the two-pass system is somewhat offset by the fact that, in the internal heat-exchange converter, tubes are anchored at only one end so that possible rupture by buckling or stretching is unlikely, leaving corrosion as the only failure to be expected.

Owing to the fact that the internal heat-exchange converter requires something like 30 per cent more catalyst than is needed in the two-pass system, the cross-sectional area of such a converter must be materially greater than that of the external heat-exchange type in order to hold power requirements to the same figure. As a matter of fact, the cross-sectional areas are somewhat greater in the internal exchange converter than in the other type, and at the same time power requirements appear to be slightly greater. This varies, of course, with different plants, and the statement made should not be interpreted as applying to all installations.

The outstanding advantage of the external heat-exchange converter lies in its flexibility for use with gases of different percentages of sulfur dioxide. It is obvious that with given gas volumes, on which basis most plants operate, heat liberated in oxidation will vary almost directly with gas percentage. An internal heat-exchange converter has a fixed heat-exchange area, at least with reference to the lower layer of catalyst, and it is difficult, if not impossible, to introduce cold gas at any point except at the regular converter entrance. This means that a converter designed, for example, to operate on a 9 per cent gas will not have the proper heat-exchange surface for operation on an 8 or on a 10 per cent gas. On the other hand, in the case of the external heat-exchange converter, gas may be put through both exchangers, introduced between the primary and secondary exchangers, or introduced directly into the first converter. In other words, any desired mixture of preheated, partly preheated, and cold gas may be fed to the converter. In actual practice one of the writers has operated such a system on gases varying from 4 to 9 per cent sulfur dioxide without appreciable difference in the results obtained in so far as temperature regulation was concerned. This advantage of the two-pass system is not of particular importance in plants in which the source of sulfur is brimstone. Plants operating on brimstone have, in general, a gas of constant sulfur dioxide percentage, and in modern plants using brimstone—that is, in plants of the so-called raw gas type—temperature of gases going to the converter can be varied within certain limits, thus largely compensating for any variation in gas strength. In metallurgical gas plants, however, flexibility is of considerable importance. In such plants, gases are cooled substantially to atmospheric temperature so that no variation in temperature of gas going to the converter system is possible. Also, in such plants partial interruption of gas flow through roaster difficulty is to be expected, and at other times it may be of advantage to burn brimstone in order to supply a part of the gas. Either of these conditions usually means variation in gas strength, which can be best taken care of in the external heat-exchange system.

World Survey of Contact Plant Converters

Briefly, the situation over the world as regards contact plant converters at the present time is about as follows:

In Europe, outside of Germany, a great many Grillo converters are still in use. Most of them are of the double-shell type with the annular space for gas passage around the converter proper, and most of them are operated with one external heat exchanger. In some cases heat exchange is adequate for operation, and in others a certain amount of extraneous fuel is used. In one European installation radial fins have been installed in the annular gas passage around the converter, and it is stated that it is possible to operate that particular plant on a 4 per cent gas without preheat. The heat exchange surface involved in this converter is much less per ton of capacity than in any other installation of which the writers have knowledge. In Europe also there are in use a considerable number of Tentelew converters, some of which have been modified to a sort of two-pass system with two external heat exchangers. Wherever such modification has been adopted, catalyst has been changed from platinized asbestos to vanadium. Most units in Europe are small as compared to American practice, the larger plants consisting of a multiplicity of small units.

In Canada the Grillo converter has been very largely abandoned. There are in that country a few installations of the two-pass system using platinum, and some installations of a combined Tentelew and shelf type using vanadium. Canadian units are in general considerably larger than European units, being comparable to all except the largest American units.

In Australia, Grillo converters are used principally, some jacketed and some unjacketed. Most units are relatively small.

In Japan the majority of installations are of Grillo converters, although one company has a Tentelew installation, and one of the larger firms is now installing the two-pass system. Units in general are relatively small, being comparable to European rather than to American practice. Units now being installed, however, are of the American order.

In Mexico and Central and South America there are not many plants of any type. The majority of installations are Grillo converters, though there is at least one each of the two-pass and of the internal heat-exchange systems.

In the United States there are still in use a good many Grillo converters, both jacketed and unjacketed. These installations are for the most part in metallurgical gas plants in which conversion is not a large item, or in plants in which the proprietors do not at present consider warranted the expense of a change to a more modern type. Practically all installations made within the last six or seven years have been either the two-pass system or the internal heat-exchange system, and most installations have used vanadium catalyst. The tendency in this country is toward larger single units, installations as large as 100 tons daily capacity in a single two-pass system having been made. There is nothing, incidentally, to indicate that even larger units could not be constructed if desired, and it might be noted that one of the writers has operated two-pass converter systems at as low as 40 per cent of their rated capacity without difficulty in heat balance.

In general, the present work in this country consists of the further development and simplification of the two types of converter systems now considered modern. Development work has pointed toward a balance between low first cost and low operating expense, and covers such points as arrangement, size, and construction materials. In the latter feature most manufacturers have held to cast iron for converter bodies and internal fittings. It seems probable that no superior metal will be found for the fittings, but one large company has changed to steel for converter shells on the theory that possible corrosion will be more than offset by lowered first cost. To date, the anticipated corrosion has not developed. Little or no work has been done with the newer chromium steels on account of their cost, but it seems possible that could that cost be somewhat reduced such steel might find quite a field for heat-exchange tubes; preliminary investigations indicate that, while it does not resist weaker grades of sulfuric acid, it is extremely resistant to sulfur trioxide. A tube which would not corrode and would not coat with ferrous sulfate should result in a material reduction in the area of heat-exchange surface required, since the heat-exchange coefficient now used is of the order of one-half the theoretical, because of allowance which must be made for coating of steel surfaces.

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Esterification Processes and Equipment

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A review is given of the various modern esterification processes used in the industries. The material for this paper is taken largely from the patent literature. Hook-ups are shown and general methods of operation. The use of fractionating columns in these processes is discussed, as well as the fundamental factors of the processes.

ESTERIFICATION as a chemical reaction has been well known for many years. It has reached its commercial significance only in recent times.

History of Use of Ester Solvents

Organic solvents, with the exception of ethyl alcohol and methanol, had little commercial use until 1914 and the start of the World War. Amyl acetate in the form of fusel oil acetate was the best-known ester solvent at that time. It was not, however, used in large quantities. The demand for airplane dope and the corresponding need for cellulose nitrate and cellulose acetate solvents increased rapidly during the war period. The only ester that was developed on a large scale during the war to replace amyl acetate was methyl acetate.

Immediately after the war there was available an enormous quantity of nitrocellulose and a correspondingly large potential source of this product in the United States. The manufacture of ethyl alcohol increased enormously during the war, and the stocks of this solvent were unusually great at that time. Fermentation process which produced acetone used as a gelatinizing agent for the British cordite also produced enormous quantities of *n*-butyl alcohol. This product had little or no peace-time use. Furthermore, in order to obtain a satisfactory production of acetone, various processes for the manufacture of acetic acid had been developed, notably the fermentation of ethyl alcohol to acetic acid. The acetone was produced from this product by the heat treatment of calcium acetate. In brief, the situation in the United States at the close of the war was such that there was an overproduction of nitrocellulose, ethyl alcohol, butyl alcohol, and acetic acid.

It was natural that the course of development should be to produce acetic acid esters of both amyl and butyl alcohol and to mix these solvents with nitrocellulose in the hope of utilizing the final solution as a covering material. Another factor in this development was the formation of a low-viscosity nitrocellulose which would permit the dissolving of an unusually large amount of nitrocellulose in these solvents without the resulting solution becoming too viscous for practical use. Nitrocellulose recovered from smokeless powder was largely of this variety, and special methods to produce the original product with this low-viscosity property were also developed at this time.

The resulting solution containing (in addition to the constituents mentioned above) natural resins, diluents such as the hydrocarbons, and plasticizing agents and pigments, constituted the beginning of our modern lacquer. At that time the varnishes and enamels used on automobiles were far from satisfactory, in that the time of application was enormous if the resulting product were to show any durability. Manufacturers of automobiles in the United States were anxious to obtain a quick-drying enamel that would be durable, would not check on exposure to the atmosphere, and could be readily washed and polished without removing an appreciable amount of the surface. The solution of esters and nitrocellulose together with the other constituents seemed to answer this particular problem. The film was formed by evaporation, and the pigmented nitrocellulose was apparently quite resistant toward light and general atmospheric conditions. The application could be carried out in a matter of minutes, whereas the old finish, consisting of many layers of varnish, required several months. The economic advantage of this covering from the standpoint of the automobile and of the furniture manufacturer was easily appreciated.

It was necessary to develop, first of all, methods of esterification so that it would be possible to produce by a continuous and efficient process enormous quantities of both amyl and butyl acetates. This development of esterification processes did not take place overnight but required several years to attain the present state of perfection.

Chemical Reactions

The simple reaction between an alcohol and an ester was well worked out by Berthelot and St. Gilles in 1862 (*2*). They found in general that this was an equilibrium reaction, in that appreciable quantities of both alcohol and ester were present under equilibrium conditions. This fact is of distinct commercial interest because all that is necessary to obtain 100 per cent yields (based on the acid composition and the ester formation) is to add an excess of ethyl alcohol and to remove from the scene of the reaction ethyl acetate and water as fast as they are formed. Strictly speaking, this is impossible by the ordinary commercial methods because, owing to the presence of azeotropic or constant-boiling mixtures, some of the alcohol is removed along with the ester and the water. Nevertheless, this fundamental fact is sufficient to indicate the desirability of running such a reaction inside an ordinary fractionating column.

Later investigators at the beginning of the twentieth century showed that a catalyst such as sulfuric acid increased the speed of this reaction but had to be present only in a small amount—for example, one per cent. It had been originally believed that, as water was one of the products, sulfuric acid in large quantities acting as a dehydrating agent would be required to produce satisfactory yields. Unfortunately the acid in large quantities has a tendency to dehydrate the alcohol and to produce various by-products. If, on the other hand, the acid is treated as a catalyst and is present in exceedingly small quantities, these by-products are rarely produced.

Another interesting scientific development regarding esterification occurred early in the twentieth century when it was found that in the case of an ordinary alcohol, such as ethyl, the hydroxyl group does not break off from the alcohol but from the acid. In other words, the bond between the hydrogen and the oxygen of the alcohol is the weak one. The summation of the reaction is the union of the hydrogen from the alcohol and the hydroxyl from the acid to form water. Later investigations showed that in the case of a tertiary alcohol, such as *tert*-amyl, the hydroxyl of the alcohol breaks off in place of the hydrogen. This explains why it is difficult to produce efficiently ethyl chloride from ethyl alcohol and hydrochloric acid, whereas it is quite simple to produce amyl chloride from *tert*-amyl alcohol and hydrochloric acid. The reverse is also true. It is relatively simple to make ethyl acetate from ethyl alcohol and acetic acid and comparatively difficult to make amyl acetate from *tert*-amyl alcohol and acetic acid. In brief, the two alcohols do not react alike and show a distinct difference in their molecular characteristics. It is sometimes thought that it would be beneficial for pedagogical reasons to differentiate between these two types of alcohols by calling the primary alcohols "alcohols," and the tertiary alcohols "alkyl hydroxides."

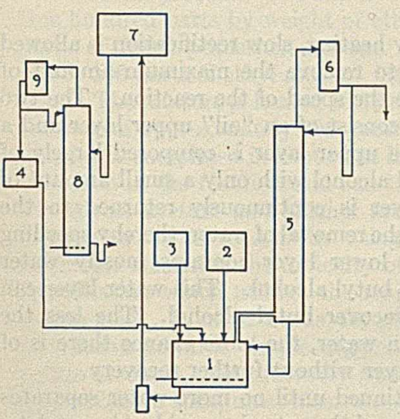

Figure 1. Batch Ethyl Acetate Process

Common Methods and Equipment for Batch Esterification Processes

Ethyl Acetate. The use of a still and an ordinary fractionating column—the batch method of producing ethyl acetate—is an excellent example of the general process. Figure 1 is a sketch of a process for the batch method of manufacture of ethyl acetate (U. S. Patent 1,425,625, Aug. 15, 1922).

The esterification chamber, 1, consists of a cylindrical tank or still containing a closed-coil steam pipe. Storage tank 2 contains a solution of 8 per cent acetic acid. Storage tank 3 contains sulfuric acid of 50–66° Bé. concentration; storage tank 4 contains 95 per cent by volume ethyl alcohol. The acetic acid, sulfuric acid, and alcohol are mixed in still 1 in the proportion of 10 parts by weight of acetic acid solution, 10 parts ethyl alcohol, and 0.33 part sulfuric acid. The vapor from this mixture generated by the heat from the steam coil is led into the fractionating column, 5. The construction of this column is similar to the ordinary bell-cap column, the details of which will be given later. The fractionation in this column is carried out so that the temperature on the top plate is approximately 70° C., which is the boiling point under atmospheric pressure of an azeotropic mixture of ethyl acetate, alcohol, and water containing approximately 83 per cent ethyl acetate, 9 per cent alcohol, and 8 per cent water. The reflux from this column is returned to the reaction chamber or still, 1. The vapors from the top of the column are run into a reflux condenser, 6, part of the condensate is sent back to the top of the column as reflux, and the remainder is sent to a storage tank not shown in the diagram. The reaction is carried out in reaction chamber 1 until the esterification is complete; then alcohol, sulfuric acid, and water (the acetic acid has been entirely consumed) are withdrawn and forced by a pump to a storage tank, 7. This mixture is led into the recovery column, 8, which is of similar design to column 5, except that at the bottom, in place of the heating coil, is inserted a perforated pipe to permit live steam to enter.

The separation within this column is such that water and sulfuric acid are withdrawn at the bottom and sent to the sewer. The composition on the top plate is approximately 95 per cent alcohol or the constant-boiling binary mixture. The vapors from the top of this column are condensed in the reflux condenser, 9, and returned to the top of the column as reflux. The rest of the condensate is led to storage chamber 4 where it may be again used in reaction vessel 1.

Practically no ethyl acetate is returned to esterification chamber 1, but is entirely removed in the form of a constant-boiling ternary mixture from the top of column 5. This materially increases the efficiency of the process in that it increases the speed of the reaction in the still by the constant removal of one of the products. There is at all times present a large excess of ethyl alcohol in the reaction vessel. This likewise materially increases the rate of esterification.

Another feature of this process is the removal of the alcohol-water mixture in the bottom of still 1 and the rectification to produce 95 per cent alcohol so that it can be again utilized.

This process can be used for the manufacture of similar esters—for example, methyl acetate—and takes full advantage of the fundamental principles and characteristics of esterification reactions in general. The use of a still and a fractionating column as the reaction equipment (it should be remembered that some of the esterification takes place within the column) has a definite economic advantage. This advantage will be even more marked when continuous esterification processes are considered.

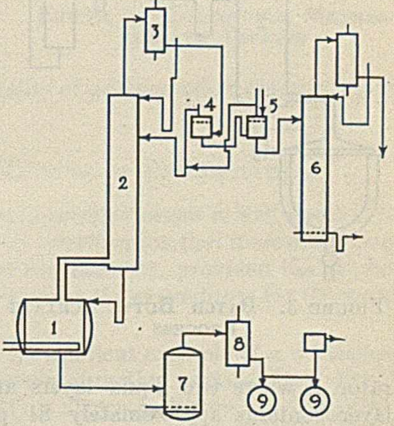

Figure 2. Batch Ethyl Lactate Process

The product of this particular process is not pure ethyl acetate, but a constant-boiling ternary mixture which contains approximately 83 per cent ethyl acetate, 9 per cent alcohol, and 8 per cent water. For many commercial purposes this is quite satisfactory. On the other hand, there are processes that require an ethyl acetate free from alcohol and water. In these cases it is necessary to utilize some method of breaking down the constant-boiling mixture so that it can be separated. The details of such a scheme will be explained later in the discussion of a continuous method for making ethyl acetate.

Ethyl Lactate. A method for the manufacture of ethyl lactate (U. S. Patent 1,421,604, July 4, 1932) is an excellent example of what can be done to increase the rate of esterification by the use of additional inert liquid—in this case, benzene.

It is well known in the fractionation of binary liquids that the addition of a third liquid will often reduce the partial pressure of one constituent much more than it does the other and therefore facilitate separation. This principle can be applied to esterification and can be utilized within the fractionating chamber, especially if it is a column.

Figure 2 shows a sketch of equipment for the manufacture of ethyl lactate, a high-boiling (low vapor pressure) ester. One chemical equivalent of lactic acid having an approximate strength of 80 per cent, together with two or three chemical equivalents of ethyl alcohol having a strength of 95 per cent, are run into the still, 1. Benzene is added to the extent of about one-half of the volume of the alcohol present. These are distilled into column 2, the heat coming from a steam coil in the bottom of the still, 1. Benzene is added to the extent of about one-half of the volume of the alcohol present. These are distilled into column 3, the heat coming from a steam coil in the bottom of the still. Ethyl lactate is formed in the still, and the alcohol, benzene, and water pass in vapor form into the fractionating column. The composition of the vapors from the top of the column are approximately 7 per cent by weight of water, 74 per cent benzene, and 19 per cent alcohol. The ratio between water and alcohol is considerably higher than would be the case if the benzene were not present. This is the fundamental factor in the process and the underlying cause for the increased rate of esterification.

The vapors are condensed in condenser 3, part of the condensate is returned as reflux to the top of column 2, and the rest passes on to separator 4, where two liquid layers are formed. The upper layer contains approximately 81 per cent by weight of benzene, 15 per cent alcohol, and 4 per cent water. The lower layer contains 35 per cent by weight of water, 55 per cent alcohol, and 10 per cent benzene. The so-called water layer is conveyed to a second separator in which additional pure water is added, in order to reduce the concentration of alcohol which acts as a blending agent for the benzene-water mixture. The upper two layers, containing most of the benzene, are returned from the two separators to a point somewhat below the top of column 2. This is done in order to use the benzene again. The water layer from the final scrubber, 5, is fed to rectifying column 6.

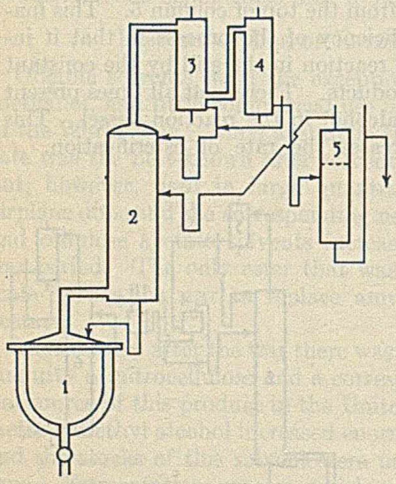

FIGURE 3. BATCH BUTYL ACETATE PROCESS

Fractionation occurs in column 6 to produce a condensate which is approximately 95 per cent alcohol. The water accumulated as a product in the reaction and also the water added in separator 5 are withdrawn from the system at the bottom of column 6.

When the reaction is complete and all of the lactic acid has been consumed, the ethyl lactate containing alcohol and benzene is allowed to run into vacuum still 7. Heat is applied to this still, and the alcohol and benzene are condensed in condenser 8 and sent to reservoir 9, leaving behind in still 7 a high quality ethyl lactate. The benzene not only decreases the partial pressure of the ethyl alcohol more than the water and thus speeds up the reaction, but, owing to its insolubility in water, it can be readily separated by decantation and used again.

BUTYL ACETATE AND BUTYL TARTRATE. Some alcohols are quite insoluble in water, as are also their corresponding esters. An example of this type is butyl acetate whose property of insolubility somewhat simplifies the batch process. A satisfactory method for the manufacture of butyl acetate and also butyl tartrate, taking advantage of this insolubility factor, is shown in Figure 3. The illustration shows a still, 1, an ordinary fractionating column, 2, a reflux condenser, 3, a total condenser, 4, and a separating vessel, 5.

Glacial acetic acid is mixed in still 1 with more than the theoretical amount of butyl alcohol required. A small amount of sulfuric acid is added as a catalyst, the acid having a concentration of 66° Bé. This mixture is brought to equilibrium by heating for several hours. The still is equipped with a steam jacket for this purpose. Any vapor from the reaction passing up through the column is condensed and brought back. The condensate in the column is led back into the still.

After this preliminary heating, slow rectification is allowed to take place in order to remove the maximum amount of water and thus increase the speed of the reaction. The two layers in the separator consist of an "oil" upper layer and a water lower layer. The upper layer is composed largely of butyl acetate and butyl alcohol with only a small amount of water. This upper layer is continuously returned to the column where it aids in the removal of water, thereby speeding up the reaction. The lower layer contains mostly water with a small amount of butyl alcohol. This water layer can be further treated to recover butyl alcohol. The less the solubility of the ester in water, the more chance there is of discarding this water layer without further recovery.

The operation is continued until no more water separates out; then the formation of the ester is considered complete. The temperature at the top of the column at this point rises and the percentage of acetic acid from the distillate increases. In order to obtain a satisfactory product, it is necessary in most cases to neutralize the small amount of remaining acid in the still before further distillation. This is done with a caustic soda solution. The mixture is allowed to stand and form a water layer, and this water layer is separated. The ester or "oil" layer is then washed with water and distilled to obtain a butyl acetate having an approximate strength of 75 to 85 per cent, the remainder being *n*-butyl alcohol.

It is sometimes desirable to obtain a higher strength of ester. In this case the acid should be in slight excess instead of the butyl alcohol. A more dilute form of acid than glacial should be used. The product in this case, following the general operation, should be considerably higher in butyl acetate.

In order to manufacture butyl tartrate by a similar process the reaction mixture should contain an excess of butyl alcohol and a small percentage of sulfuric acid. This mixture is heated for 24 hours. Any vapors are condensed and returned to the system. At the end of this time rectification is allowed to take place, and the product is drawn off in the regular manner. The vapors contain more butyl alcohol than water. Two layers will be formed on condensation. The lower layer will be mostly water with some butyl alcohol, and the upper will have the reverse composition. The lower water layer is removed. The butyl alcohol recovered by rectification in the upper layer is continually returned to the reaction mixture in the column. When the reaction is completed, as shown by the lack of water coming over, the excess alcohol may be removed by vacuum distillation. The impure ester is washed and rectified as in the former case. It is then dried in a vacuum still. The *n*-butyl tartrate obtained by this process will have an approximate strength of 97 to 98 per cent.

The principles involved in this particular method of esterification are applicable to the manufacture of many different esters. This is more or less the common method of esterification used for the higher-boiling, less-soluble type of esters. Full advantage is taken of the insolubility of the ester and alcohol in water. The alcohol separated in both cases is returned to the reaction column in order to increase the concentration of one of the reactants whereas most of the water is removed from the reaction zone as soon as formed. This method of operation appreciably reduces the time necessary for esterification and increases materially the capacity of the unit.

Ethylene Glycol Diacetate. It is sometimes more feasible to use the chloride instead of the alcohol in esterifications. Such a case may be cited in the manufacture of ethylene glycol diacetate from ethylene dichloride. (U. S. Patent 1,430,324, Sept. 26, 1922.)

In this case it is not necessary to use a column in the actual esterification process. The still is replaced with an autoclave. One hundred parts by weight of ethylene dichloride and 150 parts of fused potassium acetate are added together with 150 to 200 parts of ethyl alcohol, having a strength of 95 per cent. The mixture is heated to 180° C. with a corresponding pressure of approximately 150 pounds per square inch. The reaction is completed in about one hour. Potassium chloride is formed in the reaction and can be separated by filtration. The glycol acetate and alcohol are separated by fractional distillation. The reason for using this method with this particular alcohol is the difficulty of the ordinary scheme of esterification which utilizes the reaction between an alcohol and an acid. In other words, the polyhydric alcohols are not as reactive towards simple organic acids as are the monohydric alcohols. Considerably higher temperature is necessary which, in turn, must mean the utilization of a high pressure in order to maintain the liquid phase and a proper contact between potassium acetate and ethylene chloride.

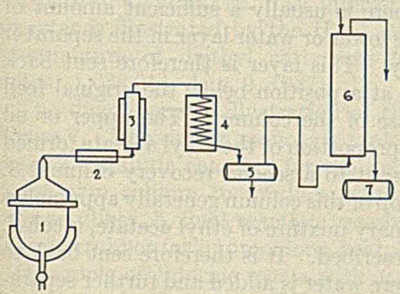

Figure 4. Batch Methyl Formate Process

This particular method is not popular because of the expense involved and the lack of capacity necessitated by the use of small autoclaves.

Methyl Formate. The dehydrogenation of alcohols to produce aldehydes and hydrogen by heating in the presence of a catalyst such as metallic copper is a well-known chemical reaction. The condensation of aldehyde to produce an ester is also well known. Fortunately the necessary conditions for both reactions are more or less the same. An illustration of this method (U. S. Patent 1,400,195, Dec. 13, 1921) used in the production of methyl formate is shown in Figure 4. A steam-jacketed kettle, 1, the preheater for the vapors, 2, the catalyst chamber, 3, a condenser, 4, a receiver, 5, a scrubbing tower, 6, and a final receiver, 7, are shown.

Methanol is placed in the steam-jacketed kettle and distilled. The vapors pass through the preheater where heat is obtained presumably from a hot oil, such as diphenyl, or, better, some oil that can be heated to 450° F. without cracking. The preheated vapors then pass through the catalyst chamber where they come in contact with metallic copper. The copper can be impregnated on the surface of pumice stone, charcoal, etc. The reaction is carried out between 350° and 450° F., or an average of 400°. The products are methyl formate and hydrogen. The condenser is maintained at a temperature of 20–30° C. The condensate in the first receiver, 5, consists of methanol and methyl formate. This may be fractionated in the ordinary manner to produce a relatively pure product. The methanol is used again. The vapors from this condenser pass into the bottom of scrubbing column 6, and the desirable products, with the exception of the hydrogen, may be scrubbed out by means of water or methanol. The liquid is collected in receiver 7. It can then be fractionated in the ordinary manner. The impure hydrogen coming from the top of the scrubbing column may be collected from the gas receiver and used for other purposes.

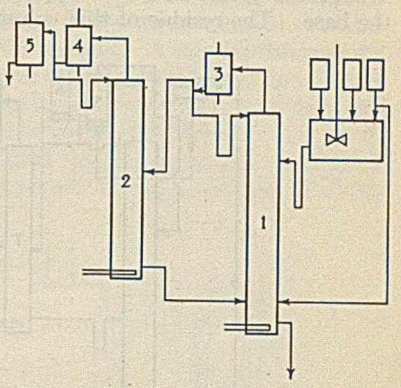

Figure 5. Continuous Methyl Acetate Process

This process is not highly efficient. There may be conditions, however, where it would be economically desirable. An example of this case would be a plant that was making products from the hydrogen and in which a source of hydrogen was desirable. Problems in fractionation of the product might possibly occur. Perhaps it would be desirable to make the process a continuous one and thereby gain added efficiency. Very little use is made of this process in industry. It is cited here only as an example of the possibility of utilizing other chemical methods of esterification.

Continuous Methods of Esterification

The advantage of continuous processes is well known. It so happens in methods of esterification that most of the processes can be carried out continuously, provided the production is large enough to warrant the expenditure for the necessary equipment.

Methyl Acetate. An excellent example of a continuous process for the manufacture of methyl acetate (U. S. Patent 1,400,849, Dec. 20, 1921) is shown in Figure 5. Columns 1 and 2 are the reaction and recovery columns, respectively. Condenser 3 is used to create a reflux for column 1. Condenser 4 is a reflux condenser for column 2, and condenser 5 is a total condenser.

Sulfuric acid as the catalyst is continuously fed to a point near the top of column 1. This acid has a strength of 50–66° Bé. It is sometimes distinctly advantageous to use an 8 per cent acetic acid solution because of its ease of manufacture, especially from ethyl alcohol by fermentation. For this case 0.33 part by weight of sulfuric acid is added to the column while 10 parts of 8 per cent acetic acid are being added. Methanol at an approximate concentration of 95 per cent is also fed into the column, but near the bottom as indicated in Figure 5.

It is sometimes desirable to use glacial acetic acid. If this is done, it has been found effective to mix the acid with the methanol and the sulfuric acid catalyst in a mixing tank prior to its entrance into the column. This mixture is inserted into the column at about the same plate as the acetic acid was formerly. Excess methanol, however, is added near the base of the column as formerly.

The actual reaction takes place within the column. No still is used. There is an excess of methanol always present in the reaction zone; therefore the acetic acid is entirely consumed in the reaction. Water and the sulfuric acid are withdrawn as waste products at the bottom of the reaction column. The column is heated by a tubular heater at the bottom. The vapors from the top of the column have approximately 30 parts by weight of methyl acetate and 70 parts of methanol. Some of this mixture is condensed in reflux condenser 3 and returned to the top of reaction column 1.

The remainder of the mixture is then sent to recovery column 2. As there are no constant-boiling mixtures present, the fractionation of this binary mixture is relatively simple. The vapor from the top of the recovery column is largely methyl acetate. Part of this is condensed as a reflux and the remainder is condensed as a product of the reaction. This recovery column is also supplied with a tubular heater at the base. The residue of this column, consisting largely of methanol, is returned to the plate on reaction column 1 that was formerly used to receive the excess methanol as a raw material.

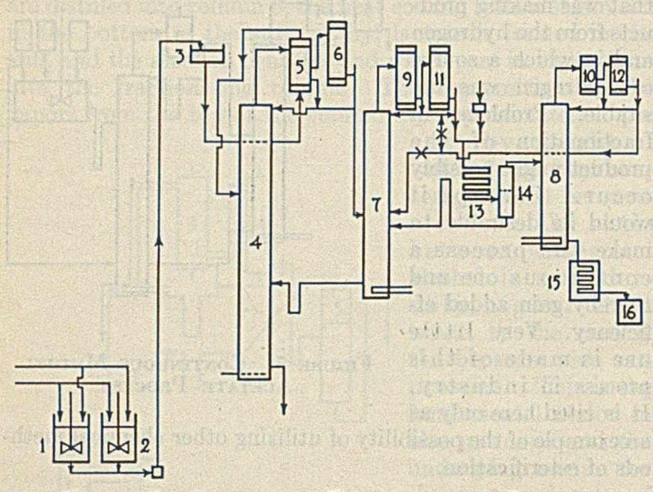

Figure 6. Continuous Ethyl Acetate Process

The ordinary type of bubble-cap plate is used, as well as proper construction throughout. The principle of the reaction equipment is always to maintain an excess of the reactants, especially the methanol, and at the same time to withdraw as rapidly as possible the products methyl acetate and water. This is readily accomplished by the utilization of two simple fractionating columns, largely because there are no conflicting constant-boiling mixtures present.

Ethyl Acetate. Frequently the mixtures of esters and water, of alcohols and water, and of esters, alcohols, and water present azeotropic mixtures. This situation renders difficult the manufacture of pure esters. In order to break up these constant-boiling mixtures, it becomes necessary to adjust the concentrations of the constituents to a point where two liquid phases appear. It will usually be found at this point that a separate layer can be fractionated with the production of only a small amount of constant-boiling ternary mixtures, for example, because of the insufficiency of one constituent. This insufficiency is brought about by a lack of solubility. This fundamental idea was used in devising a worthwhile method for the continuous manufacture of ethyl acetate (U. S. Patents 1,454,462 and 1,454,463, May 8, 1923).

The diagram showing this method is given in Figure 6. Containers where the initial mixture can be brought to an equilibrium are shown as 1 and 2; 3 is the receiving tank, 4 the reaction column, 5 a reflux condenser, 6 a total condenser, 7 and 8 are recovery columns, 9 and 10 reflux condensers, 11 and 12 total condensers, 13 is a mixing coil, 14 a separator, 15 a cooling coil, and 16 a receiver.

Eight per cent acetic acid is used in this particular process. Sulfuric acid, having a strength of 50–66° Bé., and 95 per cent ethyl alcohol in excess are mixed with the acetic acid in the reaction tanks. These tanks are supplied with agitators. The mixture is brought to equilibrium and pumped to receiving tank 3. Figure 6 shows that this reaction mixture is used for condensing purposes in reflux condenser 5. At the same time it is preheated before it enters near the top of the reaction column 4. The temperature maintained at the top of this column is approximately 80° C. Live steam to produce this heat enters at the base of the column. An additional feed of recovered alcohol, approximately 70 to 90 per cent in concentration, is led into the reaction column near the base. Vapors from this column when finally condensed and conducted to recovery column 7 contain approximately 10 per cent by weight of water. The excess water, including the sulfuric acid catalyst, passes out at the bottom of reaction column 4. The acetic acid is entirely consumed because in the reaction zone there is always present an excess of alcohol, and the ethyl acetate and water are constantly removed.

Recovery column 7 has an indirect heater in the bottom—for example, steam coils—which serves to remove the excess alcohol from the ternary mixture. The excess alcohol is returned to reaction column 4 as previously indicated. The ternary mixture of ethyl acetate, alcohol, and water coming from the top of column 7 approaches the composition of the constant-boiling ternary mixture. It contains approximately 83 per cent ethyl acetate, 9 per cent ethyl alcohol, and 8 per cent water. If for any reason the ester is less than 80 per cent of the mixture, it is led back into recovery column 7 at approximately the same position as the original feed.

If, on the other hand, it more closely approximates the constant-boiling ternary mixture, it is led to mixing coil 13 where water is added in order to form two liquid layers in separator 14. The lower layer contains a small percentage of ethyl acetate and alcohol. The upper layer is approximately 93 per cent by weight of ethyl acetate, 5 per cent water, and 2 per cent alcohol. There is usually a sufficient amount of valuable products in the lower or water layer in the separator to justify their recovery. This layer is therefore sent back into recovery column 7 at a position below the original feed plate but above the base of the column. The upper or oil layer containing a large proportion of the ethyl acetate formed in the reaction is then sent to a second recovery column, 8. A condensate from the top of this column generally approaches the constant-boiling ternary mixture of ethyl acetate, alcohol, and water previously described. It is therefore sent back to the mixing chamber where water is added and further separation of ethyl acetate is obtained. From the bottom of this column ethyl acetate, having a strength of 95 to 100 per cent, passes out as the main production of the reaction. It goes through a cooling coil and to receiver 16.

Sufficient time of contact between acetic acid, ethyl alcohol, and the catalyst should be permitted in reaction column 4 to obtain high yields of ester. This is accomplished by having a sufficient number of plates in this column. It might also be advisable to maintain pools of liquid at the boiling temperature between plates in the column. Experience has shown that this is not necessary provided a sufficient number of plates are used in the column. Practice demands approximately fifty plates.

Not only is there a constant excess of reactants present and a steady removal of products from the reaction column, but the constant-boiling mixtures are broken down by adding an excess of water and separating the mixtures into two liquid phases. The "oil" or upper layer can then be fractionated to produce a relatively small amount of constant-boiling mixture, the excess product being ethyl acetate which is obtained in a fairly pure condition. The water layer is utilized again in order to produce more of the ternary mixture, and the excess alcohol is returned to the reaction column.

Ethyl Chloride. It is sometimes desirable to make an ester from an alcohol and an inorganic acid such as hydrochloric in place of an organic acid such as acetic. Since the bond between the oxygen and the carbon in the ordinary primary alcohol is rather strong, it must be broken in this case; therefore special methods must be devised to accomplish this. An excellent example of such a process is the manufacture of ethyl chloride (U. S. Patent 1,509,463, Sept. 23, 1924).

The catalyst in this case is fused zinc chloride. This must be maintained at a point sufficiently high to drive off any water formed in the reaction. Hydrochloric acid gas and ethyl alcohol vapors are passed into the fused chloride. It is rather difficult to conceive of any commercial type of equipment that would satisfactorily handle this reaction. The equipment must be heated, presumably by some internal heating system, since any external heating system with stoneware equipment would be impractical. Stoneware equipment is necessary because hydrochloric acid at this temperature in the presence of water is extremely corrosive.

Vapors from this reaction vessel consist of water, ethyl chloride, ethyl alcohol, and some hydrochloric acid. The reaction should be run in such a manner as to produce a minimum amount of residual hydrochloric acid. The alcohol and water must be condensed in a glass or stoneware condenser and separated from the ethyl chloride vapors. The final traces of hydrochloric acid are removed by passing the ethyl chloride gas through water scrubbers such as are now used in hydrochloric acid manufacture. The scrubbing column may contain in its upper units an alkaline solution to remove the last traces of hydrochloric acid.

This process is continuous, as the zinc chloride is maintained in its original form and the condensate on the condenser is continuously removed.

Diethyl Carbonate. An interesting method of making an ester is illustrated by the H. G. Mitchell process for the manufacture of diethyl carbonate from phosgene (U. S. Patent 1,638,014, Aug. 9, 1927).

The diagrammatic illustration of this process is shown in Figure 7. The carbon monoxide tank is shown as 1, chlorine tank, 2, catalytic chamber for the manufacture of phosgene, 3, reaction column to produce ethyl chlorocarbonate, 4, a vent scrubber, 5, final reaction vessels, 6, alcohol condenser, 7, and scrubber for hydrochloric acid, 8.

One mole of chlorine reacts with carbon monoxide to produce one mole of phosgene (Cl_2CO). This in turn reacts with one mole of ethyl alcohol to produce one mole of ethyl chlorocarbonate (C_2H_5COOCl) and one mole of hydrochloric acid. Finally the ethyl chlorocarbonate reacts with one mole of ethyl alcohol to form one mole of diethyl carbonate $(C_2H_3)_2$-CO_3 and one mole of hydrochloric acid. It is quite possible to produce a gas containing 25 to 40 per cent carbon monoxide and 60 to 65 per cent nitrogen by a modified gas producer. Care must be taken to eliminate carbon monoxide, hydrogen, and water, as these will absorb the chlorine and decrease the efficiency of the process. The production of the phosgene is relatively simple. A desirable catalyst is activated charcoal. The catalytic chamber, however, must be water-cooled, and the temperature maintained below 250° C. in order to avoid decomposition of the phosgene. The reaction is exothermic and considerable heat is evolved. The final temperature of the gases leaving the phosgene reaction chamber should not exceed 110° C. They pass into the base of a filled column which acts as a scrubber and reaction equipment. Alcohol is drawn in at the top. The reaction producing ethyl chlorocarbonate is also exothermic. Therefore the reaction column must be cooled. The gases are corrosive, and the column should be constructed preferably of stoneware, glass, or lead.

The amount of alcohol fed to the column is somewhat in excess of the theoretical amount necessary for the reaction. The temperature maintained in the column should not exceed 40° C. In small vent scrubber, 5, water is used to prevent hydrochloric acid from passing into the air.

The ethyl chlorocarbonate with excess alcohol also contains dissolved hydrochloric acid gas. It is led to the reaction vessels, 6, at the base of reaction column 4. Nitrogen in the meantime has passed through the vent scrubber and out into the air. The first reaction vessel is not heated. The remaining two are heated. Overflow is permitted from one vessel to the next. Vapors coming from these reaction vessels are led through alcohol condenser 7, the alcohol being returned to the reaction zone. Hydrochloric acid passes on and is collected in scrubbing column 8 as a water solution. Water is admitted at the top of the column. A standardized quartz equipment for the scrubbing of hydrochloric acid has proved fairly successful in this particular operation. A simply designed glass column might be equally effective.

The product from the final reaction vessels is neutralized with a solution of caustic potash having a strength of about 30 per cent. In order to prevent hydrolysis of the ester, this operation is carried out at 10–30° C. The mixture is allowed to separate into two layers. The upper layer consists of approximately 80 per cent diethyl carbonate and 20 per cent alcohol. The lower layer is largely a sodium chloride solution in water.

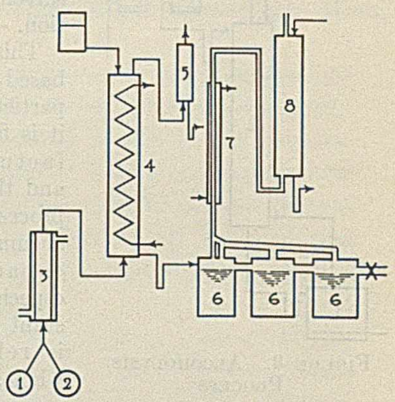

Figure 7. Continuous Diethyl Carbonate Process

Another modification of this method is the utilization of 100 per cent excess ethyl alcohol. The final reaction takes place at room temperature and no heat is required. Most of the hydrochloric acid is retained in the liquid.

It has also been found expedient to separate the diethyl carbonate into a distinct liquid layer by the addition of water without any neutralization. Another scheme of separation is the use of inert solvents such as benzene, toluene, ethyl ether, etc. They completely dissolve the diethyl carbonate, forming two layers of the water solution.

The method described above has no great commercial significance. It does, however, show the possibility of utilizing such a reaction, especially in the formation of carbonates. It also gives an indication of the type of equipment that has been found suitable for these particular reactions. From this standpoint the material is well worth consideration in the light of future possibilities.

Amyl Acetate by Alcoholysis. The high-boiling esters, such as amyl acetate, can be made by a process similar to the one described under butyl acetate. These same esters, however, can also be made by what is known as alcoholysis (U. S. Patent 1,491,076, April 22, 1924).

A sketch showing the equipment is given in Figure 8. An ordinary steam still is shown as 1, 2 is a fractionating column, and 3 and 4 are condensers. The principle of this process is the reaction of a low-boiling ester with a high-boiling alcohol to produce the corresponding ester of the high-boiling alcohol.

Methyl acetate and amyl alcohol are run into the top of column 1. Methyl acetate has a composition of about 85 per cent ester, the remainder being methanol. Sulfuric acid is added to the extent of 0.3 to 0.5 per cent by weight of the materials present and consists of the regular 66° Bé. acid. Four parts by weight of the commercial methyl acetate are added to one part of amyl alcohol. The vapors at the top of the column are largely methanol and methyl acetate. The percentage of methanol is approximately 18 per cent and is higher than the original percentage. Part of the condensate is returned to a point below the top of the column and the remainder is drawn off from condenser 4. Methanol is formed in the reaction and amyl alcohol is consumed. The reaction takes place largely within the column. The equilibrium is disturbed by the removal of a higher percentage of methanol, the lower-boiling alcohol. The mixture drawn off from the second condenser, 4, contains only 18 per cent methanol; therefore it limits somewhat the capacity of the equipment.

It is necessary in this process to recover the low-boiling ester. This can be accomplished by distillation (including the addition of water and separation) and also by salting out or extraction of the solvents followed by fractionation.

This process of esterification based on alcoholysis is not particularly popular because it is first necessary to manufacture the low-boiling ester and then to apply this second process, thereby causing an accumulation of losses. The capacity of this equipment, especially when there are constant boiling mixtures present, is relatively low. On the whole, the process is uneconomical except where special conditions exist, such as a surplus of the lower-boiling ester and an excess demand for the high-boiling ester.

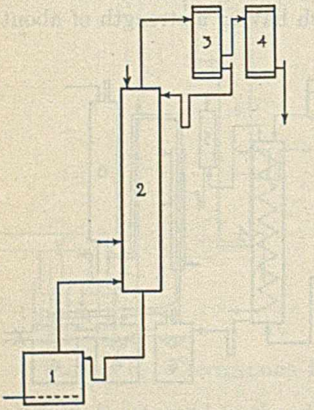

FIGURE 8. ALCOHOLYSIS PROCESS

ESTER GUM. There is at least one industrially common case of esterification which cannot be carried out by any of the processes given. There has been published (*1*) an excellent description of both laboratory and commercial units for the manufacture of this particular ester. The reaction involves the esterification of the acids in rosin by glycerol. The equipment consists only of an ordinary copper kettle with a copper lid and a short tower. Apparently, however, aluminum kettles are more efficient and capable of carrying out three 600- to 700-pound batches per day each.

It is claimed that a good grade of ester gum can be made in the large copper kettles in about 2 hours and 45 minutes. The temperature is slowly raised from 340° to 375° F. in order to prevent frothing. It is then raised from 450° to 520° F. in 15-minute intervals at 450°, 478°, and 500° F. The danger is that the frothing will cause the glycerol to come out, pass down the side of the kettle, and catch fire. The stack is used as an air condenser to condense the glycerol vapors. The materials used are 600 pounds of rosin, 75 pounds of glycerol, and 9 pounds of China wood oil.

This type of esterification is interesting because a high temperature is necessary in the process. No particular catalyst is used and the acid is first in a solid condition. Since aluminum is thought to have a certain amount of catalytic action on esterification, it is recommended as material for the construction of the unit. Wood oil seems to have some slight catalytic activity. It is interesting also to note that no vacuum or pressure is required in this reaction.

TYPES OF COLUMNS USED FOR ESTERIFICATION. The basic requirements of a column used for esterification reactions are more or less the same as the requirements of a column for fractionating purposes. All the heat should be put in at the bottom, and all condensation should occur at the top. There should be no heat transfer through the walls of the column. The process is continuous, the reaction taking place entirely within the column, and the feed should enter somewhere between the top and bottom of the column. Any recovered material is sent to the appropriate plate where the composition most closely resembles the composition of the return liquid.

It is necessary to have as intimate contact as possible between the vapor and the liquid. This means that the ordinary bubble-cap plate is appropriate in most cases. This in turn requires metallic construction and, therefore, when corrosive vapors or liquids are present in the reaction, this type is not always feasible. It becomes necessary in those cases to resort to the filled type of column, usually made of stoneware and acid-resisting filler. It is sometimes desirable to carry a rather deep liquid seal on each plate since many of these esterification reactions require time to bring them to equilibrium. The depth of seal determines the length of time the liquid remains on the plate. Experience has shown, however, that a deep liquid seal is not necessary to produce the required amount of contact. Apparently the type of froth and bubbles immediately above the surface of the liquid has a great deal to do with this estimate of contact. A test plate with the actual dimensions is made of galvanized iron and utilizes water and compressed air. This will easily show the designer, after some experience, whether or not these desirable conditions will prevail in the actual column. It is sometimes difficult to determine the actual amount of overflow and vapor velocity that will be present in a column for satisfactory running conditions. It is necessary, however, to have some idea of these rates in order to maintain similar conditions on the experimental plate.

The required number of plates in the column for a particular esterification is something that cannot be calculated. The amount of reflux is also a factor that can be determined only by experience. It has been found advisable in practice, however, to put in more plates than have been found satisfactory for the simple separation of a corresponding binary mixture. It is a relatively simple matter, if corrosive materials are not present, to make several trial runs with an experimental column containing fifty plates and to obtain a fairly accurate estimate of the actual number of plates required in a commercial unit.

Needless to say, no products are continually removed from the side of one of these columns. It is only possible to make a separation into two parts which might be called the heads and tails.

Most of these esterifications produce relatively small amounts of heat. This is fortunate because the creation of heat units means a corresponding creation of vapors within the column at a point above the bottom; this interferes in the fractionation, necessitates an increased reflux, and thereby materially decreases the capacity of the unit. Sometimes, however, gas is produced and the reactions exhibit a high heat of solution. This release of heat not only disturbs the equilibrium as far as fractionation is concerned, but also causes a rise in temperature which is often likely to increase side reactions. These side reactions mean a decrease in yield. It becomes necessary in such cases to use cooling coils on those plates where the heat is liberated. It has been found expedient to use perforated plates in this case. However, if perforated plates are used, there must be a constant pressure of gases throughout the column; otherwise the liquid will be no longer supported on the plates and will fall to the bottom. The operation of the column will cease until the pressure is built up again and each plate is covered with the proper amount of liquid. This problem becomes even more complicated when corrosive gases are present because it is impractical to use stoneware plates with stoneware cooling coils. In cases where heat is liberated and corrosive material is present, lead-lined plates are not always effective. Vacuum fractionation using filled columns or columns containing whirling disks have been found effective for fractionation purposes. It is doubtful whether this type of equipment would prove more effective for most esterifications than the ordinary pressure type using bubble caps.

Generally speaking, for continuous fractionation where the vapors and liquids are not particularly corrosive the ordinary bubble-cap column made of copper is reasonably satisfactory. It is certainly far more effective than attempting to run esterifications by the batch process in ordinary steam-heated stills.

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Methods and Apparatus for Oxidation of Hydrocarbons

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Aromatic hydrocarbons require considerable oxidation in the presence of a catalyst at an elevated temperature before desirable intermediate products are formed. The intermediate products represent definite resistance points in the oxidation, and permit high per-pass yields. Apparatus, consisting of a large number of small, vertically supported catalyst tubes immersed in a liquid boiling at reaction temperature, permits the removal of large quantities of reaction heat at a reaction temperature of 400° to 450° C., and has been successfully used in the manufacture of phthalic anhydride, maleic anhydride, etc.

Aliphatic hydrocarbons, particularly in the range of ethane to hexane, require only small proportions of oxygen to form the desired intermediate oxidation products. Resistance points in the stepwise reactions are not apparent, and a different technic is necessary. Oxygen concentrations must be controlled at a low value, reaction must be rapid, and recirculation with intermediate-product recovery employed.

The application of high pressures to this oxidation has resulted in interesting yields of alcohols, acids, and other intermediate oxidation products. Numerous difficulties have prevented the extensive industrial application of these methods, but they present interesting possibilities.

CONSIDERABLE study has been given to the catalytic vapor-phase oxidation of hydrocarbons, and a mass of data is available in the literature. However, interpretation of the data is frequently confusing because the reactions are complex, mixtures of products are generally obtained, and a great variety of conditions may be imposed on the reaction. In certain cases, available information is far from complete and many opportunities for development exist. It is not possible to propound rules and regulations for these oxidations and have them apply rigidly to all classes of hydrocarbons, or even to members of the same class having different molecular weights or isomeric structures. It is possible, however, to make certain generalizations provided they are not too specific in nature and are not applied in too narrow a sense.

Measured by their behavior toward air oxidation in the vapor phase, the hydrocarbons may be broadly classed into two large groups: aromatics, which are relatively stable and require large proportions of oxygen for conversion to useful products; and aliphatics, which are not so stable to elevated temperatures, are more reactive toward oxygen, and in general require the addition of only small amounts of oxygen to yield useful products. There are exceptions to this classification and its application is subject to rigid restrictions. For instance, aromatic hydrocarbons with aliphatic side chains may behave like aliphatics until the substituent has been destroyed. Also, anthracene is converted to anthraquinone by oxidation with the interaction of a total of only 3 atoms of oxygen. However, even this amount of oxygen is large relative to the single atom required to change butane to butyl alcohol.

Obviously, the conditions under which oxidations may be conducted are various, and a review of the literature discloses a diverse array of methods. Oxidation may be either catalytic or noncatalytic, may be conducted in either the liquid or the gas phase, and may be at essentially atmospheric pressure or under considerable pressure. The conditions must be chosen with consideration for the mechanism by which the particular oxidation occurs, for the rates of the individual steps in the reaction, and for the stability of the products.

Since oxidation reactions are exothermic in character, means must be provided for the removal of heat and for the control of temperature. These two factors have necessitated the greatest amount of thought in the design of apparatus, and the differences in converter design bear principally on these factors.

The method used for the introduction of oxygen depends considerably upon the reactivity, stability, and volatility of the reactant hydrocarbon and product. Oxygen may be passed into the hydrocarbon material which is already at reaction temperature, a mixture of oxygen and gaseous hydrocarbon may be passed in the vapor phase into the heated reaction zone, a liquid hydrocarbon containing dissolved oxygen may be passed into a heated chamber where the hydrocarbon either may or may not vaporize, or liquid hydrocarbon plus dissolved oxygen may encounter a heated stream of similar hydrocarbon, but without oxygen, and the combined streams passed into a hot reactor.

Being the seat of the reaction and consequently the point at which reaction heat is generated, the catalyst chamber or converter, as it is called, is an important part of an oxidation installation. It is with the reaction chamber or reaction zone that this paper is mainly concerned. Auxiliary equipment, such as vaporizers and recovery systems, are important but do not present the design and construction problems that the reaction chamber does.

AROMATIC HYDROCARBONS

The aromatic compounds are characterized by offering several points of resistance to further oxidation or decomposition during the course of the interaction with oxygen. For instance, in the case of naphthalene oxidation, the interaction of 3 atoms of oxygen results in the formation of α-naphthaquinone—a point of resistance, since this compound may be obtained in good yield under the proper conditions. The interaction of a total of 9 oxygen atoms results in the formation of phthalic anhydride. Another resistance point occurs after the reaction of 18 oxygen atoms when maleic anhydride is formed. These definite resistance points make possible the isolation of intermediate oxidation products in good yields. Thus, it is possible to obtain commercial yields of phthalic anhydride from naphthalene, maleic acid from benzene, anthraquinone from anthracene, etc. Because of the thermal stability and resistance to oxidation of the aromatic hydrocarbons and the intermediate reaction products, it is necessary to employ excess oxygen, operate at elevated temperatures, and make use of active catalysts. These factors make it possible to conduct the oxidation so as to obtain practically complete reaction of raw material with only a single pass over the catalyst.

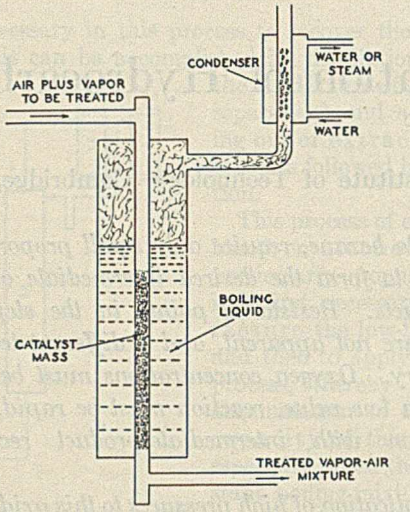

FIGURE 1. SECTION OF SINGLE-TUBE REACTOR

Noncatalytic oxidation of the aromatic hydrocarbons by air is slow at temperatures below 500° C. Benzene is not vigorously oxidized in glass chambers until temperatures near 700° C. are attained. Under similar conditions toluene is noticeably oxidized at 650° C., and xylene at 575° C. (*3*). Even with an active catalyst such as vanadium pentoxide, a temperature of 400° to 450° C. is required for the industrial oxidation of naphthalene to phthalic anhydride by the use of air. Furthermore, quantities of air from one to three times that theoretically necessary for the conversion must be used. This means that from 20 to 60 moles of air must be used per mole of naphthalene introduced to the reaction chamber.

The apparatus for such oxidation must be designed to permit the maintenance of constant elevated temperatures, to permit the removal of large quantities of heat at these elevated temperatures, and to provide adequate catalyst surface to promote reaction. To accomplish these ends the general type of converter consisting of numerous small catalyst tubes immersed in a liquid bath has been developed (*1*). The liquid bath may remove heat from the reaction as latent heat of evaporation of the liquid; it may be subjected to forced circulation in contact with the catalyst tubes and cooled in an external heat exchanger; or it may be used as a means of getting reaction heat to the outer shell of a converter where radiation and convection carry it to the atmosphere. The form of converter using a liquid boiling at reaction temperature has been successfully used for oxidation of aromatic hydrocarbons and will be described here.

Figure 1 is a diagrammatic section of a single tube reactor and is useful in showing the principles involved. The entering air-hydrocarbon (naphthalene is a good example) mixture first comes in direct heat-transferring contact with the heated vapors of the boiling liquid, and is thus preheated before coming in direct contact with the catalyst. Cooling of the first section of the catalyst is thus avoided and the whole made effective toward promoting the reaction. Reaction heat, liberated at the catalyst surface, passes from the catalyst mass through the tube wall and to the surrounding liquid, where it is removed at constant temperature by the vaporization of the liquid. The evolved vapors from the bath may be condensed outside, and the relatively cool liquid returned to the bath. Operation is thus made continuous.

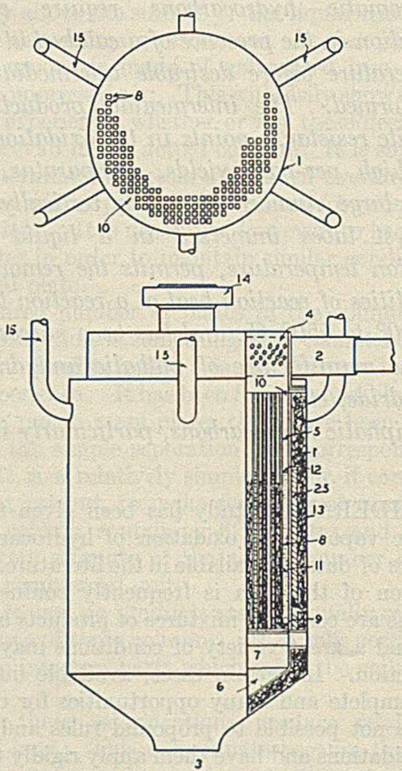

FIGURE 2. ASSEMBLY OF SQUARE TUBES ARRANGED IN SHELL

1. Shell
2. Feed inlet
3. Product outlet
4. Inlet header
5. Vapor space
6. Outlet header
7. Lower support
8. Catalyst tube
9. Tube sheet (lower)
10. Tube sheet (upper)
11. Catalyst
12. Bath level
13. Shell insulation
14. Safety disk
15. Vapor outlets to condenser
25. Heater for starting

In practice it is customary to use a large number of such tubular catalyst chambers in parallel, connected at the top and bottom by common headers. Square tubes $^5/_8$ to $^3/_4$ inch (1.6 to 1.9 cm.) to the side, and approximately a yard (0.9 meter) long are assembled in numbers that may reach nine to twelve hundred for a single converter. Figure 2 shows such an assembly of tubes arranged in a shell provided with the proper connections for reaction mixture intake, product outlet, and vapor lines. Mercury has been successfully used as the bath liquid in such an apparatus, having a boiling point and latent heat satisfactory for practical use. Construction is of welded steel.

Square catalyst tubes present a larger area for heat transfer than do round tubes on the basis of comparable volume, and may be placed closer together in the assemblage. Although the ratio of catalyst volume to mercury volume may be made large, as long as liquid mercury is kept in complete contact with the tubes in the catalyst zone, the ratio of catalyst volume to tube surface and the maximum distance of catalyst from tube surface must be controlled within limits. As the distance that heat has to travel in leaving the catalyst zone is increased, the temperature differential between boiling liquid and catalyst must be larger in order for the same amount of heat to be transferred. It is desirable to have the catalyst temperature as nearly that of the liquid (commensurate with adequate heat transfer) as is possible for purposes of control. It is imperative that no point of the catalyst mass exceed a maximum temperature, which depends upon the activity of the catalyst, to prevent undue losses of raw material by complete oxidation and contamination of product by undesired substances. For these reasons a minimum ratio of 3 square inches of tube surface per cubic inch (1.2 sq. cm. per cc.) of catalyst volume has been claimed as a limit for tube size in this particular converter.

Such a converter is largely automatic in operation and does not depend upon atmospheric conditions for satisfactory operation. As shown in Figure 3, a suitable air and water-cooled condensing system returns the mercury to the liquid reservoir and removes the heat of reaction thereby. The mercury (liquid and vapor) is thus the means for removing the heat of a reaction at a constant temperature of about 425° C. and for dissipating it to cooling water at a temperature of about 100° C. Heat is thus effectively removed without affecting the temperature of the catalyst adversely.

By varying the pressure on the two-phase mercury system, it is possible to control the temperature of the liquid bath and of the catalyst mass. This may be accomplished by the use of nitrogen pressure. It is also possible to alter the boiling point of the mercury by introducing alloying metals such as cadmium.

The capacity of such a converter is from 1500 to 1800 pounds (816.5 kg.), or even more, of phthalic anhydride per 24 hours, depending upon catalyst activity, rate of feed, etc. Production at this rate means the generation of large quantities of heat in the converter. Although the heat of oxidation of naphthalene to phthalic anhydride is about 6000 B. t. u. per pound (3330 Cal. per kg.) of naphthalene, the occurrence of a certain amount of complete combustion during the oxidation reaction brings the heat evolution up to approximately 10,000 B. t. u. per pound (5550 Cal. per kg.) of naphthalene fed to the converter. About 21,000,000 B. t. u. (5,300,000 Cal.) are generated per day and removed by the boiling mercury and as sensible heat in the hot exit products during operation on the above basis.

Figure 4 shows a diagrammatic layout for a phthalic anhydride plant.

Mercury has both advantages and disadvantages for use as the heat-removing fluid. Its boiling point of 357° C. at atmospheric pressure may be easily raised to 400–425° C. by the application of nitrogen pressure. It is fluid at room temperature and introduces no hazard of equipment damage due to solidification through accidental cooling due to shutdown of equipment. Latent heat of evaporation at 357° C. is 117 B. t. u. per pound (65 calories per gram). Mercury vapor is toxic, the liquid is heavy, and leaks in the pressure system are difficult to prevent. These latter factors, together with cost, operate as disadvantages.

The objectionable features have been largely overcome in practice. Proper construction and design have reduced mercury loss by leakage to about one per cent per year. Aside from this small loss, the only mercury expense is the charge against the investment, since the resale value is almost as high as first cost—differing only by the cost of purification. Mercury has a low coefficient of thermal conductivity and does not wet the steel tube walls. However, the violent motion given to the mercury by its own boiling tends to counteract these effects.

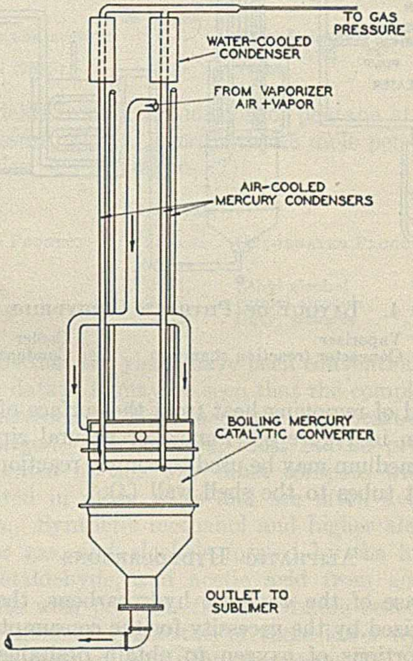

FIGURE 3. CONVERTER USING TWO-PHASE MERCURY SYSTEM

The oxidation reaction occurs at the surface of a catalyst, usually vanadium pentoxide supported on small fragments of a catalytically inert carrier. The early use of pumice as this carrier was abandoned because of the tendency for reaction with the acid catalyst at the elevated temperatures. The development of carriers that were inert to the catalytic material has eliminated the lowered productivity formerly encountered on continued use of the catalyst. Vanadium pentoxide supported on an inert carrier is quite active and promotes the rapid oxidation of naphthalene to phthalic anhydride at temperatures near 400° C. when freshly prepared; temperatures nearer 450° C. are required after aging. For complete and efficient conversion of naphthalene, it is essential that the gaseous reaction mixture make thorough contact with the catalyst. The use of small-sized catalyst particles contained in vertical tubes, and the introduction of the reaction mixture at the top of these tubes insures this good contact and prevents channeling of the gases. Since the usual catalyst support of inert material is generally a poor heat conductor, and since the different catalyst particles are only in point-to-point contact, heat transfer from catalyst to tube wall by solid conduction is relatively small. Radiation and gaseous transfer account for the greater part of the transfer. Indeed, it has been reported that the use of a good heat-conducting catalyst support such as metallic aluminum does not materially alter the capacity of a converter. The use of aluminum as a carrier is advantageous since it is neither catalytically active itself nor does it form compounds of lower productivity with vanadium pentoxide. Because of the importance of radiation in the removal of heat from the reaction, the black-body coefficient of the inner tube wall is of more importance than the thermal conductivity of the metal. In this respect steel tubes are suitable.

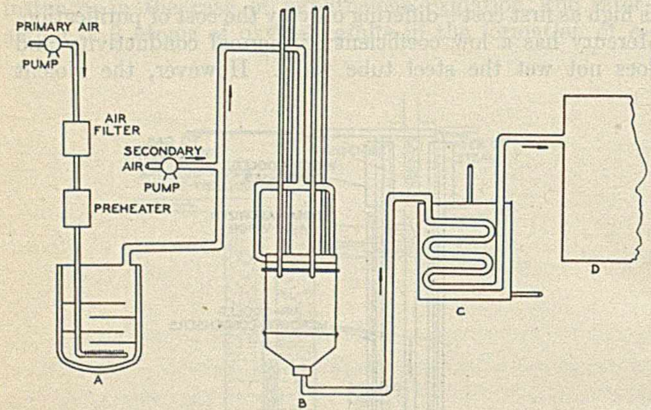

Figure 4. Layout of Phthalic Anhydride Plant

A. Vaporizer
B. Converter (reaction chamber)
C. Cooler
D. Condenser

A method of removing heat from the surface of a shell by air is shown in Figure 5. Forced or natural circulation of some fluid medium may be used to convey reaction heat from the catalyst tubes to the shell wall (*4*).

Aliphatic Hydrocarbons

In the case of the aliphatic hydrocarbons, the oxidation is characterized by the necessity for the consumption of only small proportions of oxygen to obtain desirable oxidation products. Also, the oxidation, once started, proceeds rapidly through the various intermediate stages to the final products—carbon oxides and water—if sufficient oxygen is present. Even with insufficient oxygen for complete oxidation, decomposition of the intermediate oxidation products may occur and must be guarded against. The branched-chain saturated hydrocarbons constitute a possible exception to this rule, inasmuch as ketones may form as intermediates; since ketones are more stable than the aldehydes obtained in the case of the normal-chain hydrocarbons, they may offer a point of resistance to oxidation or decomposition (*6*). But this resistance point appears not to have the significance that the resistance points of the aromatic series do, since it has not been shown possible to convert 70 to 80 per cent of the hydrocarbon per pass to a single "useful" oxygenated product, as is true of the aromatic oxidation. The nature of the oxidation reactions with the aliphatic compounds is such that good conversions of hydrocarbons to product can be obtained only under conditions which limit the extent to which oxidation is permitted to occur. In general, these conditions are best met by limiting the amount of oxygen that is capable of reacting at any one time. This means the use of low oxygen concentrations, and recycle operation with intermediate recovery of product and replenishment of oxygen. However, even by operating under these conditions the conversions to "useful" products are low, and the products consist of aldehydes, acids, carbon oxides, and water. Per-pass yields are, of course, low.

It is essential not only to limit the amount of oxygen present at any one time but also to operate at as low a temperature and as short a time of contact as possible in order to prevent thermal decomposition of the oxygenated products which are usually thermodynamically unstable at the temperature of oxidation. The use of solid catalysts alone for this purpose in the case of the lower-paraffin hydrocarbons, such as propane, butane, pentane, etc., has not been found to be successful in lowering the oxidation temperature to a point where the desired products could be obtained in good yields with high per-pass conversions. With the petroleum hydrocarbons of higher molecular weight, such as are found in kerosene, catalysts of vanadium and molybdenum oxides have been used in processes similar to that developed by James. Without a restricted oxygen supply and adequate temperature control, catalysts may easily promote the reaction to the extent that only complete oxidation products result. Catalysts alone, as far as has been shown up to the present, cannot be used for the large-scale efficient conversion of the lower-paraffin hydrocarbons by oxidation into useful products, which are capable of ready separation into pure constituents.

It has been shown, however, that by the application of elevated pressures to the oxidation of the paraffin hydrocarbons of lower molecular weight, it is possible to form alcohols of the same number of carbon atoms as the parent hydrocarbons. Concomitant yields of aldehydes may also be higher than in the case of atmospheric pressure oxidation. This is apparently true even for methane which normally requires so high a temperature for oxidation that only small yields of formaldehyde and no methanol are obtained. The results of Newitt and Haffner (*5*) have shown that the temperature required for the oxidation of methane in an 8.1 methane–1.0 oxygen mixture is markedly lowered by increasing the pressure up to 150 atmospheres, at which point a temperature of 343° C. causes rapid oxidation. Increase in pressure also increases the amounts of methanol and formaldehyde surviving, and increases the ratio of alcohol to aldehyde in the product. At 150 atmospheres this ratio may become as large as 52.7 to 1 at 343° C.

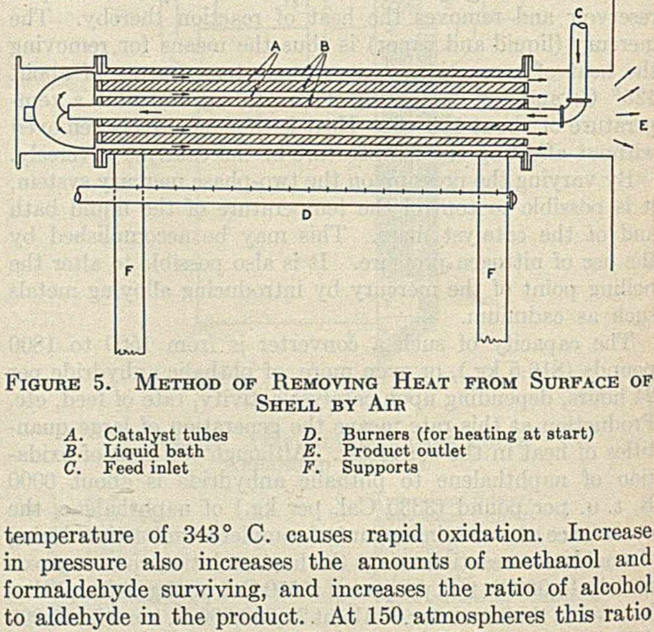

Figure 5. Method of Removing Heat from Surface of Shell by Air

A. Catalyst tubes
B. Liquid bath
C. Feed inlet
D. Burners (for heating at start)
E. Product outlet
F. Supports

The nature and diversity of catalysts that have been claimed for this pressure type of oxidation make it seem as though the principal effect of their presence was due to the surface exposed to the reaction rather than to any specific chemical effect. In the work mentioned above, it was found that the oxidation in a steel apparatus was largely heterogeneous in nature. Reaction rate was increased several times by an increase in the surface : volume ratio of the reactor.

In the pressure oxidation process, temperatures as low as 200° C. may be used with the hydrocarbons of higher molecular weight, such as hexane. In general, a range of 300° to 400° C. has been specified for the process. The pressures may range from 1500 to 3500 pounds per square inch (105 to 246 kg. per sq. cm.). Very low oxygen concentrations, limited to a maximum of about 15 mole per cent, and very short times of contact must be used (*8*).

Besides lowering the temperature necessary for oxidation, pressure is effective in stabilizing the "useful" products, decomposition of which occurs with an increase in volume. Temperature control is easier than in the case of atmospheric pressure processes, where the volumes are larger and times of contact are more readily controlled.

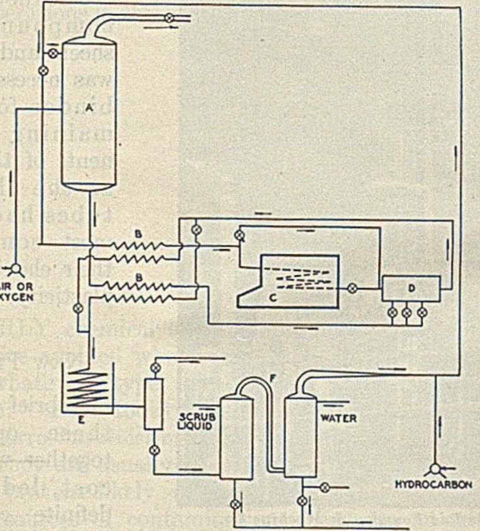

Figure 6. Hypothetical Layout for Pressure Oxidation of Aliphatic Hydrocarbons

A. Oxygen saturator
B. Heat interchangers
C. Preheat furnace
D. Reaction chamber
E. Condenser
F. Recovery system

To offset the advantages, there are several difficulties in the pressure oxidation of the aliphatic hydrocarbons, not the least of which is hazard from explosions. The danger from explosions arises whenever the ratio of oxygen to hydrocarbon is in the explosive range, a condition most likely to be met during the introduction of oxygen. To eliminate any possibility of having explosive mixtures enter the hot reaction zone, it has been proposed to saturate the liquid hydrocarbon at room temperature with oxygen at a predetermined pressure which is so chosen that the desired ratio of oxygen to hydrocarbon is obtained. Air under pressure may be used to obtain this desired ratio, and control of the air pressure automatically controls the oxygen concentration if the temperature is maintained constant (*7*).

It is essential that the hydrocarbon-air mixture be rapidly brought up to reaction temperature, held at that temperature for a short time, and then cooled. In small-scale laboratory apparatus this may be accomplished by pumping the reaction mixture (directly, by displacement, or by gas pressure) through a coil of capillary pressure tubing heated at the desired temperature by molten lead or by other means insuring a steady temperature. For large-scale operation a somewhat different technic may be adopted. If a portion of the hydrocarbon under treatment is saturated with oxygen under pressure, another portion heated rapidly in a tube furnace, and the two portions mixed under suitable conditions, it is possible to bring the whole to reaction temperature without ever directly heating the hydrocarbon-oxygen mixture. Figure 6 shows a hypothetical layout for such a plant.

The difficulties involved in the industrialization of such a process for the utilization of such hydrocarbons as ethane, propane, butane, etc., are readily apparent. Because only low oxygen concentrations may be used, the per-pass conversions of hydrocarbon to products is low, and recovery of this small amount of product from a large body of unreacted hydrocarbon is difficult. The oxygenated product does not consist of a preponderance of any one compound as in the case of the aromatic hydrocarbons, but may, on the contrary, consist of a mixture made up of several compounds which are difficult to separate. A typical product from the oxidation of propane at 136 atmospheres pressure and a temperature of 300° to 350° C. is as follows (*2*):

Oxygenated Product	Yield *% of total*	Oxygenated Product	Yield *% of total*
Acetaldehyde and acetone	6.0	Propyl alcohols (78%)	7.0
Methanol	22.0	Formic acid	1.5
Ethyl alcohol (95%)	37.0	Water	26.5

Data on yields from the oxidation of pentane at 150 atmospheres pressure, 278° C., and with 5.5 mole per cent oxygen concentration are as follows (*7*):

Oxygenated Product	Yield per Liter of Propane *Grams*	Oxygenated Product	Yield per Liter of Propane *Grams*
Acetaldehyde	3.84	Ethyl alcohol	4.52
Acetic acid	3.47	Propyl alcohols	4.00
Acetone	1.12	Butyl alcohols	1.20

It is obvious that the yields have been conventionalized from distillation data. It may be seen that the complexity of the product increases as the size of the hydrocarbon molecule becomes larger. Furthermore, most of the products that may be formed in this way must compete with products manufactured in other ways and are often available in a purer form. Synthetic methanol and higher alcohols made from water gas, and alcohols formed by the hydration of olefins, acetaldehyde, and acetic acid from acetylene—all can compete with products from oxidation reactions.

But the immense quantities of these lower hydrocarbons that are available in relatively pure form, the ready supply of oxygen, the exothermic nature of the reaction, and the economic necessity for finding new outlets for refinery waste products have stimulated research in this field, which may become of considerable importance in the future.

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Manufacture of Hard Rubber Dust

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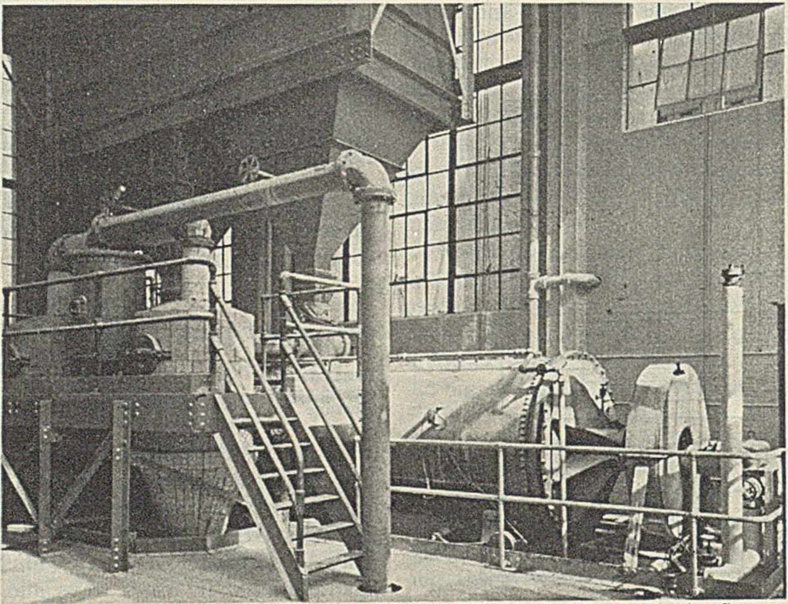

Courtesy of Buffalo Foundry & Machine Co.

Machine Used in Experiments

A process is described for mixing rubber with sulfur and accomplishing vulcanization at the same time. The resulting product is in granulated form ready for fine grinding. Standard equipment, designed for other purposes, is used in carrying out the process.

A FACTORY producing a variety of hard rubber articles frequently finds it desirable, in compounding a stock for the hard rubber, to have an appreciable amount of hard rubber dust in the compound. This method of operation has several advantages: It offers an outlet for the hard rubber scrap, coming from the factory's manufacturing operations, by converting the hard rubber scrap to dust; it assists in securing complete and rapid vulcanization of the hard rubber article and produces a rubber stock which is easier to form.

Old Process of Manufacture

A factory, operating in conformity with the description just given, was utilizing old inner tubes as a cheap source and as the chief source of rubber entering into the production of hard rubber dust. The process employed in making the dust at the inception of the investigation herewith described involved the following operations:

1. Disintegration of the old inner tubes by milling on rubber rolls.
2. Breaking down washed Para sheets.
3. Mixing Para sheets with reclaim.
4. Compounding mixed rubber with sulfur.
5. Stock sheeted out 1 inch thick.
6. Vulcanizing in trays in a pressure vulcanizer for 14 hours.
7. Vulcanized slabs broken up with a hammer by hand.
8. Pieces broken down on rolls to pass a No. 12 screen.
9. Screenings ground in a Raymond impact mill to approximately 100 mesh, classification by air separation accompanying the grinding operation.

The ground classified product was then ready for use after nine operations from raw materials to finished product.

The stock used in making dust was:

	Pounds
Ground tubes	660
Sulfur	420
B soap oil	120
Para sheets	120
Reclaim rubber	180
Total	1500

The system of vulcanizing used at that time necessitated the milling of this stock in the same manner as would be required for the milling of a rubber stock intended for the production of a finished molded article.

The rubber in the compound (Para sheets and reclaim) was necessary as a binder for the remaining components of the stock, as the old inner tubes had lost almost completely their elasticity and plasticity.

New Process

A brief study of these operations, together with their cost, led to the definite conclusion that a better process for making rubber dust had to be evolved; otherwise the factory could not afford to make and use the material. A series of laboratory experiments, using only rubber and sulfur in the mixture, gave indications that, under proper conditions of operation, a satisfactory vulcanization could be secured. These experiments demonstrated that one of the essentials for a satisfactory process would be the mixing of the sulfur with the rubber when both had been raised to a temperature at which they would be plastic.

A further study of the operation indicated the selection of a mixer and vulcanizer in which the material could be heated with fairly close temperature control, and where the material would be continuously stirred while being heated; it was also found that operating under a vacuum was desirable. An investigation of the equipment on hand in the factory, which might be found to function satisfactorily, disclosed a vacuum rotary drier (made by the Buffalo Foundry and Machinery Company) which was not then in use. This equipment seemed to possess the characteristics desired, and it was decided to attempt to use it as the mixer and vulcanizer.

The machine was size R3, 3 feet in diameter by 10 feet long; it could be operated satisfactorily with a charge of 2000 pounds of disintegrated tubes together with the required amount of sulfur.

Maintaining a temperature of 340° F., satisfactory vulcanization could be secured from 4.5 to 6 hours. The vulcanizer was kept under a vacuum of approximately 22 inches for the major portion of the time. It was noted, however, that after vulcanizing about 3 to 3.5 hours, there was a marked rise in temperature of the material being vulcanized and, accompanying this, a copious evolution of hydrogen sulfide. The rise in temperature, along with the gas evolved, completely destroyed the vacuum at times.

The stream to the vulcanizer was shut off at the conclusion of the vulcanizing period, but the stirring was continued during the cooling of the material in the vulcanizer.

The material, when cool, was finely granulated and in such condition as to pass directly to the Raymond impact pulverizer for the final grinding.

The materials charged into the drier for vulcanizing consisted of 2000 pounds of ground tubes and 1200 pounds of sulfur. No other materials were added, nor were others necessary.

The operations in this system of procedure were:

1. Disintegration of the tubes.
2. Vulcanization.
3. Fine grinding, accompanied by air separation.

Three operations were used in place of nine as in the original process. The total time necessary for the new process was 8 hours, as compared with 2 days and 1 night on the process it replaced.

The savings represented by the change in process amounted to 50 per cent of the cost of the rubber dust.

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[End of Symposium]

Pumps

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Early chemical and metallurgical engineering practice avoided wherever possible the use of pumps of whatever "type, sex, color, or previous condition of servitude." Even today, in spite of the wonderful development in corrosion-resisting materials, pumps are to be avoided because they are usually secondary to the chemical process; even the best are likely sources of trouble and expense; they may be sources of contamination; they are an additional cost for power in the flow sheet; and they are sometimes not so corrosion-resisting as the manufacturer would lead us to believe.

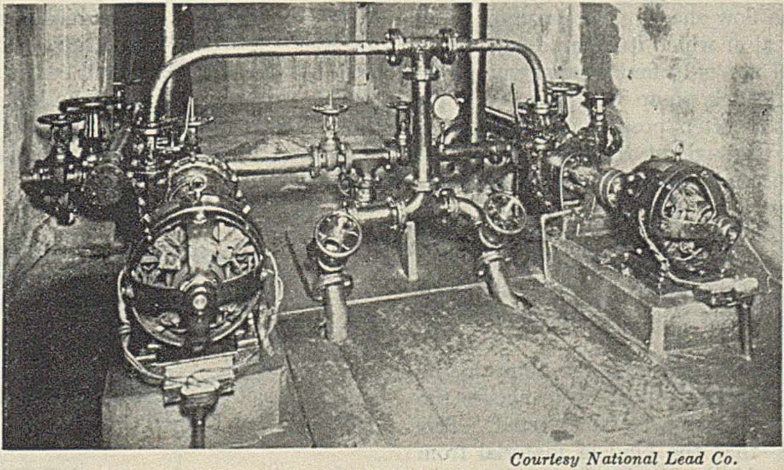
Corrosion-Resisting Materials

There is no all-purpose corrosion-resisting material. Acid-proof stoneware, porcelain, and glass come perhaps nearer than any, but stoneware is heavy and easily broken because of its high coefficient of expansion, and glass has not so far come into commercial use. Porcelain, stoneware, and glass-lined pumps are on the market, but their high cost has limited them to very special uses.

Next on the list as a fairly universal corrosion-resistant material is Duriron, a high-silicon iron. It is, however, very hard and brittle, has high thermal expansion, and can be ground but not machined.

Lead is much used because of its resistance to sulfuric acid solutions. Its principal disadvantages are its softness and low elastic limit. Very excellent lead-lined equipment is now on the market, but can be recommended only for certain types of pumps, and its uses are limited by the solubility of lead in many reagents.

Equipment may also be lined with rubber. A new vulcanizing process bonds this material very satisfactorily to steel. Its use, with the exception of hard rubber, has been limited almost wholly to centrifugal pumps.


Courtesy National Lead Co.

Centrifugal Acid Pump of "United" Hard Lead, Direct Drive, Wrought Steel Pipe, Fittings, and Valves Lead-Lined

Copper and copper-base alloys are used extensively, chiefly because of their cheapness and excellent machinability. The iron-base materials, such as alloys of chromium and nickel, are also coming to the fore. Many of these are readily machinable, are very hard, and have high tensile strength. Their largest use, however, is in thermal equipment because of their resistance to corrosion at high temperature.

Monel metal, a nickel-base alloy containing about 60 per cent nickel and 30 per cent copper, finds considerable use because of its strength, its workability, and its resistance to many solutions. Tin, aluminum, aluminum-base alloys, magnesium alloys, hard rubber, Bakelite, and vulcanite may be mentioned, but this by no means completes the list.

Uses of Pumps

The several uses of pumps and kindred devices may be classified as follows:

1. The simple transfer of gases, liquids, colloid solutions, or solids suspended in either liquids or gases, from one point to another, usually with comparatively small changes in pressure. This is by far the largest use.
2. Where such transfer is incident to or combined with a marked change in pressure or "head," the latter being the main object.
3. For the purpose of producing high-pressure or high-vacuum phenomena in conjunction with heat or cold, the object being to aid physical or chemical change.

In discussing the first grouping—the simple transfer of gases, liquids, etc., with nominal changes in pressure—the use of a pump in these cases has the same justification as the use of elevators and belts in the transfer of solids—that is, the additional expense of so arranging the flow sheet in order to take advantage of the force

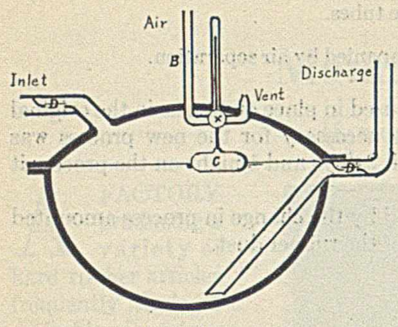


Figure 1. Acid Egg or Blow Case

of gravity is greater than that of the cost of the pump plus its operating expense over a period of from ten to twenty years.

The side-hill concentrating and flotation mills of the West are good examples of such gravity flow to avoid the use of pumps. In case of gases, the directional flow is of course reversed. We still build high chimneys for steam plants and smelters instead of using suction fans and blowers. There is an additional reason for doing so in that we wish to discharge the obnoxious gases as high into the air as possible.

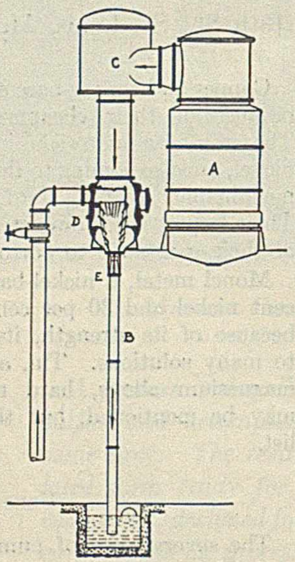


Figure 2. Barometric Leg Using Water-Jet Ejector

It goes without saying, also, that in such simple transfers, the less change in pressure or head, the more efficient the operation, just as in the transfer of solids the level or slightly inclined conveyor belt is more efficient than the vertical elevator.

In the chemical plant the position of the pump in the flow sheet is usually very important. In a simple leaching process, the logical place for the pump is at the head of the operation where it feeds only clear water, the rest of the system being under pressure. In other operations it may be best to place it at the end. In the manufacture of sulfuric acid, the blower or fan is logically placed in the middle of the operation just before the converters and after the sulfur dioxide has been purified, for obvious reasons. In the coke plant the compressors are placed after the ammonia extractors so that the system up to that point is under slight suction, and after that point, under pressure.

The first important point to be decided is the position of the pump or pumps in the flow sheet. This position often dictates the kind of material of which it is to be fabricated. The chemical engineer will not only find a great variety of pumps on the market, but each pump will be suitable for a variety of purposes. It is often possible to standardize on a single type and size throughout the plant. The experienced operator will appreciate what this means in everyday plant operation.

As a rule the pumping cost is a minor item in the chemical process. The chemical engineer is not so much interested, therefore, in rated efficiency as in materials of construction and the trouble the pump is likely to give owing to corrosion or other failure.

After determining the proper location of the pump in the flow sheet, the second consideration must be to choose the material from which the pump must be constructed. This leads to the second point—that the kind of material from which the pump must be made often limits the type of pump which can be used.

Types of Equipment

With such background, we may now examine the different types of pumping equipment and determine in a general way their adaptability to special chemical processes.

If we broaden the definition to include all devices designed to lift fluids against the force of gravity, pumping devices may be classified as follows:

1. Those devices having no moving parts, usually not classed as pumps
   - Siphons
   - Acid eggs, monte-jus, blow cases
   - Barometric legs
   - Air lifts
   - Ejectors, injectors, aspirators
2. Reciprocating devices, with valve action and positive displacement
   - Piston pumps
   - Plunger pumps
   - Diaphragm pumps
3. Centrifugal devices, one moving part, no valves, relative displacement
   - Volute centrifugal pumps
   - Turbine centrifugal pumps
   - Blowers
   - Fans
4. Rotary devices, usually but two moving parts, no valves, more or less positive displacement
   - Rotary pumps, cycloidal blowers
   - Screw pumps
   - Special design

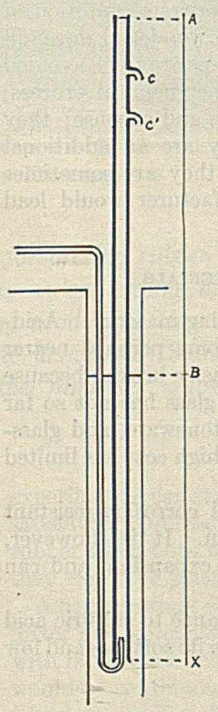


Figure 3. Air Lift

Siphon. The siphon has application wherever the level of the receiving vessel is lower than that of the discharging—that is, wherever the sum total of the lift is less than the drop, provided always that the lift does not exceed 34 feet for water and corresponding heights for other liquids. For mercury the theoretical lift cannot exceed 29 inches, in practice somewhat less.

The siphon is the usual method of emptying the cast-iron melting pot in a lead refinery. The main reason for using a siphon instead of a valve cast into the bottom is because of the high thermal expansion of cast iron. Shaped like a huge evaporating dish, it expands uniformly, whereas a heavier portion for the valve would cause strains, uneven expansion, and perhaps cracking at the first firing. A siphon must be filled with the liquid before it begins to operate. To fill it in this case, the workman immerses the whole pipe into the molten lead, then closes a valve at one end and carefully withdraws it, always keeping the open end below the level of the liquid.

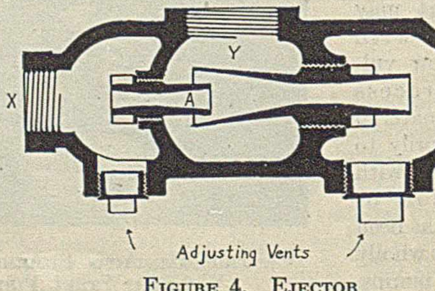


Figure 4. Ejector

If the siphon is stationary, it can be "primed" by pressure applied on the discharging vessel, or suction upon the receiving vessel.

Acid Egg. If we close the lead vat as in Figure 1 and apply pressure at *B*, we have an acid egg, monte-jus, or blow case. Inserting float *C* and inlet and check valves *D* and *D′* makes the acid egg automatic. The flow is intermittent and irregular. The height that the liquid can be lifted depends on the air pressure. The advantages are that it can be constructed of almost any noncorroding material, it is inexpensive, and causes little trouble. Its efficiency is low and capacity small.

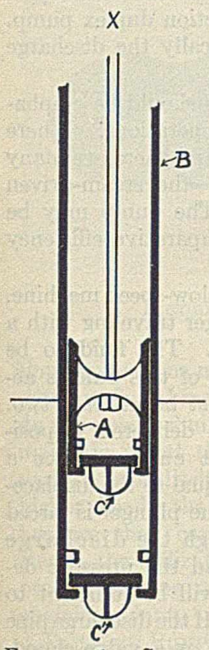


Figure 5. Simple Well Pump Showing Essentials of Reciprocating Pumps

Barometric Leg. A modification of the siphon principle is the barometric leg illustrated in Figure 2. In this, evaporator *A* is kept under partial vacuum by the liquid column in the barometric leg, *B*, which theoretically must be slightly longer than 34 feet for water. The vapor continually condenses at *C*. In practice, as nitrogen and oxygen are soluble in practically all solutions, air tends to trap at the highest part of the leg and the efficiency drops unless this is removed by a suction pump or aspirator connected at *D*. If the condensate is valuable, it should have a by-pass to *B*, or it may be made to operate intermittently by a float or mercoid switch at *E*.

Air Lift. The air lift shown in Figure 3 is a somewhat more efficient method of utilizing compressed air in lifting liquids. It necessitates a considerable submergence of the leg in the liquid to be elevated. It is evident that the total lift (lift plus submergence) cannot in theory be more than the equivalent of air and water mixture equal in weight to the water column of the leg—that is, the weight of the water-air mixture *AX* is equivalent to a similar column of water alone of the height *BX*. In practice 80 per cent of this figure is hardly reached.

The ratio lift : (lift plus submergence) decreases with increased lift (*AB*). For a lift of 20 feet (*AB*), this ratio equals 0.64 to 0.66—that is, *BX*, the leg, equals 10 to 11 feet. For 500 feet this ratio decreases to about 0.40, or *BX*, the submergence, must be more than 700 feet. The air lift is simple in mechanical construction, but no definite mathematical formula has been advanced for its action. It may, without confusion, be considered a sort of inverted siphon where the weight of column of water *BX* serves to balance the weight of water-air mixture *AX*. Any aperture lower than *A* at *C* or *C′* would therefore cause a continuous flow of water. Modifications of the air lift have a number of important industrial applications, such as lifting salt brines in the salt mines of Kansas, and sulfur in the sulfur mines of Louisiana and Texas.

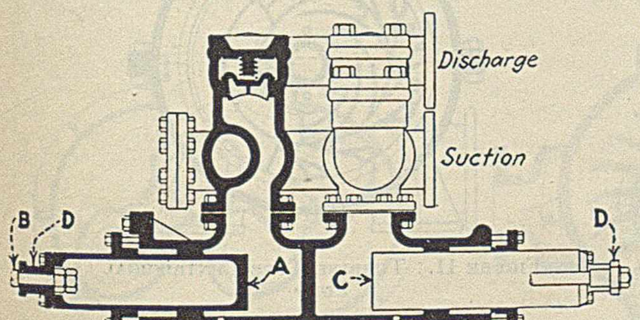
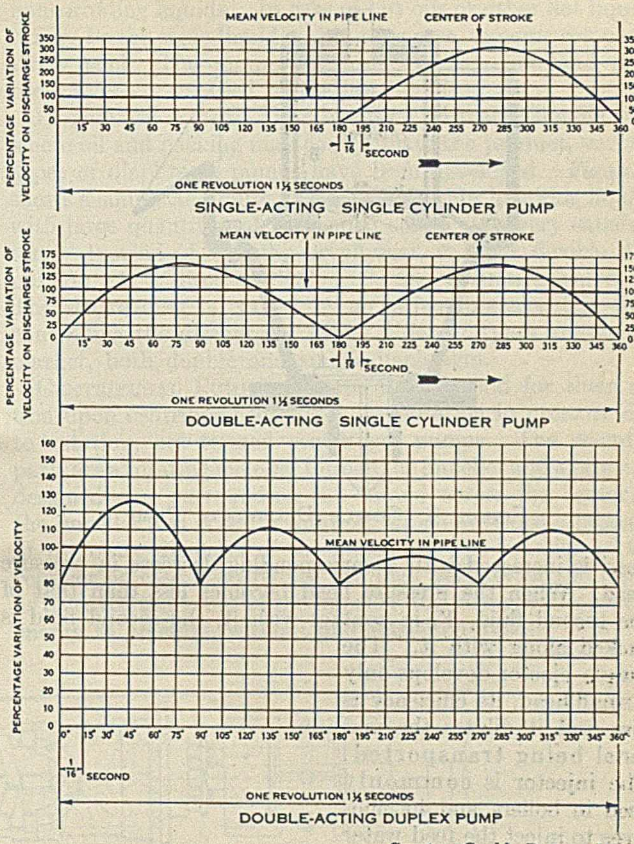


Figure 7. End-Packed Single-Action Duplex Plunger Pump



Courtesy Goulds Pumps, Inc.

Figure 6. Graphic Characteristics of Reciprocating Pumps

Ejectors, Injectors, and Aspirators. Another method of moving a fluid without using moving parts is by use of the ejector, a type of which is shown in Figure 4. Fluid *X* under pressure expands through nozzle *A*. Its velocity

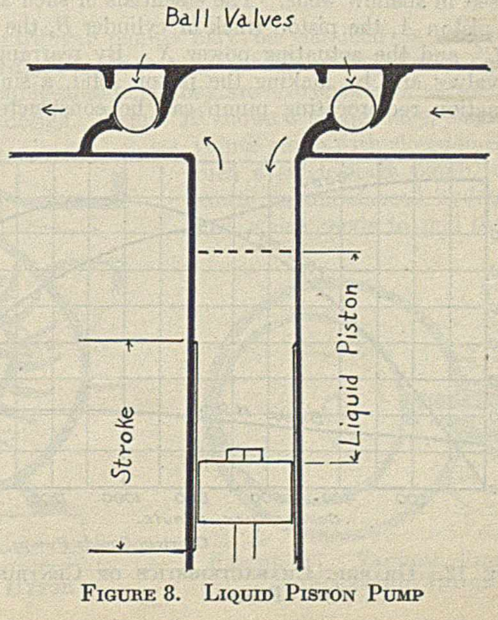


Figure 8. Liquid Piston Pump

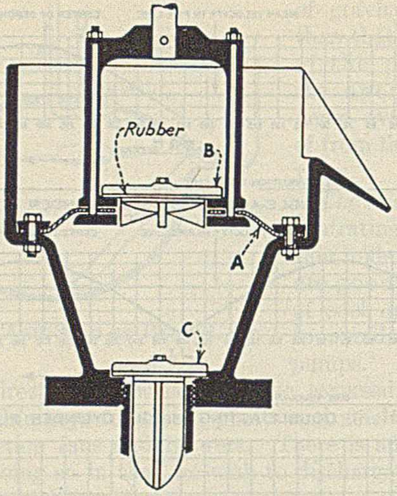


FIGURE 9. SIMPLE DIAPHRAGM PUMP

head is increased with a corresponding decrease in pressure head. When the pressure head becomes less than that of the second fluid, *Y*, in contact with it, the second fluid is sucked along with it. The simple ejector develops only a small head, its efficiency is low, and it dilutes the material being transported. The injector is commonly used in boilers and locomotives to inject the feed water by means of a steam jet. These have been developed to such a degree that they will inject quite warm water into the boiler against the full steam pressure. Operated by steam or compressed air, they serve to transfer liquids from tank to tank. They are the basis for spray nozzles, oil burners, etc. In modified form (aspirators) they make very efficient vacuum pumps.

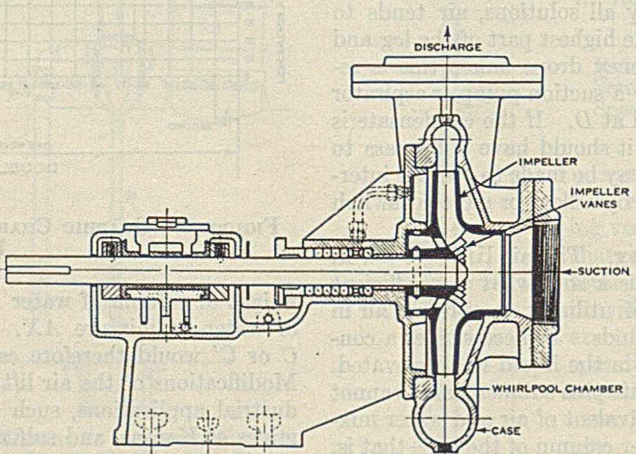
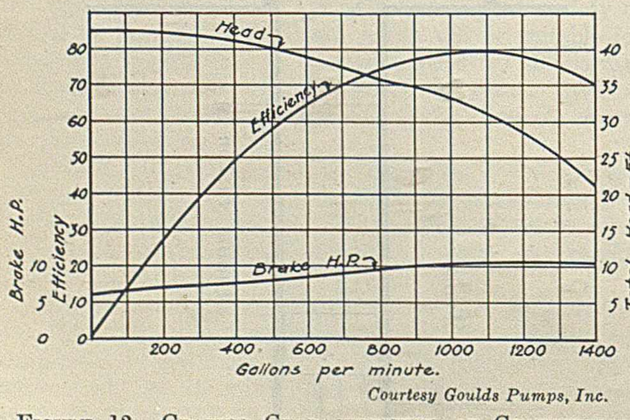


FIGURE 10. SINGLE-STAGE SINGLE-SUCTION VOLUTE PUMP WITH CLOSED IMPELLER

RECIPROCATING PUMPS. One of the earlier types of positive-action pumps, illustrated in Figure 5, is even today being used in shallow wells. The essentials of such a pump are the piston *A*, the piston track or cylinder *B*, the valves *C* and *C'*, and the actuating power *X*. By rearrangement of the valves and by making the piston solid, a single- or double-action reciprocating pump can be constructed.



Courtesy Goulds Pumps, Inc.

FIGURE 12. GRAPHIC CHARACTERISTICS OF CENTRIFUGAL PUMPS

It is well to remember that for every cycle of piston *A* the same liquid flows from suction one half the time and is discharged the other half. The flow is therefore intermittent. In order partly to smooth out this discharge, a double-action pump is used. Even then there is a variation in discharge, because at the end of every stroke neither cylinder is discharging and there is no flow. The next step is to use two such double-action cylinders arranged with the crank pins 90 degrees apart. This gives a double-action duplex pump. The diagrams, Figure 6, compare graphically the discharge of these several types.

The importance of reciprocating pumps should be emphasized. They are still standard in many operations. Where steam is to be used for process heating—and there are many such possibilities in the chemical plant—the steam-driven reciprocating pump fits in admirably. The pump may be regarded as a reducing valve and its comparative efficiency to other types of pumps be disregarded.

The reciprocating pump is essentially a slow-speed machine. Its main moving part is a piston or plunger traveling with a to-and-fro motion past a tight packing. The fluid to be pumped follows. The undirectional flow of this fluid is accomplished by valves of which there must be at least two. The head delivered is positive. At each stroke a volume equal to the displacement of the plunger is forced out through the discharge valves, and the pressure developed will be sufficient to do this. If the discharge pipe is choked or a valve closed, the pressure will continue to increase until the pipe bursts or some other part gives way. It is therefore necessary to have a relief or by-pass valve in the line, which opens at any undue pressure and allows the liquid to flow back to suction. The quantity delivered depends upon the speed. Every stroke means a definite amount of liquid. The only way to change the discharge is to change the speed. The flow is also intermittent. It is this unsteady flow which leads to pressure surges and often to tremendous thumps in the discharge line and sometimes in the suction line also. For this reason, reciprocating pumps are supplied with an air chamber on the discharge side and sometimes on the suction side, to even the pressure by means of an air cushion.

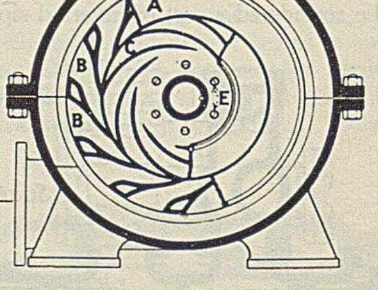


FIGURE 11. TURBINE TYPE CENTRIFUGAL PUMP

The advantages of reciprocating pumps are that the suc-

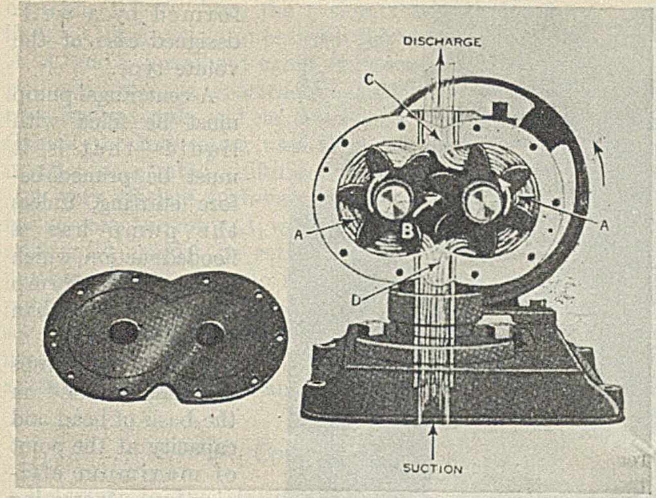


Figure 13. Rotary Pump in Action

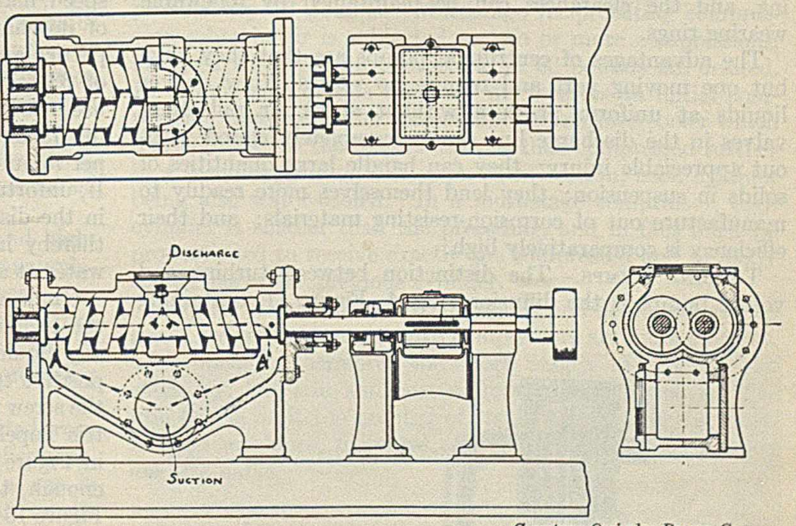
tion connections may be under less than atmospheric pressure without "air binding," and unlike centrifugal pumps they do not need priming; they are more flexible in operation and maintain about the same efficiency over wide variations of discharge; they are designed for higher heads than centrifugal pumps; and because they can be connected with direct steam, the utilization of the exhaust steam for process heating may be of advantage in the chemical plant.

Plunger Pumps. In the pumps so far described, the piston carries the packing with it. When these pumps are made larger or when they must handle much suspended matter, frequent replacement of packing becomes necessary. In the plunger type of pump, the plunger moves past stationary packing. An illustration is the end-packed single-action duplex pump in Figure 7.

An important modification of the plunger type of pump is the "liquid piston" pump illustrated diagrammatically in Figure 8, the essential feature of which is the volume entrapped between valves, which must be at least twice the volume of the stroke of the piston. It can readily be seen that with every cycle of the piston, the amount of liquid over and above the suction and discharge volume remains with and moves with the piston, acting as a buffer. The pumps are usually placed vertically to avoid diffusion and flow losses. The liquid pistons may be mercury or other noncorroding liquids. In case of hot oils or other hot liquid, it may be the same liquid which, of course, remains comparatively cool. The pump therefore remains cool, and only the valves are exposed to the hot liquids.

Diaphragm Pumps. For handling corrosive liquids and where oil and packing may contaminate the product, various types of diaphragm pumps have been developed. Figure 9 shows a simple and quite efficient type. For handling liquids with large quantities of suspended solids, it is very satisfactory. Instead of a piston or plunger, it has a flexible diaphragm, *A*, a discharge valve, *B*, and a suction valve, *C*. The stroke may be varied by an adjustable eccentric, thus controlling the discharge. Many different types are on the market, both double and single diaphragm.

Centrifugal Pumps. Pumps that depend for their action upon centrifugal force, or the variation in pressure due to rotation, are termed centrifugal pumps. The essential parts are a rotating member termed the impeller and a properly designed case surrounding it. Liquid enters the center of the impeller and is set in rotation, which develops a pressure at the outer diameter of the impeller. The function of the receiver or case is to reduce the high velocity of the liquid as it leaves the vanes of the impeller and changes this kinetic energy to pressure, without undue friction losses.



Courtesy Quimby Pump Co.

Figure 14. Screw Pump

Centrifugal pumps may be classified as single-stage or multistage, open-impeller or closed-impeller, single-suction or double-suction. They are also spoken of as volute or turbine design. Figure 10 shows a single-stage, single-suction, volute pump with closed impeller. In such a single-stage pump, the liquid exerts an unbalanced hydraulic pressure which tends to pull the impeller

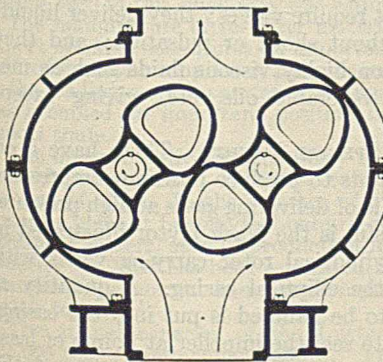


Figure 15. Roots Type Cycloidal Blower

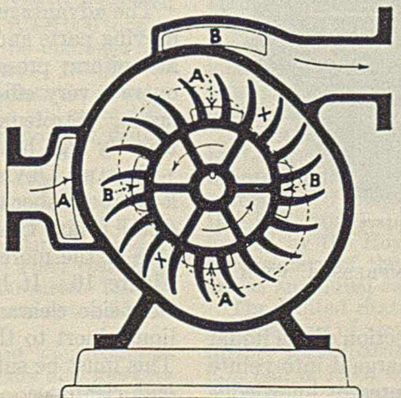


Figure 16. Nash Hytor

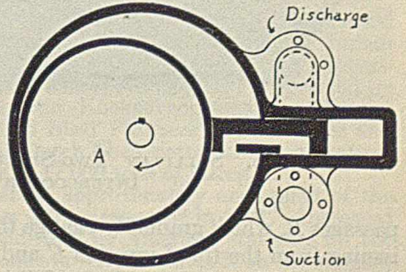
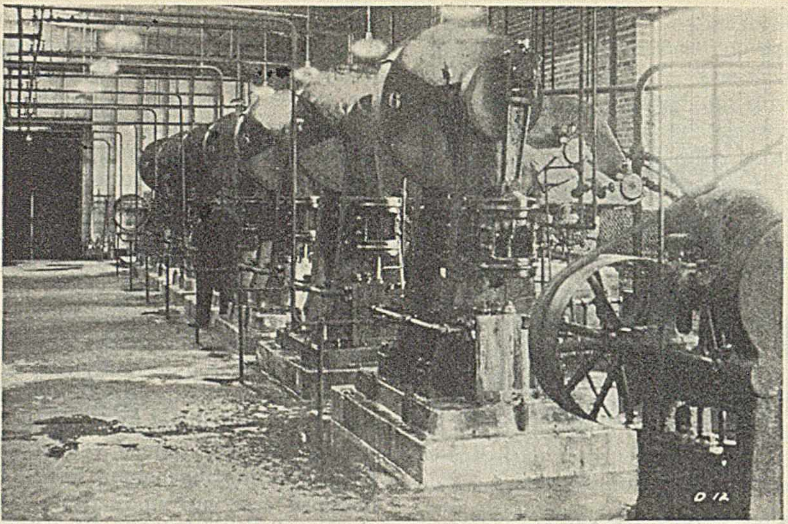


Figure 17. Vacuum Pump with Eccentric Rotor



Courtesy Dow Chemical Co.

Hydraulic Pumps for Pumping Raw Material through High-Pressure Autoclaves in Phenol Production

away from the shaft. The two-stage double-suction pump has therefore come greatly into favor.

The open impeller consists essentially of a series of curved vanes extending from a central hub. As these vanes are not in actual contact with the casing, there is always a certain amount of back leakage which increases with the wearing of the pump. To remedy this, the closed impeller has been developed. The vanes of the impeller are enclosed between two sheets or rings of metal. A closer fit can be maintained between the outer circumference of these rings and the casing, and the clearances can be maintained by renewable wearing rings.

The advantages of centrifugal pumps are that they have but one moving part and require no valves; they deliver liquids at uniform pressure without shock or pulsation; valves in the discharge line can be completely closed without appreciable injury; they can handle large quantities of solids in suspension; they lend themselves more readily to manufacture out of corrosion-resisting materials; and their efficiency is comparatively high.

Turbine Pumps. The distinction between turbine and volute pumps is the diffusion ring *A*, Figure 11, containing passages *B*, which gradually change the direction of the liquid issuing from the tip of impeller *C* and discharge it into volute *E* with minimum friction loss. With our present knowledge of hydrodynamics, this function can be more cheaply performed by a well-designed case of the volute type.

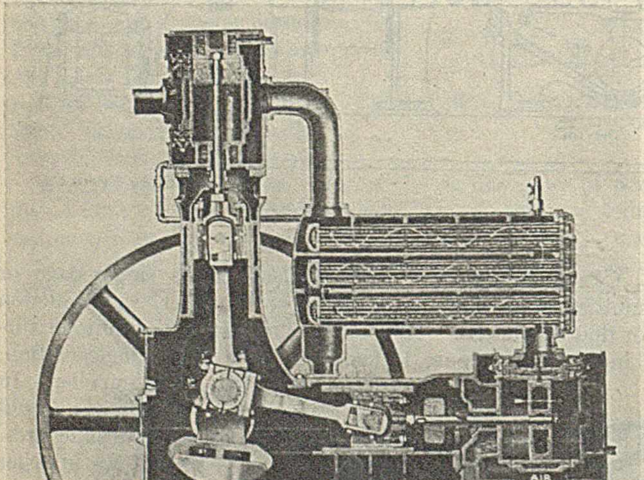


Figure 18. Sullivan Two-Stage Compressor with Intercooler

A centrifugal pump must be filled with liquid—that is, it must be primed before starting, unless the pump has a flooded suction, which means if the pump elevation is lower than the liquid supply.

Centrifugal pumps are usually rated on the basis of head and capacity at the point of maximum efficiency. Increasing the speed usually increases the head for any given rate of discharge. As the principal operating characteristic of a centrifugal pump is this relation between head and discharge at constant speed, manufacturers usually supply with each pump a graph of its characteristics curves similar to Figure 12. For this particular pump the rating would be 1100 gallons at a head of 32 feet (point of maximum efficiency), the horsepower used about 11. But the chart gives much more interesting facts. If the head is reduced to 21 feet, 1400 gallons per minute can be delivered at about the same horsepower. If, unfortunately, the pipe fitter should put a few extra kinks in the discharge line for the sake of beauty and symmetry, thereby increasing the head to 45 feet, there would be no water at all at that speed.

Gear and Screw Pumps. Of interest to engineers with the problem of moving heavy viscous solutions, or in fact any liquid without appreciable solids in suspension, is the positive type of rotary pump exemplified by the gear pump, the screw pump, and various special designs such as the eccentric impeller, oval case, etc. The gear pump is illustrated in Figure 13 and the screw pump in Figure 14. Curiously enough, the cycloidal blower of the Roots type illustrated in Figure 15 was among the first of the rotary type of blowers developed, and found application in supplying air in large quantities at comparatively low pressures for blast furnaces, etc.

In Figure 13, the gears, *B*, entrap slugs of liquid at *D* and carry them around to *C*, where they are forced out and upward because of the meshing of the gears. A modification of this is the screw pump shown in Figure 14. The liquid entrapped at the ends, *A*, is carried by the screw action to the center, the meshed screws producing a positive head at *B*.

The advantages of such pumps are that they have but two moving parts and do not require valves; they deliver liquids at uniform pressure without shock or pulsation; and they operate very efficiently on highly viscous fluids such as molasses, petroleum oils, vegetable oils, etc., giving exceptionally high heads.

Rotary Devices of Special Design. There have been a great number of attempts to produce positive compressors of the rotary type capable of delivering gases at high pressure. One of the more successful is the Nash Hytor illustrated in Figure 16. It has a cylindrical rotor carrying vanes with close side clearance to the elliptical casing. A quantity of liquid inert to the gas to be handled is put into the casing. This must be sufficient to seal the impeller at points of least end clearance, *X*, *X*, when rotated. The rotation of the impeller causes the liquid to rotate with it. This, due to centrifugal force, hugs the casing, as shown by the dotted lines. Gas is sucked in between the vanes at the inlet ports, *A*, *A*, and is forced out again at the outlet ports, *B*, *B*. The pump is simple in construction, may be made of corrosion-resisting materials, and can develop pressures up to 20 pounds. One of the interesting uses is in compressing chlorine gas using concentrated sulfuric acid as the liquid.

A very efficient high-vacuum pump, shown in Figure 17, has an eccentric rotor, *A*, with a sliding partition valve pressed constantly against its rotating circumference. The sliding partition valve serves to separate the inlet from the outlet port at all positions of the rotor, the rotation of the latter serving alternately to suck gas from the inlet port and force it out of the outlet port. The pump is built with close clearances and operates with an oil seal.

CONCLUSIONS

Referring to the classification at the beginning of this article, we find that the chemical engineer is little concerned with classification 2, where the transfer of fluids under high pressure or head is the main object. Such objectives fall more in the realm of the mechanical engineer and find large application in water works and the transfer of oil and gas over pipe lines. But in classification 3, where high-pressure or high-vacuum phenomena in conjunction with heat or cold are used to aid physical or chemical change, we find a major present-day interest and one where the pump or compressor is an important item in the flow sheet. We need mention only a few of the newer chemical engineering processes, such as synthetic ammonia, solid carbon dioxide, liquid chlorine, liquid sulfur dioxide, recovery of helium, synthetic methanol, etc. So marked has been this change that we have coined the phrase, the high-pressure industries.

We note the following: that the high-pressure and high-vacuum industries are chiefly concerned with the manipulation of gases; that for low pressures, fans, blowers, and rotary type compressors can be employed; that for partial vacuum effects, condensers, barometric legs, and aspirators can be used; but for high-pressure effects, the reciprocating compressor is still standard.

The compressor shown in Figure 18, as differentiated from the reciprocating pump, shows only minor modifications. Valves are lighter and clearances smaller. When a gas is compressed, its volume decreases. Work is done on it. This together with the friction losses appear as heat. In blowers, fans, etc., where the pressure is low, this rise in temperature can be neglected. It must be taken care of in the high-compression engine, not only because of the effect of heat on the cylinders and packing, but for efficiency of operation. Table I gives the theoretical final temperatures at various pressures when compression is completed, the air being taken into the cylinder at 60° F.

TABLE I. CYLINDER TEMPERATURES AT END OF PISTON STROKE

AIR COMPRESSION	FINAL TEMPERATURE Single stage	FINAL TEMPERATURE Two stage
Lb. gage	*° F.*	*° F.*
10	145	
20	207	
30	255	
40	302	
50	339	188
60	375	203
70	405	214
80	432	224
90	459	234
100	485	243
110	507	250
120	529	257
130	550	265
140	570	272
150	589	279
200	672	309
250	749	331

Single-stage compressors are built both single and double action. They are used for the compression of air up to approximately 80 pounds. Multistage reciprocating compressors, wherein air is subjected to two or more compressions, are used when pressures in excess of 80 pounds are desired. In compressors of this type, the air receives an initial compression in one cylinder, passes through an intercooler which serves to reduce the temperature, is then compressed further in a second cylinder, and so on in succession, each cylinder being also water-cooled. In a multistage compressor, each cylinder is smaller than the preceding, and in fact must be proportioned to receive exactly the compressed and properly cooled gas of the previous cylinder.

Because of the more effective cooling and because clearance losses are reduced, multistage compressors are more efficient. Theoretically, therefore, the more stages the higher the efficiency, but size and cost of machinery, as well as friction losses, limit the number of stages to seven at the most. In such machines, pressures of from 1000 to 15,000 pounds are attainable.

RECEIVED April 21, 1932.

The Netherland Fertilizer Industry

In normal years the Netherlands uses more artificial plant food per acre of crop and improved pasture and hay land than any other country. Nearly 40 per cent of its area of 12,640 square miles consists of pasture and 26.5 per cent of arable land. The total quantity of chemical basic fertilizer materials consumed during 1930 in this small area was estimated at 1,300,000 tons.

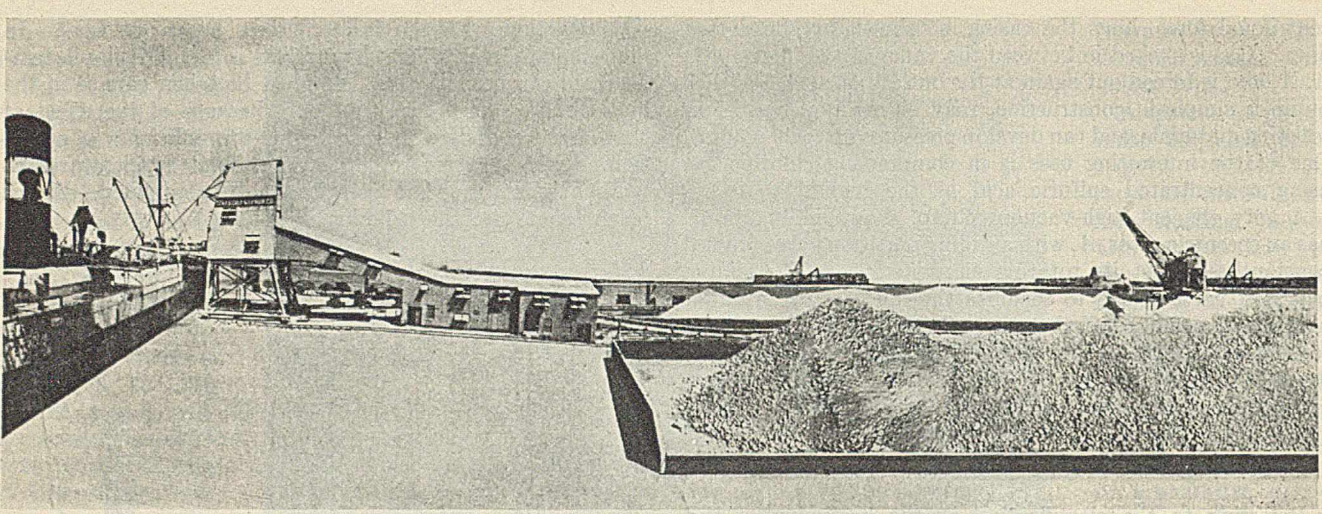
The manufacture of fertilizer materials for the domestic and export markets constitutes an important industry. Despite the lack of domestic supplies of phosphates and sulfur, the country is the leading world exporter of superphosphate and since 1930 has occupied an important position in the ammonium sulfate export trade.

The first synthetic nitrogen plant in the Netherlands, located near blast furnaces at Ijmuiden, commenced operations in the autumn of 1929. In the summer of 1930 the state coal mines opened a plant at Lutterade, Limburg, while the plant at Sluiskil, Zeeland Flanders, started production in 1931. Their combined capacity for 1932 has been estimated at 122,000 metric tons of nitrogen; the normal home consumption approximates 65,000 metric tons.

The annual capacity of the Lutterade plant approximates 225,000 tons of ammonium sulfate. The company also markets aqua ammonia for industrial purposes and in March, 1932, completed a new plant with an annual production capacity of 47,000 tons of ammonium nitrate, 12,000 tons of ammonium sulfate–nitrate, and a by-product yield of 2000 tons of sodium nitrate. The total output of about 55,000 metric tons of synthetic nitrogen does not include approximately 15,000 tons of ammonium sulfate obtained annually as a by-product in the coke works of the state coal mines. The plant has storage capacity for 40,000 tons of ammonium sulfate and facilities for loading either bulk or bagged products at the rate of 100 tons hourly. It produces about one-third of its sulfuric acid requirements from Spanish pyrites.

The annual capacity of the Sluiskil nitrogen plant, operated by Compagnie Néerlandaise de l'Azote, formed by the Italian Montecatini, the Belgian Coppée company, and others, approximates 50,000 tons nitrogen. The Ijmuiden plant is operated by the Mij. tot Exploitatie van Kooksovengassen, a company formed by the Royal Dutch Blast Furnaces and Factories and a subsidiary of the Royal Dutch Shell petroleum organization. It has an annual capacity of 17,000 tons of nitrogen.

The United States received approximately one-fourth of the 254,685 tons of ammonium sulfate exported in 1931. Increased further participation is evidenced by American statistics for the first half of 1932, which indicate the Netherlands as the supplier of 107,670 long tons of the all-time record receipts of 165,441 long tons.



Courtesy of Texas Gulf Sulphur Co.

SULFUR CARGO-LOADING PLANT, GALVESTON, TEXAS

Economic Position of Sulfur

A. M. TAYLOR, 50 East 41st Street, New York, N. Y.

FROM time immemorial sulfur has been the backlog of the chemical industry and, to use a trite expression, its rate of consumption has been considered the barometer of general trade activity. There is hardly an industry into which it or one of its products does not enter. No other element plays such an active part in our chemical processes. Yet we ask the question: "What of the future of sulfur?"

Clarke (*7*) has estimated the world's reserves at from 56,000,000 to 121,000,000 metric tons, so that there is little immediate danger of any scarcity. The largest reserves are in Italy and the United States, conservatively estimated at 25,000,000 and 40,000,000 tons, respectively. Chile is reported to have 5,500,000 tons averaging 70 to 90 per cent; Spain 500,000 to 1,750,000 tons averaging 15 to 30 per cent, and Japan several million tons of 50 per cent ore. The producing deposits of Italy and Texas have the advantage of the lowest cost of production. If Clarke is correct in his estimate of 40,000,000 metric tons being the available resources of the United States, then the supply will be exhausted in fifteen years if our consumption and exportation continue at the present rate of 2,525,000 tons yearly. Even if our reserves were sufficient for fifty years, conservation of sulfur should receive our serious consideration if we are to continue to use it as a raw material in our basic industries.

SOURCES OF SULFUR (*5*)

	1930 *Long tons*	1929 *Long tons*
World production	2,900,000	2,800,000
United States	2,525,000	2,362,389
Sicily	245,000	237,000
Italy	88,000	.....
Japan	75,000	75,000
Spain	70,000	....
Chile	10,000	....

U. S. EXPORTS OF SULFUR

	1931 *Long tons*	1930 *Long tons*	1929 *Long tons*
Canada	....	166,943	200,012
Germany	....	120,569	169,474
Australia	....	65,036	104,538
France	....	59,190	136,732
Netherlands	....	35,073	50,707
United Kingdom	....	28,683	43,856
New Zealand	....	18,212	37,048
Total exports	407,586	593,312	855,183

Of the sulfur produced in the United States, 86 per cent of the total comes from the deposits of the Texas Gulf Sulfur, the Freeport Sulfur, and the Duval Sulfur Companies located in Texas. No sulfur was produced in 1929 and 1930 in Nevada, California, or Utah, which made small contributions during preceding years.

PRODUCTION OF PYRITES

Production of pyrites in the United States, including by-product pyrites and pyrrhotite concentrates from Tennessee, pyrites concentrates from New York, and partly desulfurized tailings from Wisconsin, is as follows:

YEAR	PYRITES *Tons*	SULFUR EQUIVALENT *Tons*
1930	347,512	124,226
1929	333,465	120,371
1928	312,315	113,305

The imports of pyrites amounted in 1930 to 368,114 tons (equivalent to 184,000 tons of sulfur), and in 1929 to 514,336 tons (equivalent to 257,168 tons of sulfur). Of these imports in 1930 Spain furnished 325,992 tons, Canada 42,117 tons, and Russia 5 tons.

The shipment of sulfur direct to the consumer amounted in 1928 to 1,396,000 tons, in 1929 to 1,555,000 tons, and 1930 to 1,465,000 tons. Of the total sulfur shipped to the consumer, brimstone represented 82.7 per cent, imported pyrites 6.4, and domestic pyrites 6.9.

Sulfur used in various industries in 1929 has been estimated as follows (*26*):

	Tons
Heavy chemicals	560,000
Fertilizer and insecticides	415,000
Pulp and paper	265,000
Explosives	67,000
Dye and coal tars	47,000
Rubber	43,000
Electrochemical	23,000
Paints and varnishes	5,000
Food products	....
Miscellaneous	136,000
Total	1,581,000

The production of sulfuric acid in 1929 was as follows:

INDUSTRY	EQUIVALENT IN 50° BÉ ACID (*6*)	EQUIVALENT IN SULFUR
	Tons	*Tons*
Fertilizers	2,418,000	483,600
Petroleum refining	1,570,000	132,000
Chemicals	890,000	178,000
Coal	935,000	187,000
Iron and steel	800,000	160,000
Other metallurgical	675,000	135,000
Paints and pigments	225,000	45,000
Explosives	195,000	39,000
Rayon	150,000	30,000
Textiles	90,000	18,000
Miscellaneous	390,000	78,000
Total	8,338,000	1,355,600

In 1882 brimstone furnished 85 per cent of our sulfuric acid and in 1895 only 75 per cent. In this latter year the zinc smelters began to recover their roaster gases as sulfuric acid, and in 1907 copper blast-furnace gases were first recovered commercially for acid production. Our production of brimstone in 1907 was only 188,878 of the world production of 648,324 tons. In 1914 our production of brimstone was 417,690 tons out of the world total of 880,292 tons and our sulfuric acid production (*4*) came from the following sources:

	%		%
Domestic and foreign pyrites	73.7	Copper smelters	10.5
Zinc smelters	13.2	Sulfur	2.6

This was a direct reversal of the old practice. In 1929, of the world's production of 2,800,000 tons of brimstone we produced 2,362,389 tons, and the tables were again turned; 66 per cent of the acid production came from brimstone, 17 from pyrites, and 17 from smelters.

The cause for this reversal in consumption from sulfur to pyrites and then from pyrites to brimstone is not a difficult question to answer. In 1900 the United States produced only 3147 tons of sulfur of a total of 555,282 tons, Italy producing 535,525 tons. In 1900 it was stated (*17a*) that there was a decided increase in the production of sulfur for the year as compared with the 1565 tons in 1899. Nevada contributed the greater part. The balance came from Utah, and only 50 tons came from Lake Charles, La., where deposits had just been reopened.

Pyrites acid could be produced comparatively free from impurities (especially arsenic) by precipitation with hydrogen sulfide. This method was not only dangerous but expensive, yet its product did not compare in cost or purity with the brimstone acid. At this time rapid strides were being made by the Europeans in producing acid by the so-called contact process. Pyrites gases laden with lead, zinc, arsenic, selenium, chlorides, etc., were thoroughly purified by washing with water or acid, cooled and filtered through asbestos, coke, or other materials, and finally delivered to a platinum catalyst. The sulfur dioxide was thereby converted to sulfur trioxide which was absorbed in strong sulfuric acid. Two processes, the Schoeder-Grillo and the Mannheim, were imported; the Herreshoff process was developed in this country. The quality of acid made in this way was even better than that from sulfur made by the chamber process which was then the common practice. The acid produced by the new method was not only of 66° Bé. and 98 per cent concentration, but contained free sulfur trioxide for which there was no demand or for which there appeared at the time to be but little use. It was soon realized that this so-called oleum, containing from 10 to 60 per cent sulfur trioxide, was especially useful in making anhydrous mixtures of sulfuric and nitric acids, giving much improved yields of nitroglycerin, and that it was invaluable in the refining of petroleum and in the manufacture of dyestuffs.

This simpler contact system replaced the chamber process with its purification and still bench and was the only type of new construction for strong acid up to 1916, when our supplies of pyrites were seriously curtailed. Our domestic production of sulfur in 1916 was 649,683 tons, but in 1917 it was increased to 1,134,412 tons. Sulfur was again our raw material and all the war plants were constructed to use it.

During these strenuous days the Department of the Interior at Washington kept up an aggressive search for sulfide ores suitable for acid manufacture, but only a few scattered deposits were developed. Sulfur was the backlog of forced production, and instructions were then issued by the Committee of the Council of National Defense showing how the equipment used for burning pyrites and zinc blend could be adapted to burning sulfur. All developments were favorable to the use of brimstone and detrimental to pyrites.

Early in 1918 construction of a plant for the production of sulfur at the Big Hill deposit in Texas was begun by the Texas Gulf Sulphur Company. This development came into production in March, 1919, after our most urgent demands were over, but after our plants were fully equipped for the use of sulfur. The Freeport, Texas, and Duval Companies now furnish us the cheap supplies that account for our continuing to consume more sulfur than pyrites.

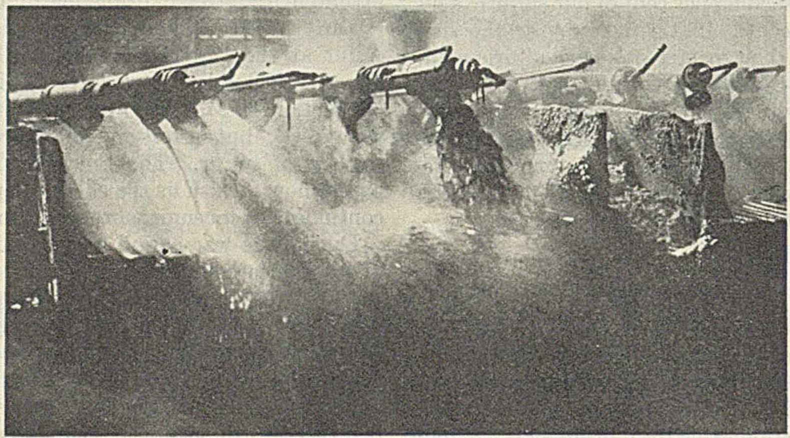
During the war period we learned more about the quality of our domestic brimstone. It was sufficiently pure to enable the acid manufacturer practically to eliminate purification. The "acid mist" which was the bugbear of purification was overcome by predrying the air used for combustion, maintaining the temperature of the sulfur gas above the dew point, and admitting it to the contact system at the desired temperature for conversion. This was a real advance in the art, as it cut the cost of construction in half.

Today we are equipped to burn brimstone which requires low cost plants with large capacities and low operating costs, and it would appear that we shall continue to use this as a raw material until such time as the unit cost of sulfur in pyrites makes it uneconomical. This now appears improbable. Our supplies of sulfur are adequate for this generation's requirements, but, unless more deposits of sulfur are discovered, we must expect higher costs of production and a new economic equilibrium between sulfur and pyrites.

The current price of brimstone at Atlantic ports is $22 per ton; Spanish pyrites is 12 to 13 cents per unit, or the equivalent number of dollars per ton of sulfur. This pyrites price includes the cost of mining, handling, and transportation from Spain to the Atlantic seaboard and has changed very little during the past thirty years. It would appear that there is a sufficient spread between these two prices to warrant increased use of pyrites; yet it must be remembered that for each ton of sulfur two tons at least must be handled, together with the resulting iron oxide calcine weighing 70 per cent of the ore. In burning pyrites there is left some uncalcined sulfide averaging 2 per cent of the original ore, and 4 to 6 per cent of the sulfur is converted into impure sulfuric acid in the roaster owing to the iron oxide catalyst. Expensive roasters are required, and the gases demand a positive purification with scrubbers, coolers, Cottrells, and/or coke box filters—all expensive and elaborate equipment. These operations add to the cost of available sulfur.

Formerly, purification of the gases from brimstone received this same scrupulous care, necessitating identical equipment with that already outlined for pyrites, a practice still continued in a few plants. The cost of the plant for each raw material was the same except for the burners, which for ore were invariably of the multiple hearth type, and except for apparatus for removing the entrained dust. Yet it has been estimated that a differential of not more than $5 per ton between these two raw materials would put them on an equivalent basis.

Today, with commercially pure domestic brimstone and the elimination of sulfuric acid mist formation, brimstone plants are constructed with practically no purification apparatus, whether platinum or vanadium is used as a catalyst; power as steam is generated as a by-product in the cooling of the hot sulfur gas; installations are built with a capacity of 50 tons of sulfur instead of 12 to 15 as with pyrites; and these are almost automatically controlled. These developments have completely changed the picture. The price differential per ton sulfur, instead of being only $5, is now between $8 and $10, and we can see little likelihood of pyrites replacing brimstone even on the Atlantic seaboard. Pyrites have not been available in the Great Lakes district since 1913, nor are there pyrites at hand for the fertilizer producer, except perhaps in Tennessee.



Courtesy of Texas Gulf Sulphur Co.

WELLS DISCHARGING INTO SUMP AT GULF, TEXAS

RECOVERY OF SULFUR FROM GASES

Another source of sulfur is the gases from the smelting of copper, zinc, and nickel sulfide ores, which are now being converted to a certain extent to sulfuric acid by the International Nickel, Anaconda Copper, and Consolidated Smelting companies, and from the various zinc smelters in this country and in Europe, but these gases do not yield sulfur as desired for economical distribution and use. M. C. Boswell (*2*) of Toronto University has suggested the recovery as elemental sulfur and has done considerable investigation in this direction, but none has been produced on a plant scale.

Our largest reserves of sulfur are unquestionably combined with iron as pyrites and well distributed over the whole world. Ridgeway (*22*) states that there are over 907,000,000 tons of pyrites available, not including totals for North and South America and Africa.

To recover this sulfur as brimstone is no new thought. The Chinese for several hundred years distilled pyrites, and others too numerous to mention have suggested the same procedure. Chaddick (*3*) states that this practice is common all over the world. As early as 1863 some 2440 tons of sulfur were thus produced in Bohemia. Other processes he mentions are those of Labin (*15*) who heats pyrites with producer gas; Urbasch (*3*) who uses a vertical retort externally heated by producer gas, the oxygen-free gas being then conducted through the charge; Piederson (*19*) who heats the sulfide ore with coke, regulating the air supply; and Hall (*12*) who passes producer gas and steam over the ore on a shelf burner. According to German Patent 313,122 (*3*) ore is heated in the presence of a gas inert to sulfur to a temperature at which the molten sulfide decomposes; part of the sulfur is distilled and a material high in sulfur is obtained; Marchal (*17*) heats pyrites in a vacuum or in an atmosphere of nitrogen; Riggs (*23*) and the New Jersey Zinc Company heat pyrites with the exclusion of air to 600–800° C. until it has been converted to the magnetic sulfide. German Patent 310,526 (*3*) describes an electric furnace in which pyrites is heated with silica at a temperature of 1500° C. out of contact with air; sulfur is distilled and ferrosilicon obtained. Wright (*3*) uses an electric tilting furnace with a single carbon electrode at the top and a metallic plate at the bottom to produce a temperature of 3000° C., the sulfur being volatilized. The Norsk Hydro-Elektrisk Kvaelstof Aktieselskab (*3*) also proposes the electric furnace; Frehling (*3*) heats pyrites in a stream of carbon monoxide or nitrogen with an insufficient supply of oxygen, the iron being converted to oxide and the sulfur eliminated. Lelay (*26*) reduces sulfur dioxide by drawing it through carbon heated to a "yellow heat," sulfur, carbon monoxide, hydrogen sulfide, and carbon disulfide being formed; Carpenter (*26*) in 1908 burned sulfur dioxide in a reducing atmosphere.

The Thiogen process (*27*) proposes to reduce sulfur dioxide with natural gas using a catalyst; Beekman (*26*) reduces sulfur dioxide with methane or carbon monoxide; Bacon (*1*) subjects the pyrites to the action of oxygenated air and steam, condenses the sulfur, and returns the exhausted condenser gases to the process.

These and many others have attempted to reclaim sulfur, but so far as the writer is aware no process is in commercial operation.

A plant for the recovery of sulfur from pyrites has been built in Norway at Orkla Grube (*24*) where satisfactory operations are being carried out. No details of this process or of that operated in Spain are available.

All sulfur reclaimed by the above method is likely to be impure, as the pyrites is never pure FeS_2 but contains admixtures of other base sulfides, together with arsenic, selenium, etc. It is therefore necessary that these gases be purified before sulfur can be obtained that is fit for general use. Several methods for this operation have been proposed but all add to the cost of production. The most recent suggestion for this purification is to burn the pyrites to sulfur dioxide and iron oxide, the heat of the burner gases being converted into steam; the sulfur dioxide is absorbed in water and stripped by use of the steam generated, and finally this 100 per cent sulfur dioxide is reduced to sulfur with coke. It is stated that the steam generated is sufficient for the process. This method should give a high grade sulfur, as the volatile impurities in the ore would not affect the sulfur dioxide recovered in this manner. Its success would depend on several factors, such as the original value of the pyrites, available supply of water, the disposition of the iron oxide calcine, the value of coke, the cost of freight to consuming points, etc.

It would appear that the cost of reclaiming sulfur from pyrites has not been a profitable operation, but all of this work does indicate that the user of sulfur is convinced that elemental sulfur is much more desirable than combined sulfur.

The only successful process for recovery is that of Chance and Claus from the sodium carbonate wastes of the LeBlanc process. This has produced 30,000 tons per year, but it is unimportant in our consideration of a source of sulfur, especially in view of the fact that this process of producing sodium carbonate is now almost obsolete.

Europeans are obtaining sulfur and sulfate from gypsum. The Bayer factory at Leverkusen is said to have a yearly capacity of 40,000 to 50,000 tons of sulfuric acid. This process involves the heating of gypsum, clay, and coal with the addition of sand, the sulfur dioxide being converted to sulfuric acid and the cinder to cement. This source of sulfur, too, is especially favorable to the production of ammonium sulfate.

Salt cake (*13*) or sodium sulfate, of which there are millions of tons in Canada and the United States, offers a source of sulfur by interaction with barium carbonate and coal. The barium sulfide is decomposed with water and carbon dioxide, barium carbonate being thus regenerated, and the hydrogen sulfide is oxidized to sulfur.

In the Tern process (*8*) sulfur dioxide is recovered from spent oxide made in coke-oven gas purification. Sulfur dioxide from this source is oxidized by an electric arc to sulfur trioxide; ammonia from gas liquor and the sulfur dioxide are then led in proper proportions into the reaction chamber and combined to form dry ammonium sulfate, sufficient moisture being present in the atmosphere to hydrolyze the sulfur dioxide. The Koppers method (*20*) for removal of sulfur from coke-oven gas with sodium carbonate uses nickel as a catalyst, and the Englehardt process (*25*) uses activated carbon, recovering sulfur as ammonium polysulfide.

This recovery of sulfur from coke-oven gases does not offer a particularly cheap source of sulfur. It is more interesting from the standpoint of gas purification; our future supply of gas, it would seem, is more likely to come from our enormous resources of natural gas than from coal. A potential future supply of sulfur is from smelter fume, which is carrying more sulfur into the atmosphere than we consume, and from the sulfur combined with the coal we burn, which is now polluting the air we breathe. The recovery of this sulfur from coal is being thoroughly investigated by the London (England) Power Company and by the Chemical Engineering Division of the University of Illinois under the direction of Johnstone (*14*).

It is obvious that conservation of our sulfur resources is receiving intensive study, but all processes studied or proposed are handicapped by a cost that precludes their competing with the brimstone which Frasch made so easily available. If the cost of sulfur used for our production of chemicals becomes exorbitant, then we must develop processes which will eliminate its use.

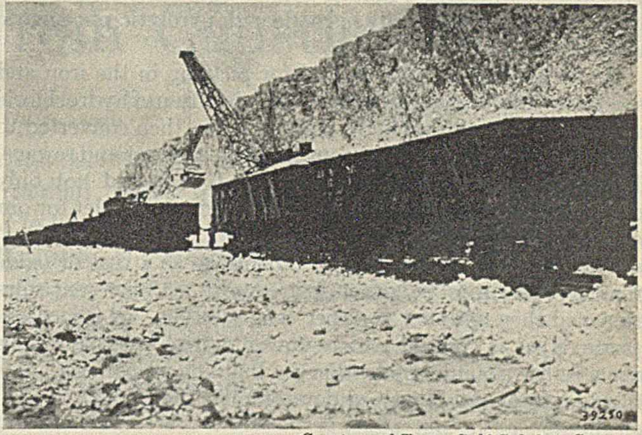
CONSUMPTION OF SULFUR

Sulfuric acid consumes about 65 per cent of the sulfur supply, and pulp and paper 17 per cent, leaving 18 per cent for miscellaneous uses such as explosives, dyes, rubber, electro-chemicals, etc. Of the sulfuric acid produced, 30 per cent is used for decomposing phosphate rock, 11 per cent in the coal industry for ammonium sulfate (thus totaling approximately 41 per cent for the fertilizer industry), 10 per cent in chemical manufacture, 20 per cent in oil refining, and 10 per cent in the iron and steel industry.

The demand for some method of producing soluble calcium phosphate other than decomposing phosphate rock with sulfuric acid was realized long ago by the Bureau of Chemistry of the U. S. Department of Agriculture as is evidenced by the work of Carruthers, Southgate, Waggerman, and others, and also by the commercial developments of the Federal Phosphorus, the Victor Chemical, and the Coronet Companies. All of these methods are pyrolytic—either pyroelectric or blast furnace operations. Little detailed information is available, but the advantages claimed are "utilization of low grade phosphate rock which is unfit for treatment with acid, elimination of the raw rock treatment (that is the washing with the attendant loss of fines), and elimination of the gypsum in the finished product equivalent to the weight of the superphosphate (thus eliminating 50 per cent of the handling, bagging and freight charges)."

The materials used are phosphate rock, coke, and silica. The evolved gases consisting of carbon monoxide and phosphorus are burned, the resulting P_2O_5 collected by the Cottrell precipitator giving an acid of any desired strength and of unusual purity. The principal cost with the pyroelectric furnace is power; that with the blast furnace is coke. In both cases the plant investment is considerable. That these processes are economical is evidenced by the fact that the producers are not only continuing to operate but are continuing to expand.

Ammonia produced in the coking of coal could be as easily converted to the phosphate as the sulfate and thus made into a much more valuable and useful product. Under present business conditions this ammonia is hardly worth the expense of recovery, as it cannot compete with the synthetic salts made in Europe where the sulfate radical is obtained to a large extent from gypsum by the Bayer process already referred to.


Courtesy of Texas Gulf Sulphur Co.

LOADING SULFUR AT GULF, TEXAS

Some coke plants recover their ammonia as ammonium hydroxide and sell it as such, but because of the concentration of the solution (26° Bé.), the value per unit of ammonia is much less than that of anhydrous ammonia.

For the production of chemicals we use 10 per cent of our sulfur largely as sulfuric acid, which is frequently only a means to an end, producing a by-product of little or no value. The principal products in which it is used are aluminum sulfate, nitric acid, hydrochloric acid and salt cake, acetic acid, hydrofluoric acid, and sodium and calcium phosphates.

Demand for aluminum sulfate, made by decomposing bauxite with sulfuric acid, and used for purification of water and as a size for paper, has been increasing annually. The sulfate radical is only the carrier. It takes no active part in the reaction, and it is the alumina that is desired. Yet according to Dreshfield (*9*) it is claimed that paper can be sized without aluminum sulfate, if the rosin is in solution in an organic solvent, by applying this solution to the paper in a vacuum drier after the sheet has been formed and practically dried.

Hydrochloric acid and salt cake, made by decomposing common salt with sulfuric acid or sodium acid sulfate, is an unbalanced operation, as is usual when only one of the two products is in demand. There is always too much of one and not enough of the other. At present we have no sodium acid sulfate as the by-product of the production of nitric acid, since our nitric acid requires no sodium nitrate and sulfuric acid but is made almost exclusively by the oxidation of ammonia. The loss of this raw material increases the ratio of hydrochloric acid to salt cake, and the latter is in greater demand now than ever before because of the production of kraft paper. The demand for salt cake is now being satisfied from the enormous deposits of natural cake in Canada and the United States, and importations from Germany where it is made by the double decomposition of magnesium sulfate and sodium chloride. Our hydrochloric acid is also produced by combining hydrogen and chlorine which are produced in the electrolysis of common salt or by passing chlorine with steam through incandescent coke, a process which further reduces salt cake production.

Not only do we need no sulfuric acid for the production of hydrochloric and nitric acids, but each may replace sulfuric acid in the decomposition of phosphate rock. Acetic acid (*18*) no longer requires calcium acetate and sulfuric acid, being now made by several catalytic processes. The most important of these processes is perhaps that from calcium carbide by way of acetylene and acetaldehyde.

Calcium and sodium phosphates, produced by decomposing phosphate rock with sulfuric acid and neutralizing the phosphoric acid with either lime or sodium carbonate and sodium hydroxide, can more easily be made with pyrolytic phosphoric acid.

As for the use of sulfuric acid for pickling in the iron and steel industry, it may be more economical to use hydrochloric acid, the ferrous chloride by-product being then converted to the ferric salt and used in the purification of water and sewage. If this process were further developed, it would not only eliminate the use of sulfuric acid but furnish an outlet for our excess production of chlorine.

Phosphoric acid also has an advantage as a rust or oxide remover, the iron being first treated with a 15 per cent solution and then with a 1 to 2 per cent solution. A thin phosphate layer is formed which prevents fresh rusting. This process has found application in building apparatus, pipe manufacture, and bicycle and automobile industries.

Sulfur in Pulp and Paper

Pyrites as a substitute for brimstone has been used with little success in sulfite pulp manufacture because of its impurities, the low strength and uneven flow of the sulfur dioxide gas, heavy charges for labor and equipment for handling large tonnage of ore and cinder, and the inconvenience and difficulty of intermittent operations that are necessary in the plant. Europeans have had a greater incentive to perfect this substitution, yet they continue to use large tonnages of brimstone for the purpose.

The shaft type of furnace (*11*) appears to offer a solution to some of the objections, such as the strength and low sulfuric acid content of the sulfur dioxide gas, ease of operation, etc., but one must either have an ore of the required quality or must purify the gas. Since it is possible to recover approximately 2 pounds of steam per pound of pyrites burned in cooling the gases (which are generated at 1000° to 1100° C.), it would appear feasible to absorb the sulfur dioxide in water and then to strip the solution with this steam, obtaining thereby pure sulfur dioxide of 100 per cent concentration, or to strip it with a steam-air mixture that would be required to bring it to the desired concentration. This method offers a solution to the difficulties outlined but increases the cost of the sulfur. It could be utilized where operations are of sufficient size and the cost of pyrites warrants the expense.

Sulfuric Acid in Petroleum Industry

Petroleum refining called for some 132,000 tons of sulfur in 1929, about 10 per cent of our acid production. It may be the cheapest reagent for this work, but other methods of refining have already been developed which not only give the oil the desired characteristics but yield side products of value.

The major threat is probably the hydrogenation process which requires little sulfuric acid but has the added advantage of eliminating the sulfur in the oil as hydrogen sulfide which can easily be reclaimed.

Edeleanu (*10*), using liquid sulfur dioxide as the treating agent, shows excellent results especially in removing the sulfur and nitrogenous compounds. The sulfur gas is easily recovered for re-use.

Lachman (*16*) describes the use of zinc chloride, showing not only a decreased cost of treatment but extra values in the by-products obtained.

Methods have been proposed of regenerating the sulfuric acid in the so-called oil sludge, this acid being decomposed with the carbon of the oil by heat; the sulfur dioxide thus evolved is converted to sulfuric acid by the contact process.

Sulfuric acid is used almost exclusively as an acid reagent, and the resulting sulfate is seldom of value. This is illustrated by the calcium sulfate left in the superphosphate fertilizer, by the sulfuric acid cokes left in the refining of petroleum, and by aluminum and ammonium sulfates. If sulfates are valuable to the soil as in the case of fertilizer, there are other sources much less expensive than the sulfur which has been converted into sulfuric acid. Our use of sulfur in this way would appear to be an economic waste.

In the production of sulfuric acid, the raw material (brimstone) accounts for over 70 per cent of the total cost, and further development of the method of production offers little opportunity for the chemical engineer. According to the trade journals of 1900, 50° Bé. sulfuric acid in bulk in tanks cars was quoted at $14.00 per ton. Sulfur was $19.25, and Spanish pyrites 13 to 15 cents per unit, both delivered in New York. Today 50° Bé. acid is not even quoted, but 66° acid is offered at $15.00. Yet sulfur is $22.00, and Spanish pyrites is still 13 cents per unit.

Apparently the engineer has accomplished much during this period. As outlined above, owing to the scarcity of sulfur in the early 1900's, he developed the catalytic process for converting the sulfur dioxide from pyrites to sulfur trioxide, producing an acid of higher strength at lower cost, and of greater purity than that made from brimstone by the chamber process with the necessary iron or platinum still concentration. Through the high quality of our domestic sulfur and the elimination of the purification apparatus, he developed units of 400 to 500 per cent greater capacity which cut his plant construction cost 50 per cent. By utilizing the sensible heat of the burner gas to generate steam, he obtained sufficient power to operate his plant; by installing automatic control he eliminated labor to the vanishing point; and by devising new catalysts he removed the danger of poisoning with arsenic, chlorine, or other volatile impurities in his raw material.

What is there now left for him to accomplish; what new developments can we expect in the future? The three elements of cost of production are raw material, operations, and plant. Raw material (either sulfur or pyrites) costs today the same as it did thirty years ago. The methods of recovery or mining have evidently kept pace with the increased costs of labor and materials necessary. Operators are almost eliminated. There is left then only plant, the cost of which has already been decreased about 50 per cent. Perhaps this item can be further cut by the use of 100 per cent sulfur dioxide produced from pyrites as already outlined, using oxygen for converting to sulfur dioxide and then to sulfur trioxide, the sulfur trioxide being absorbed and the residual gas recirculated with the necessary increment of sulfur dioxide. Under present conditions little remains for decreasing the cost of plant, and no new raw materials are seen to be available.

It is obvious that all major industries now using sulfur are striving to find a substitute or a different method of operation; to a large degree they have succeeded, the question of whether to use it or not depending on comparative costs. However, for the industries we have analyzed our question is: "What shall we do without sulfur?" or "What shall we do with it?"

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Extraction of Phenols from Caustic Solutions

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Many of the simple phenols have been extracted from an equivalent of 5 normal caustic by use of ether to the extent of 93 to 99 per cent. Individuals exhibit different speeds of extraction. A continuous extractor is diagrammed by means of which the extractability of a number of isomeric and homologous phenols has been determined. The essential part consists of a flow-regulating device to deliver ether at a constant rate to the extractor. Time-percentage extraction curves are shown.

The strength of caustic used is comparable with that employed in commercial practice. An extraction of this sort, if carried out on plant scale, should expedite the recovery of tar acids from tar distillates and would obviate the necessity of the springing and recausticizing operations, both of which are time-consuming and involve an added expense in materials.

In acid recovery plants it is common practice to remove phenols from tar distillates with caustic soda, and to liberate them from the latter by a springing operation which involves the use of mineral acid or carbon dioxide from stack gases. If a mineral acid neutralization process is employed, the sodium is lost from further usefulness; if carbon dioxide is used, the resulting carbonate solution may be recausticized with lime. Both processes have decided drawbacks either from the standpoint of consumption of chemicals or from that of the necessity of additional plant operations.

It was proposed to attempt the extraction of tar acids from the caustic by means of an immiscible solvent, such as ether, in a continuous extractor by taking advantage of the hydrolysis represented by the equation:

$$RONa + H_2O = ROH + NaOH$$

and, if it was found possible to recover them expeditiously, to study individual phenols by measuring their proper extractabilities under changing conditions of temperature, rate of ether flow, caustic concentration, and type of solvent. A further idea was entertained—namely, that of separation of tar acids of similar boiling range if their extractabilities were found to differ widely.

The historical background of this research is brief. Weindel (*4*), in 1925, investigated phenolate liquors from low-temperature tar and found that, by extraction with ether or benzene, a group of phenols could be removed which he termed "e-phenols." The nonextractable or "ne-phenols" had to be recovered by neutralizing with mineral acid. Three boiling ranges were studied, and the proportions of the two classes determined for each:

	230–310° C.	222–230° C.	100–107° C. (10 mm.)
e-Phenols	51.5	39.0	24.1
ne-Phenols	48.5	61.0	75.9

Exhaustive extraction was not used. It is clear from Weindel's description that he obtained only partial extractions of his phenate solutions because of the partition of phenols between caustic and solvent. That is, he arrived, not at a separation of extractable and nonextractable phenols, but at an equilibrium condition between phenols, solvent, and caustic under one set of empirical conditions.

Vavon and Zaharia (*3*) went somewhat farther and showed that all phenols are extractable from alkaline solution with immiscible solvents, the coefficients varying within wide limits. From their results they drew a number of conclusions:

> 1. Phenols are extractable from phenolate solutions by organic solvents because of hydrolysis.
> 2. The percentage of total phenols extracted increases with solubility of the phenol in the solvent used and with the relative volume of the solvent.
> 3. The percentage of total phenol extracted decreases with increasing concentration of aqueous solution or excess of alkali.
> 4. In high concentrations, aqueous phenolate solutions become miscible with ether.
> 5. The degree of hydrolysis or percentage extracted is decidedly greater with the ortho derivatives and increases with the number and size of the side chains.

By agitating 0.01 mole of sodium phenate in 10 cc. of solution with 20 cc. of ether for 10 minutes, the following percentages of extracts were obtained:

Phenol	7.5	1,4,2-Xylenol	37.7
o-Cresol	20.8	Thymol	86
m-Cresol	15.0	Thymol (by benzene)	38
p-Cresol	13.3	Thymol (by CCl_4)	25
o-Ethylphenol	44.7	Thymol (by petroleum ether)	22
p-Ethylphenol	25.3		

(The order of solubility of thymol in these solvents is the same as that indicated by the amount extracted.) These results are good as far as they go, and most of the writers' generalizations are correct. On the other hand, their extractability figures are for one equilibrium extraction only, and tell nothing of progressive behavior as the phenol content of the caustic is lowered, nor is it made clear that configuration is fully as important a factor as molecular weight.

In the present research, ten phenols have been subjected to exhaustive extraction tests at a temperature of 25–30° C. as the first phase of the investigation. It was early recognized that for this research a special type of continuous extractor would be required, so designed that fresh solvent would be delivered to and thoroughly agitated with the phenate solution at a constant rate. Various constant-temperature devices were tried for regulating the boiling off of solvent, but were not found to give reproducible results. Efforts in this direction were therefore abandoned, and attempts made to reach the same end mechanically. An apparatus (Figure 1) was finally developed and has been used continuously without modification. Two such extractors were constructed for running the tests in duplicate. The ether delivery devices were made identical; that is, when calibrated, the delivery per minute of 12.7 cc. varied less than 0.1 cc. between them.

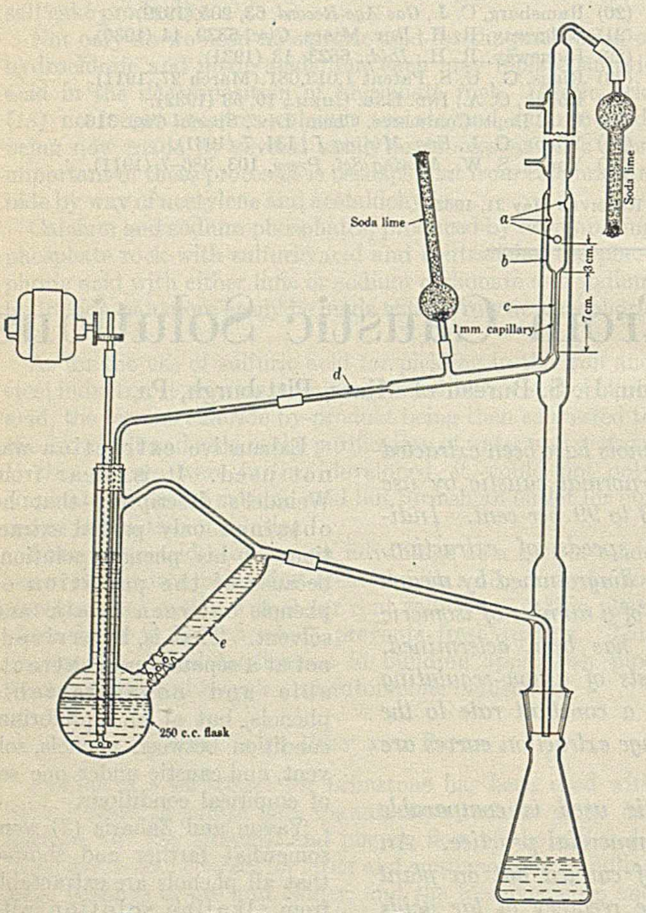

FIGURE 1. CONTINUOUS EXTRACTOR

METHOD OF EXTRACTION

The experimental procedure has been as follows:

Five-tenths mole of the phenol is dissolved in 100 cc. of caustic soda containing 0.5 mole of sodium hydroxide. In such a solution the molar ratios of phenol to caustic to water are preserved constant, even though the total volume may vary from one phenol to the next. The phenate solution is contained in the special type of extraction flask of 250 cc. capacity. Ether is added as high as the overflow. The stirring motor is started, and the two liquids are thoroughly agitated together several minutes to insure an equilibrium condition before fresh solvent is admitted from the condenser. The motor is then stopped and a hot plate placed under the Erlenmeyer flask containing about 100 cc. of ether. The latter quickly vaporizes and rises through ports *a* into the condenser whence it flows back into cup *b* and is delivered to the phenate solution through capillary *c* and tube *d*. The volatilization is rapid enough to keep cup *b* filled as far as the lower port, through which an excess of ether overflows into the Erlenmeyer flask, thereby maintaining a constant head. As soon as this condition is reached, the motor is again started and the time recorded. Ether is emulsified in the body of the flask with the phenate solution, but, as the emulsion rises into outlet tube *e* where it is free from agitating influences, the layers separate, and clear ether containing phenol overflows into the Erlenmeyer flask. The cycle is now complete. Little loss of solvent need be sustained in this apparatus even if the stirring device is not equipped with mercury seal, provided the condenser is adequate to take care of large quantities of ether. The speed of stirring is maintained at the highest possible rate, although it has been observed that the same degree of extraction is obtained with somewhat less agitation, provided that the two liquids are kept well emulsified.

At suitable time intervals, which are lengthened as the concentration decreases, the extraction is interrupted and the amount of extracted phenol determined by distilling off the ether from a tared flask. The recovered ether is invariably used for the next time period.

Difficulties are sometimes experienced with the emulsions. After a certain period of time has elapsed in an extraction, for example, the rate of separation of the emulsion diminishes—a condition which requires careful manipulation to secure a rate of stirring such that no emulsion is carried over into the Erlenmeyer flask. Later on, as the phenol becomes more attenuated, the emulsion-breaking again becomes more rapid. The naphthols, which require somewhat long periods of time for extraction, are particularly prone to form difficult emulsions (in these cases probably as a result of a small amount of oxidation). All the phenate solutions turn more or less dark with time, usually as a result of the presence of impurities. It is possible to purify C. P. phenol by recrystallization from petroleum ether and distillation to a point where it will remain almost water-white in alkaline solution. The material extracted is in every case pure enough to crystallize if the original material was itself crystalline.

Little or no sodium is actually removed from the phenate solution by the ether as dissolved sodium or as aqueous caustic mechanically entrained. This fact is quite remarkable in view of the large quantities of ether that are emulsified with the sodium phenate solution in the course of a single extraction. In the case of β-naphthol more than 108 liters of ether passed through 100 cc. of alkaline naphtholate.

In only one case was it necessary to vary the general procedure. Potassium hydroxide was used in the study of *sym*-xylenol on account of the meager solubility of the sodium salt of this compound.

Three compounds, *p*-chlorophenol, thymol, and *p*-butylphenol, proved impossible to study under the conditions used for the others, as ether was completely miscible with the phenate up to the capacity of the flask. Under modified conditions—for example, dilution—thymol and butylphenol would doubtless exhibit extreme rapidity of extraction because of the character of the alkyl substitutions. These individuals will be investigated later when the dilution effect is considered, as they are representative to some extent of the higher-boiling tar acids. It is predicted that chlorophenol will come out rather slowly because of the negative character of the chloro substituent.

EXTRACTION BEHAVIOR OF COMPOUNDS

The trend of the extraction in each case is shown by the extraction data (Table I) and the composite graph (Figure 2). From a study of these curves it is seen that the elementary phenols—that is, phenols consisting of a single or double benzenoid nucleus with one hydroxy substitution—show similarities in their extraction behavior. Phenol falls midway between α- and β-naphthol. All may be classed as being relatively difficult of extraction. The appearance of alkyl substitutions at once increases the rapidity of removal, although in this connection the importance of position as well as of enhanced molecular weight should be observed. *o*-Cresol, for example, is removable at a greater rate than *sym*-xylenol. If both ortho positions are occupied as in 1, 3, 2-xylenol, the speed is still greater.

Table I. Extraction Data

Time *Hours*	I %	II %	Mean %	Av. per Hour %	Av. per Hour Interval %
			PHENOL		
2	10.4	12.6	11.5	5.80	5.80
6	20.4	19.7	20.1	3.35	2.15
14.5	34.2	32.6	33.4	2.30	1.56
26	..	45.4	45.4	1.75	1.04
42	60.3	59.3	59.8	1.42	0.87
62	73.6	72.8	73.2	1.18	0.67
86	87.1	86.3	86.7	1.00	0.56
110	93.7	93.3	93.5	0.85	0.28
			o-CRESOL		
2	33.9	32.0	33.0	16.50	16.50
4	50.1	48.1	49.1	12.28	8.05
8	71.3	70.0	70.7	8.84	5.40
12	85.6	86.5	86.0	7.17	3.82
20	98.5	98.5	98.5	4.92	1.56
23	98.8	98.8	98.8	4.29	0.10
			m-CRESOL		
2	13.2	13.3	13.3	16.65	16.65
6	27.4	28.0	27.7	4.62	3.60
14	44.5	52.2	48.8	3.48	2.64
26	68.0	72.4	70.2	2.71	1.78
42	88.2	88.2	88.2	2.10	1.12
58	98.7	98.5	98.6	1.70	0.65
			p-CRESOL		
1	10.2	8.3	9.3	9.30	9.30
3	20.2	19.6	19.9	6.63	5.30
7	33.2	32.8	33.0	4.71	3.28
15	52.8	51.8	52.3	3.48	2.41
28	72.8	75.2	74.0	2.64	1.67
45	98.1	97.8	98.0	2.18	1.41
			sym-XYLENOL		
1	11.3	11.0	11.2	11.20	11.20
3	24.1	23.8	24.0	8.00	6.40
7	39.2	39.2	39.2	5.60	3.80
15	61.6	62.0	61.8	4.12	2.83
27	88.8	88.5	88.7	3.29	2.24
37	99.7	99.2	99.6	2.69	1.09
			1, 3, 2-XYLENOL		
1	34.8	34.9	34.9	34.90	34.90
2	58.2	57.7	58.0	29.00	23.10
3	77.3	76.6	77.0	25.67	19.00
5	96.0	96.4	96.2	19.24	9.60
7	98.2	98.2	98.2	14.03	1.00
			α-NAPHTHOL		
2	10.3	9.6	10.0	5.00	4.00
6	21.8	20.4	21.1	3.52	2.78
14	36.6	37.2	36.9	2.64	1.98
26	..	52.0	52.0	2.00	1.26
42	65.6	..	65.6	1.56	0.85
62	81.6	80.8	81.2	1.31	0.78
90.25	..	97.6	97.6	1.08	0.58
			β-NAPHTHOL		
2	6.2	6.5	6.4	3.20	3.20
6	13.2	12.7	13.5	2.25	1.78
14	24.9	..	24.9	1.78	1.43
27	36.0	..	36.0	1.33	0.85
42	49.5	44.9	47.2	1.12	0.75
62.5	62.1	..	62.1	0.99	0.73
86	75.1	..	75.1	0.87	0.55
114	88.6	89.2	88.9	0.78	0.49
142	97.9	..	97.9	0.69	0.32
			GUAIACOL		
4	15.8	..	15.8	3.95	3.95
10	24.2	..	24.2	2.42	1.40
18	30.8	30.2	30.5	1.69	0.79
34	40.6	41.0	40.8	1.20	0.64
58	49.4	52.9	51.2	0.88	0.43
84	60.0	61.8	60.9	0.72	0.37
112	66.6	70.7	68.1	0.61	0.26
			RESORCINOL		
3	40.2	..	40.2	13.40	13.40
6	42.8	..	42.8	7.13	0.87
9	44.9	..	44.9	4.99	0.70
17	47.1	..	47.1	2.77	0.28

It may be safely concluded that alkyl groups in the ortho position do more to accelerate the extraction than do the same groups in the meta and para relationships. The relative position of *o*-cresol to *m*- and *p*-cresol and of 1, 3, 2-xylenol to *sym*- or 1, 3, 5-xylenol is evidence of this fact. Negative substituents, on the other hand, lessen the speed of extraction, as is attested by the behavior of guaiacol and resorcinol.

The coincidence of the *m*- and *p*-cresol curves, just as the similarities in their boiling points, rules out extraction of alkaline phenate solutions as a possible means of separating these isomers by ether under the conditions of this experiment.

The curves (Figure 3) are not perfect parabolas, but, as a rule, approach this form over the majority of the range following the general expression,

$$y = kx^n$$

where k and n = constants for each compound for given experimental conditions

Thus, it is possible to approximate fairly closely the amount of pure compound extractable per unit time with the knowledge at hand of the proper constants to employ, which may be obtained readily for any set of empirical conditions by determining two points on the time-percentage extraction curve. The following constants satisfy the curves of Figure 3:

	n	k		n	k
sym-Xylenol	0.620	11.56	β-Naphthol	0.634	4.53
p-Cresol	0.663	8.82	Guaiacol	0.451	8.17

There is a divergence in the upper portions of the curves plotted from the equation and the experimental data. This behavior is exactly what one would anticipate, as the curves represented by the equations will cross the 100 per cent line and proceed indefinitely beyond. Also, the "driving force" of the hydrolysis reaction must weaken as the concentrations become low. It is interesting to note that *m*- and *p*-cresol follow the same equation in the early part of the extraction but diverge along different paths, the meta compound being bent down more. *o*-Cresol, 1, 3, 2-xylenol, and resorcinol exhibit extremely sharp changes of direction at the top of the curves. Resorcinol is unique in that the point of departure occurs relatively early in the extraction and in its decided change from great speed of extraction to extreme slowness.

Boyd (*1*) has determined the hydrolysis constant for a number of sodium phenates at 25° C. which are as follows:

	K_h at $V = 32$	Proportion Hydrolyzed %	$K_a \times 10^{-10}$
Guaiacol	0.000103	5.58	1.17
Phenol	0.000104	5.60	1.15
m-Cresol	0.000123	6.08	0.98
p-Cresol	0.000178	7.27	0.67
o-Cresol	0.000192	7.54	0.63
1, 2, 4-Xylenol	0.000233	8.28	0.52
1, 4, 2-Xylenol	0.000251	8.57	0.48
Carvacrol	0.000267	8.83	0.45
1, 3, 4-Xylenol	0.000352	10.07	0.34
Thymol	0.000373	10.34	0.32
2, 4, 5-Trimethylphenol (pseudocumenol)	0.000422	10.96	0.28
2, 4, 6-Trimethylphenol (mesitol)	0.000694	13.83	0.17

From his results he drew the following conclusions:

1. The acidity of phenol is diminished by introduction of alkyl groups.
2. Alkyl groups are most effective in the ortho position, slightly less effective in the para, and much less effective in the meta position. This rule applies to di- and trialkyl derivatives.
3. The isopropyl group in the ortho position acts more strongly than the methyl group, but in the meta position there is little difference.
4. The methoxy group in the ortho position scarcely alters the acidity of phenol.

The extraction experiments bear out some of these generalities but contradict others. That the introduction of alkyl groups does indeed reduce the acidity of phenol and that the ortho position is most effective are well established by both Boyd's work and the present investigation. On the other hand, the lack of harmony between the hydrolysis constants of *m*- and *p*-cresol and the extraction curves is also quite apparent. Moreover, the extraction curve of guaiacol does not bear out the statement that an *o*-methoxy group scarcely alters the acidity of phenol. It must be recalled, however, that the hydrolysis constant holds good only for dilute solutions and that one must expect fairly large deviations when dealing with normalities as high as 5.0. It is quite probable that the degree of hydrolysis in high concentrations of sodium phenates would follow the order of the curves. Another contributing factor in the extraction may be the rate at which an equilibrium condition, which is being continuously upset, is continuously approached.

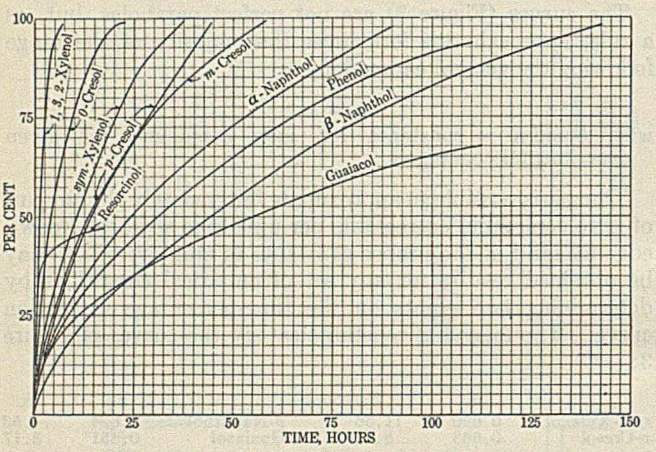

FIGURE 2. EXTRACTION CURVES OF ALKALINE PHENATE SOLUTIONS

From the data curves, Tables II and III have been calculated to show the percentages of each phenol extractable during arbitrary time intervals.

TABLE II. PERCENTAGES EXTRACTED IN SUCCESSIVE 5-HOUR PERIODS

	EXTRACTIONS IN 5-HOUR PERIODS									
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Phenol	18.5	9.0	6.5	5.5	5.0	4.5	4.5	4.0	4.0	4.0
o-Cresol	55.0	21.0	14.5	7.0	1.5	...	...	...	...	...
m-Cresol	24.0	15.0	13.0	9.5	7.5	6.5	5.5	5.0	4.0	3.5
p-Cresol	26.0	15.0	11.5	9.0	8.5	7.5	7.0	7.0	6.5	1+
sym-Xylenol	31.5	16.5	14.0	11.5	11.0	7.0	5.0	2.5+	...	...
1,3,2-Xylenol	96.0	2.5	..	..	..	...	...	...	...	...
α-Naphthol	20.0	10.5	8.0	6.5	5.5	5.0	5.0	4.5	4.0	3.5
β-Naphthol	12.0	8.0	6.0	4.5	4.5	4.0	4.0	4.0	3.5	3.5
Guaiacol	17.5	6.0	5.0	4.0	3.0	3.0	2.5	2.5	2.5	2.0
Resorcinol	42.0	3.0	2.0	..	..	...	...	..	...	...

TABLE III. TOTAL PERCENTAGES EXTRACTED FROM START OF REACTION

	HOURS									
	5	10	15	20	30	40	50	60	70	80
Phenol	18.5	27.5	34.0	39.5	49.0	57.5	65.5	72.5	78.5	84.0
o-Cresol	55.0	76.0	90.5	97.5	99+	99+	99+	99+	99+	99+
m-Cresol	24.0	39.0	52.0	61.5	75.5	86.0	93.5	99+	99+	99+
p-Cresol	26.0	41.0	52.5	61.5	77.5	91.5	99+	99+	99+	99+
sym-Xylenol	31.5	48.0	62.0	73.5	91.5	99+	99+	99+	99+	99+
1,3,2-Xylenol	96.0	99+	99+	99+	99+	99+	99+	99+	99+	99+
α-Naphthol	20.0	30.5	38.5	45.0	55.5	65.0	72.5	79.5	86.0	92.0
β-Naphthol	12.0	19.5	26.0	30.5	39.0	47.0	54.0	61.0	67.5	72.5
Guaiacol	17.5	23.5	28.5	32.5	38.5	43.5	48.0	52.0	66.0	69.5
Resorcinol	42.0	45.0	47.0	..	..	..	..	..	..	..

After a period of little more than 30 hours, these representative phenols (with the exception of β-naphthol and guaiacol) are all extracted to the extent of 50 per cent or more, inclusive of phenol itself. The extension of this idea to recovery of tar acids, which are largely phenolic, is clearly indicated. For example, if the acids should be removed from a tar distillate with 5 *N* caustic already containing 0.5 equivalent of phenols, and the resulting solution should be extracted exhaustively under conditions comparable to those described in the experimental part of this paper, they could be separated quantitatively from the caustic in 30 hours at the maximum, a time period considerably less than that which the springing operation often consumes in plant practice. Actually, much less time than 30 hours would be required because of the occurrence of large quantities of easily extractable individuals in mixed tar acids.

Additional advantage could be taken of the fact that it is possible to extract tar acids (from distillates of low-temperature tar at least) with less than an equivalent of caustic as has been shown by Cheng and Morgan (*2*). This fact is surprising and is explained on the basis of the high solubility of phenols in sodium phenate solutions.

Obviously, it would never be advantageous or practicable to attempt even an approach to the quantitative removal of high-temperature tar acids from caustic solutions at concentrations of alkali similar to that used in the present investigation, because of the relatively high proportion of elementary phenol and the slowness with which it is removed by ether in the upper regions of the extraction curve. Low-temperature acids, on the other hand, present a different picture. Here we find only a small amount of phenol but great quantities of derived phenols. The limiting percentage to the amount economically extractable would therefore be considerably greater.

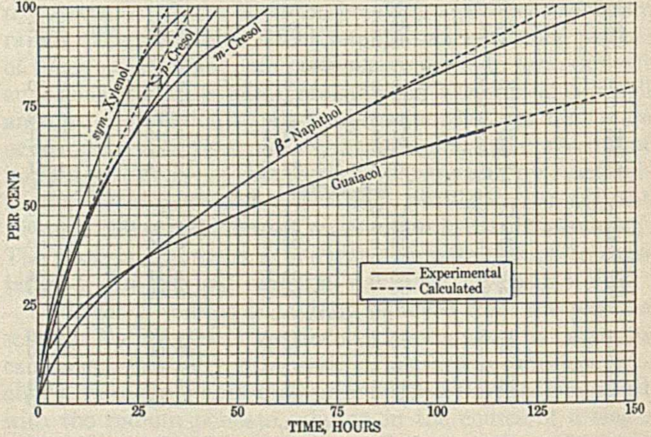

FIGURE 3. THEORETICAL AND EXPERIMENTAL CURVES OF ALKALINE EXTRACTIONS

The limits on speed of extraction have yet to be determined. Additional studies are being made of the effect of dilution, temperature, and variation of solvent. Increased throughput of ether would doubtless accelerate the extraction, but beyond a certain limit would not be proportional to it. The speed of stirring would naturally need to be slackened as the flow of ether increased to permit separation of the emulsified layers. A point would be reached when the same degree of equilibrium between caustic, phenol, and incoming ether would not be continuously established as in the case of the higher-speed stirring.

The accumulation of extraction data in connection with this problem is necessarily slow because of the long time intervals required in the extractions to establish the curves. It is inferred from the results of Vavon and Zaharia that solvents of the ether type would produce a more rapid extraction than hydrocarbons of either the aliphatic or aromatic series. Of the common solvents, however, there are numerous other possibilities not yet tried. Esters are, of course, out of the question because of the aqueous caustic, but such other volatile liquids as alcohols and ketones should be considered. Alcohols, in particular, merit study because of their generic relationship to phenols.

SUMMARY

1. It has been demonstrated that phenols are extractable from aqueous sodium hydroxide by means of ether to any attenuation desired, the time required being a function of the molecular structure (conditions of temperature, caustic concentration, and rate of ether flow being equal).
2. The time-percentage extraction curves approach the parabolic in form during the early part of the extraction but depart from the equation as the phenol becomes attenuated.
3. Alkyl substitutions favor rapidity of extraction but the ortho position is most influential in this respect. One *o*-methyl substitution accelerates the removal more than two *m*-methyl groups.
4. In the early part of the extraction *m*- and *p*-cresol follow the same equation but diverge along different paths.
5. Negative substituents affect the removal adversely.
6. The possibility of applying exhaustive ether extraction to recovery of tar acids in plant practice has been suggested as a means of short-circuiting the springing and recausticizing operations. Caustic soda containing 0.5 equivalent of tar acids could be used as a reagent for removing phenols from tar distillates, and the phenols could be recovered quantitatively in 30 hours at the maximum, the time required being a function of the number, type, and proportion of derived phenols.

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Synthetic Resins from Petroleum Hydrocarbons

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THE characteristic formation of gummy deposits in distillates has long been a problem in the petroleum industry. Numerous means are used to prevent the formation of these gums, and various cracking methods with subsequent treatments have been employed in an effort to obtain a high degree of unsaturation for antiknock value, without the troublesome gum formation in storage or when subjected to the warm parts of an internal combustion motor. The object of the present work, started several years ago, was to study the reverse of the above problem—that is, to learn if a useful resinous product could be obtained by the treatment of such unsaturated distillate. The result of this research has led to the production of a new synthetic resin, quite different in qualities and characteristics from the gummy deposit known to the petroleum industry. This resin has many interesting properties and is now being used in the paint, varnish, and plastic industries.

In the previously known methods of producing gummy materials by treatment with adsorbing agents, it is generally accepted that such gums result largely from the polymerization of the diolefin components. On the other hand, where a cracked distillate containing hydrocarbons of varying degrees of unsaturation (such, for example, as olefins and diolefins) is treated with a metallic halide catalyst in the manner described below, the reaction appears to include both condensation and polymerization to produce a new synthetic resin having valuable commercial properties. As is well known, both straight-chain and cyclic diolefins are produced by cracking charging stocks of various gas oils, but under the usual refinery practice these diolefins polymerize to aromatics and other compounds, so that, upon examination of the resulting distillate, only a small percentage of unchanged diolefins can be found. Where a high yield of this new resin is desired, conditions may be changed to produce a highly unsaturated distillate rich in diolefins and olefins. As diolefins change rapidly at high temperature, it is imperative to remove them immediately from their zone of formation during the cracking operation. Even then a large amount of aromatics will be formed, but, as explained later, these aromatics in the presence of unchanged diolefins are very useful and may enter into the resin reaction.

Numerous distillates of varying degree of unsaturation and of varying compositions have been polymerized in the course of this investigation by various methods to form resins, but in this paper only one catalyst—namely, anhydrous aluminum chloride—and one type of distillate will be discussed. The particu-

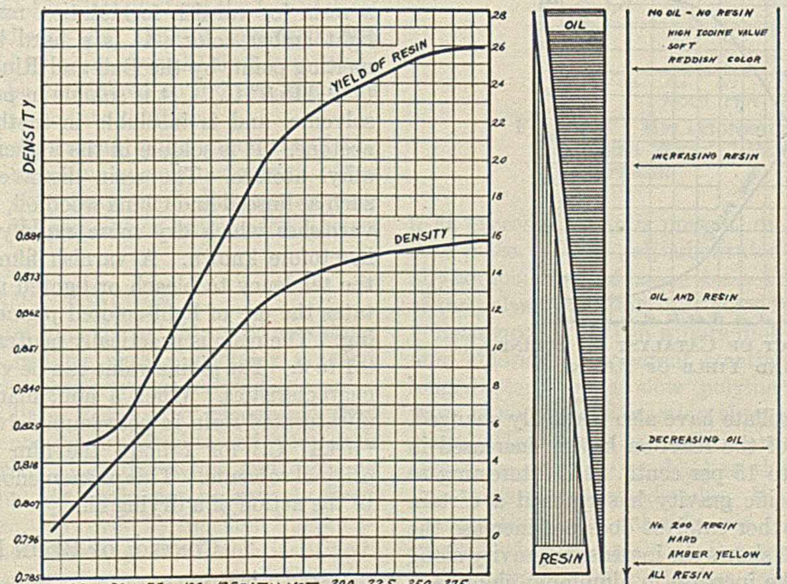

FIGURE 1. EFFECT OF CATALYST ON DENSITY AND YIELD OF RESIN

lar distillate described in this paper is one obtained by cracking at a high temperature and low pressure, and has the following characteristics:

Boiling range, ° C.	23–180
Specific gravity at 20° C.	0.84–0.86
Aromatics, %	40–55
Unsaturates, %	45–60
Bromine number, mg. per gram	1003
Refractive index	1.416–1.517
Molecular weight, average	150

The extreme tendency of such a distillate to polymerize on exposure to air, light, and heat make storage a difficult phase in working with these materials. No simple way of preventing this has been found. It has been the practice to fractionate material only slightly in advance of the needs of the plant. Storage in the raw state, with benzene and toluene as diluents, checks this loss of material to a high degree. The degree of polymerization on standing can be estimated by the change of refractive index.

A new synthetic resin having various industrial applications has been produced from highly unsaturated petroleum distillates. This resin is produced by polymerization and condensation of suitable distillates in the presence of aluminum chloride. The characteristics and yield of the resin are controlled by regulation of various factors in the resin formation. The reactions involved are many and very complex, probably including the reaction of olefins to form oily polymers, reaction of olefins with aromatics to form substituted aromatics, polymerization of diolefins and olefins to form resins, and reaction of diolefins with substituted aromatics to form resins.

EXPERIMENTAL PROCEDURE

Polymerization is carried out in vessels which are equipped with adequate cooling means, since much heat is liberated in the reaction. The catalyst, anhydrous aluminum chloride, is added in a finely divided state in a small continuous stream so as to avoid local heating as much as possible. The stream of catalyst is under control at all times, and toward the end of the reaction the rate of addition may be increased slightly. After a time a point is reached where no more heat is evolved with further addition of catalyst. In practice it is best to maintain a constant temperature in the reaction vessels. The distillate darkens in color as polymerization proceeds, and at the end of the reaction it has changed to a dark reddish brown color. The viscosity and specific gravity of the distillate have also markedly changed, the material at the end of the reaction having increased in specific gravity from 10 to 15 per cent. It is interesting to note that, when the specific gravity has reached a certain point, the addition of further catalyst does not increase the specific gravity. Figure 1 shows the increase in gravity along the vertical axis, while the increase in aluminum chloride is plotted along the horizontal axis. There is also shown the increase in yield of resin which accompanies the increase in density, and at the right is a diagrammatic explanation of the conversion of low-density oily polymers to high-density resins as polymerization progresses downward. After approximately 2 grams of aluminum chloride per 100 cc. of distillate have been added, there is no increase in specific gravity. This would indicate that no more catalyst is going into solution, and, if more catalyst is added, it will be found to be in suspension and not in solution as the previous additions.

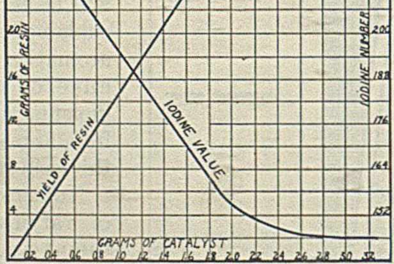

FIGURE 2. EFFECT OF CATALYST ON IODINE NUMBER AND YIELD OF RESIN

The reaction mixture obtained is then treated with a suitable alkali to break down the aluminum chloride complex, and the hydrocarbon resin remains in solution while there is precipitated the aluminum hydrate and the alkali chloride. There is also found in this precipitate an insoluble organic polymer. By filtering this solution, the inorganic material and the insoluble polymer can be separated from the solution of the resin. By repeatedly treating the solid residue with diluted acid and subsequent washing, all of the inorganic salts can be washed out, and there remains a white granular polymer, which is characterized by its insolubility in all organic solvents tried.

The resin solution may be distilled under reduced pressure to remove the solvents at as low a temperature as possible, and there is left behind a hard amber-colored resin. Superheated steam may be turned directly into the hot molten resin to remove the high-boiling oils formed during the reaction. By controlling the time and temperature of the steam treatment, the hardness of the resin can be controlled up to certain limits. Samples are taken from time to time during this operation, and, when the desired hardness is reached, the steam is shut off, and the molten resin run into shallow pans and allowed to cool.

The resulting resin is now suitable for various industrial applications, and the type of resin required may be produced by control of the factors of resin formation. For example, a resin for varnish formulation may be produced having a light amber color. It is a hard brittle material having a melting point, by the Ball and Ring method, of 230–240° F. (110–115.6° C.). It is soluble in practically all hydrocarbon solvents, and is insoluble in methanol, ethyl alcohol, and acetone. It is soluble in the higher acetates but insoluble in ethyl acetate. The resin dissolves readily in drying oils, such as linseed and China wood oil, and with the latter makes varnishes which dry more rapidly than any type of resin heretofore known. A varnish film of this composition has the tendency to bleach or lighten upon drying, which facilitates the use of light-colored pigments without after-yellowing. The resin is practically neutral, having an acid value of 0.1 to 2. The iodine value can be varied to bring out unusual characteristics. When a film, made by dissolving a highly unsaturated resin in petroleum solvents, is baked at 220° F. (104.4° C.) for 1 hour, the film becomes insoluble in its original solvents. This phenomenon is somewhat comparable to the action of a drying oil.

CONTROL OF RESIN FORMATION

In the formation of resin, an important factor is the amount of catalyst used. With all other conditions the same, the iodine value, yield, and color can be influenced by this factor alone. Figure 2 shows the increase of yield of resin with increase of aluminum chloride on a particular distillate. The vertical axis shows the amount of resin formed in grams per 100 cc. of distillate with increasing amounts of catalyst expressed in grams per 100 cc. of distillate. The yield increases with increase in catalyst to a certain point, where the curve then flattens out and the addition of more catalyst does not increase the yield of resin. There also is shown the decrease in iodine number of the resin formed with increasing amounts of catalyst, the iodine values being plotted along the right-hand vertical axis. Here again the iodine value reaches a point where it flattens out, beginning at about the point where the maximum yield is reached; as shown, the lower values are obtained as the amount of catalyst is increased. All points on these curves were obtained by taking out small samples at various intervals during the polymerization, and determining their resin content. The total time of this polymerization was 6 hours, with constant agitation.

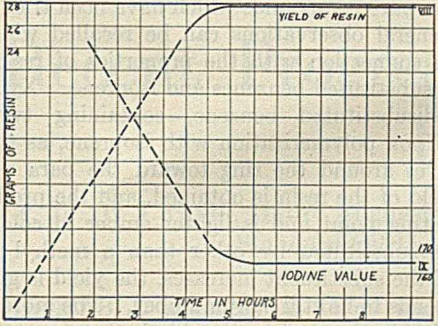

Figure 3. Effect of Time of Polymerization on Iodine Number and Yield of Resin

As pointed out in Figure 1, the effectiveness of the catalyst is believed proportional to the amount that goes into solution, and theoretically, if all of the catalyst could be put into solution immediately, time of polymerization would be greatly reduced. This is shown by curve VIII, Figure 3, which was made to study the effect of time upon yield, iodine value, and type of resin obtained. The catalyst, added as rapidly as possible without loss of material, was held constant at 2 grams per 100 cc. of distillate, while the time of polymerization varied from 4 to 9 hours.

The yield of resin obtained is plotted along the left vertical axis. This appears to indicate that time of polymerization does not increase the yield of resin after the first two points in the curve, which may be considered to indicate the time necessary for the catalyst to go into solution.

Curve IX in Figure 3 shows the iodine numbers of the resin obtained plotted against time of polymerization. It is extremely interesting to note that the iodine number remained constant and was the same after running for 9 hours as it was after 4 hours.

The Resin Reaction

It is very difficult to determine the actual reactions taking place, particularly when dealing with a complex cracked distillate. In studying the chemistry underlying the polymerization of cracked distillate, it was early recognized that specific compounds could not readily be obtained from such a source in sufficient purity. Certain olefins and diolefins were recognized as present, but could not be entirely freed from disturbing impurities. However, by repeated fractionation, many compounds have been purified and identified. Like compounds were then synthesized, and their behavior in the presence of anhydrous aluminum chloride was studied. Some unusual results were obtained in the case of the pure compounds. For the most part, these distillates consisted of both straight-chain and cyclic olefins and diolefins with aromatic compounds. There was also present a small amount of paraffin hydrocarbons which remained inert. When aluminum chloride is added to such a distillate, the four following reactions are believed to take place:

1. Reaction of olefins to form high-boiling oily polymers.
2. Reaction of olefins with aromatics to form substituted aromatics.
3. Polymerization of diolefins and olefins to form resins.
4. Reaction of diolefins with substituted aromatics to form resins.

Reaction 1. Sullivan (*1*) and his co-workers have pointed out that olefins can be polymerized with aluminum chloride to form lubricating oils. This reaction alone is detrimental in the formation of resin, and it is desirable to have no great excess of olefins present because such oils are difficult to separate from the resin. Such oils also cause the resin to have a low melting point and are not generally desirable in a resin that is to be used in the paint and varnish industry. However, it is beneficial to have a proper ratio of olefins to diolefins and to substituted aromatics.

Reaction 2. When olefins in the presence of aromatics are treated with anhydrous aluminum chloride, there is a condensation reaction resulting in the formation of substituted aromatics. Thus, *p*-amyltoluene is formed from amylene and toluene. Therefore, in the treatment of distillates such as are being described, a percentage of the olefins probably reacts to form substituted aromatics. This reaction does not stop with the monosubstituted compound, but, if an excess of olefin is present, di- and trisubstitutions may take place. These polysubstituted products are high-boiling oily compounds, and hence it is not desirable to have too much of the polysubstitution take place in this reaction.

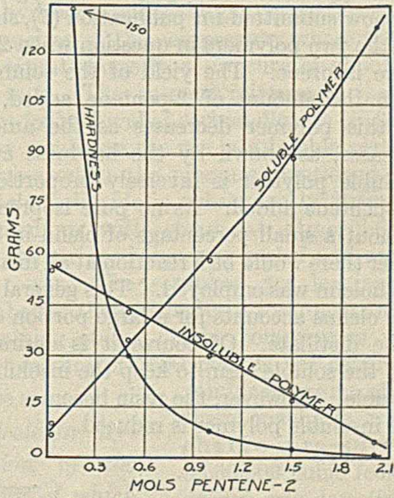

Figure 4. Relationship between Two Polymers When 2-Pentane Is Added to Isoprene

Reaction 3. When a pure diolefin is treated with aluminum chloride no apparent reaction takes place. Upon prolonged standing, a slow polymerization does occur, but there is no obvious reaction since no temperature rise takes place. However, if an olefin is present with the diolefin, and aluminum chloride is added to the mixture, a violent reaction takes place immediately. If the reaction is controlled, enough aluminum chloride can be added until a point is reached where the reaction is completed. When the aluminum chloride complex is broken down, there will be found two polymers—one soluble and the other insoluble in hydrocarbon solvents. The insoluble polymer, after purification from the inorganic matter, has been found by combustion to conform to the formula $(C_nH_{2n} - 2)_x$, which indicates that it is entirely a diolefin polymer. The insolubility of this polymer has prevented an accurate molecular weight determination.

TABLE I. REACTION OF ISOPRENE IN PRESENCE OF SUBSTITUTED BENZENE[a]

SUBSTITUTED BENZENE	ISOPRENE	AROMATIC	RESIN	PPT.	REMARKS
	Cc.	*Grams*	*Grams*	*Grams*	
Toluene	27.0	25	9.2	14.1	Extremely hard, clear, and brittle; very pale yellow-amber
o-Xylene	24.0	25	17.6	..	Hard, clear; dark cherry-red
m-Xylene	24.0	25	16.9	..	Hard, clear; dark cherry-red
p-Xylene	24.0	25	11.1	13.3	Hard, brittle, clear; amber-yellow
Ethylbenzene	48.0	50	17.7	18.9	Very hard, brittle; brownish amber
Propylbenzene	8.5	10	3.4	6.9	Very hard, clear, brittle; light amber-yellow
Isopropylbenzene	22.0	25	8.3	9.8	Very hard, clear, brittle; clear amber-yellow
Hexamethylbenzene	6.2	10	3.2	9.4	....
Hexaethylbenzene	10.0	25	4.6	9.2	Very hard and brittle, clear; deep cherry-red
sec-Butylbenzene	7.5	10	4.5	6.8	Hard, clear, brittle; deep brilliant red
tert-Butylbenzene	7.5	10	4.0	7.7	Very hard, brittle, clear; amber color
tert-Amylbenzene	28.0	48	14.0	12.9	Very hard, brittle, clear; brilliant amber-yellow

[a] Time, temperature, and catalyst were held constant.

The soluble polymer is a resin, usually of a light straw color, and its carbon-hydrogen ratio varies with the amount of olefin in the diolefin-olefin mix. The more olefin present, the softer the polymer, and combustions show it to be a mixture of the types of soluble polymers. Figure 4, taken from a paper now submitted for publication (*2*), shows the relationship of the two polymers in question when 2-pentene is added to pure isoprene. The yield of the soluble polymer increases with the amount of 2-pentene added, while the hardness of this polymer decreases as the amount of 2-pentene increases, as shown by the hardness curve. The yield of insoluble polymer is inversely proportional to the amount of 2-pentene added. As no pure isoprene could be obtained without a small percentage of olefin in it, it is not known whether there would be a reaction at all in a case where 100 per cent diolefin was employed. This general reaction of diolefins with olefins accounts for a large portion of the resin formed in the distillate. Of course it is desirable in the production of the soluble resin to keep the insoluble polymer as low as possible. However, the resin becomes softer as the proportion of insoluble polymer is reduced.

REACTION 4. It has been found that diolefins react with substituted benzenes to give hydrocarbon resins. Undoubtedly this reaction is similar to the olefin condensation with aromatics. The theory may be advanced that when diolefin is used instead of olefin, there is a double bond available in the side chain, which immediately reacts in the presence of aluminum chloride to form a hydrocarbon resin. Again studying this general type of reaction with pure materials, it has been found that this reaction takes place more easily when there is a substituted aromatic such as xylene or amylbenzene present than when ordinary benzene is present alone. In fact, no appreciable amount of resin is found in the case of a pure diolefin, such as isoprene with benzene. However, when benzene is replaced by toluene or xylene, there is an appreciable amount of resin formed. Table I gives some of the pure compounds which have been tried.

Some general observations can be recalled which are of interest in connection with the properties of resins formed from pure substituted benzenes and isoprene. Xylene is the simplest disubstituted benzene, containing two methyl groups. Upon polymerization with isoprene, as the methyl group moves around the ring toward the para position, a smaller yield of the resin is obtained, and the product has a higher melting point and is lighter amber in color. When benzene is substituted by other than a methyl group, as the size of the substituent increases, the yield is greater and the color tends to be still lighter amber. The more branched the substituent, the more noticeable is the above effect with regard to the physical properties.

Undoubtedly in the distillate all or part of these reactions take place simultaneously, probably with additional interreactions. Thus the diolefins react with the olefins and also with substituted benzenes to form resins. At the same time, substituted benzenes are being formed by the condensation of the olefins with aromatics. It must be borne in mind that the cyclic olefins and diolefins follow the same general reaction, and, usually in the case of the cyclic compounds, the reaction is much more vigorous and the resulting resin is harder and of better character.

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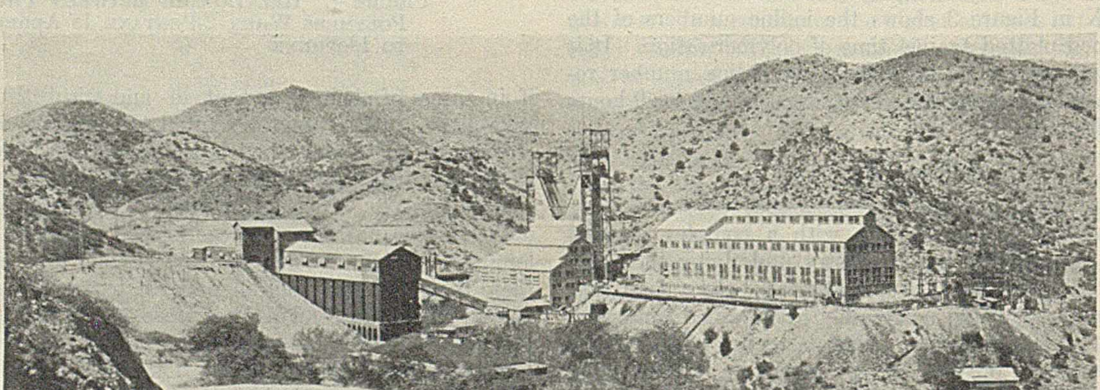

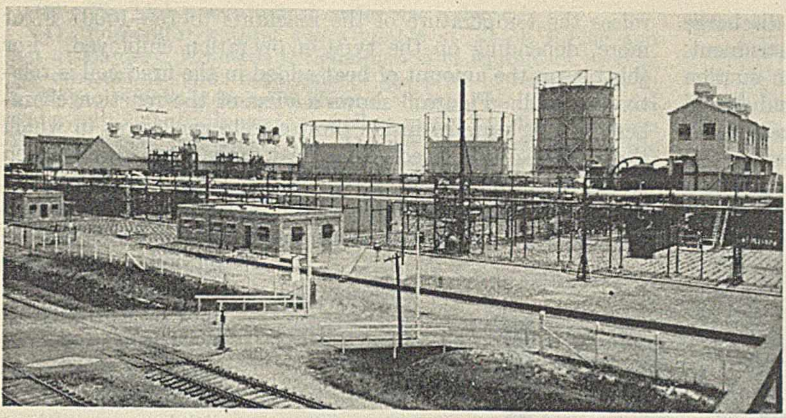

Figure 1. General View of Petroleum Hydrogenation Plant, Baton Rouge, La., Refinery of Standard Oil Company of Louisiana

Recent Progress in Hydrogenation of Petroleum

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Large-scale developments in petroleum hydrogenation include the construction of the second commercial plant, a description of which is given. Commercial runs of one year's operation without shutdown are cited to show the ruggedness of the catalyst and the workability of the process. Various examples of products made in commercial equipment are given to illustrate the flexibility of the process. Under technological developments, advances in lubricating oil hydrogenation, and antiknock gasoline production are discussed with examples. Particular emphasis is placed on the manufacture of two new products: hydrogenated high-flash safety fuel for aviation and marine use; and hydrogenated high-solvency naphthas for use as lacquer diluents, varnish thinners, rubber solvents, etc.

CONSIDERABLE advance has taken place in the commercial development and the technology of the petroleum hydrogenation process since results were last published in this journal about two years ago (*2*). The information herein presented is grouped into two major divisions: large-scale developments and technological developments.

LARGE-SCALE DEVELOPMENTS

The second large-scale commercial plant was placed in operation on May 23, 1931, at the Baton Rouge, La., refinery of the Standard Oil Company of Louisiana. This plant has an operating capacity of 4000 to 8000 barrels per day, depending on the type of feed stock. Figure 1 shows a general view of this plant.

Baton Rouge Hydrogenation Plant

Hydrogen Production. The hydrogen used in the operation of the Baton Rouge plant is obtained from natural gas according to the following reactions:

$$CH_4 + H_2O = CO + 3H_2$$
$$CO + H_2O = CO_2 + H_2$$

The first reaction is carried out in tubes packed with catalyst and heated by direct firing in a radiant-type downflow furnace to a temperature of about 1600° F. at approximately atmospheric pressure. Following this, additional steam is added, and the second reaction is carried out using a second catalyst at about 850° F. The gas leaving this stage of the operation is composed roughly of 78 per cent hydrogen, 20 per cent carbon dioxide, and 2 per cent unconverted hydrocarbons and other gases. The gas is cooled with water in a coke-packed tower and conducted to a holder for temporary storage prior to compression. Figure 2 shows a general view of the hydrogen production equipment at the Baton Rouge Hydrogenation Plant. The three units shown in Figure 2 can be operated independently and have a combined capacity of 9,000,000 cubic feet of pure hydrogen per day.

From the hydrogen holder the gas passes through a moisture trap to the suction of the compressors where the gas is compressed in several stages to a pressure of about 250 pounds per square inch. The gaseous mixture is then conducted to equipment for removal of carbon dioxide (Figure 3). This is effected by scrubbing the gas in a bubble plate tower with triethanolamine under the pressure mentioned above. The dissolved carbon dioxide is subsequently stripped from the scrubbing medium with steam at atmospheric pressure, after which the stripped liquor is cooled and recycled to the absorption tower. The scrubbed gas leaving this equipment shows better than 97 per cent hydrogen and is returned to the remaining stages of the compressors wherein it is raised to a pressure of 3600 pounds per square inch. The combined normal delivery of these machines with this discharge pressure is about 5,500,000 cubic feet of pure hydrogen per day (60° F. and 1 atm.). The compressors are operated at a rate sufficient to maintain a constant pressure in the reaction chambers. Figure 4 shows the compressor house of the Baton Rouge plant.

Safety Precautions in Handling Hydrogen. Because of the explosive nature of hydrogen-oxygen mixtures, many precautions have been taken to guard against infiltration of air to the hydrogen stream. Each compressor is provided with a recording oxygen alarm on its low-pressure side, which actuates a siren if more than

0.2 per cent oxygen is present. The combined discharge of all the machines is provided with a similar instrument. In addition, a low-pressure alarm is fitted to the suction of each compressor. This device is adjusted to sound should the suction pressure approach atmospheric. Pressure is normally maintained at about 10 inches of water at this point by the hydrogen holder. This holder, which acts as a surge chamber between the hydrogen-producing equipment and the compressors, has been provided with both high- and low-level alarms. Special precautions have been taken in all buildings to provide a high degree of ventilation in order to sweep out any hydrogen which might be vented through accidental leakage. Similarly, care has been exercised in construction to eliminate pockets beneath which this gas might collect.

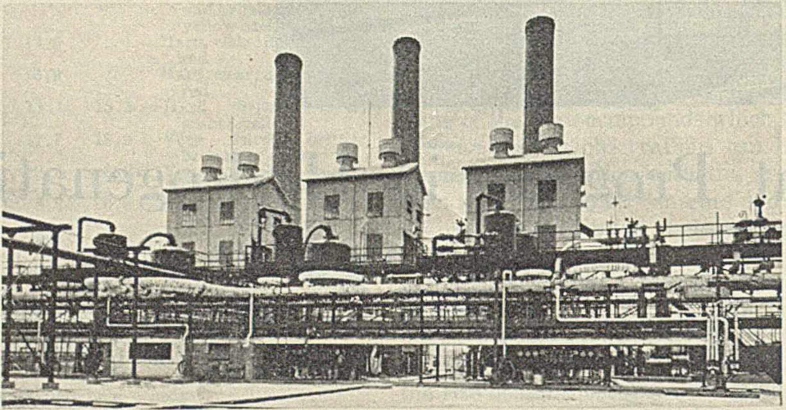

FIGURE 2. HYDROGEN PRODUCTION EQUIPMENT AT BATON ROUGE HYDROGENATION PLANT

FLOW OF OIL IN PROCESS. The stock to be hydrogenated is raised to operating pressure by steam-driven plunger pumps, the exhaust steam from which is employed in hydrogen manufacture. The high-pressure pump house, which also serves as the control room for the carbon dioxide removal system, is shown in Figure 5.

The hydrogen from the compressors, together with recycled gas, is now mixed with the oil and delivered to tubular heat exchangers where the mixture is preheated by the hot hydrogenated products coming from the reaction chambers. Following this, additional heat is supplied in a fired pipe coil wherein the temperature of the mixture is raised to about 700–850° F., after which it is introduced into the reaction chambers. These drums, which are about 40 feet in length and mounted vertically, are connected in series, three or four being used in each of the two units of the plant. The reaction space is about 3 feet in diameter. This free space is lined with a noncorrosive alloy and filled with a sulfur-resistant catalyst. Since the hydrogenation reaction is exothermic, an increase in temperature takes place as the oil and hydrogen pass through the catalyst bed. This raises the temperature of the reactants to 750–1000° F. or more, depending on the type of operation employed. For this reason the amount of heat added in the fired coil is relatively small. Figure 6 shows a view of the reaction chambers looking upward inside the concrete enclosures in which these vessels are placed. The heat exchangers may be seen at the left of the picture.

From the reaction chambers the mixture of hydrogenated products and gas pass through the heat exchangers, a cooling coil, and thence to a separator. Here the gas and liquid products are separated under full pressure, the liquid being withdrawn to a low-pressure separator from which it passes to storage. The gas from the high-pressure separator is conducted to a booster compressor where it is recompressed to an operating pressure of 3600 pounds per square inch for mixing with the fresh hydrogen coming from the compressors. The booster compressors normally operate with a pressure of about 350 to 600 pounds per square inch differential. Gases which are formed in the process are, in many cases, removed to a sufficient extent by solubility in the liquid product. However, high-pressure scrubbing equipment is provided for removal of these gases if necessary. By this means the recycle gas coming from the high-pressure separator is scrubbed with oil prior to recompression in the booster compressors.

The Baton Rouge Hydrogenation Plant, although similar in general to the first large-scale plant erected at Bayway, N. J., possesses certain improvements as a result of experience gained at the latter. These may be summarized as follows:

(1) Sea water is used at the Bayway plant for removal of carbon dioxide from the hydrogen gas. This was replaced with triethanolamine in the second plant with consequent savings in power and equipment size, inasmuch as about one-thirtieth as much scrubbing liquid is required. In addition to this, more complete removal of carbon dioxide was obtained.

(2) Piping and layout were simplified owing to experience gained in pressure drop in Bayway high-pressure equipment.

TABLE I. LUBRICATING OILS PRODUCED IN COMMERCIAL-SCALE HYDROGENATION

	FEED STOCK			
	Van Zandt lubricating dist.	Colombian lubricating dist.	Reagan lubricating dist.	East Texas pressed paraffin dist.
Gravity, ° A. P. I.	20.0	20.4	24.9	24.6
Saybolt viscosity at 100° F.	3700	1572	580	293
Saybolt viscosity at 210° F.	144	86	64	50
Viscosity index	62	35	78	73
Flash, ° F.	550	445	380	410
Pour, ° F.	125	15	115	25
Conradson carbon, %	2.70	0.86	0.45	0.07

	PRODUCTS[a]				
	S. A. E. 60[b]	S. A. E. 20[c]	S. A. E. 40	S. A. E. 20[b]	"200" Oil
Gravity, ° A. P. I.	26.6	28.8	29.7	29.8	31.2
Saybolt viscosity at 100° F.	1510	327	670	332	206
Saybolt viscosity at 210° F.	111	52	72	55	47
Viscosity index	95	81	95	100	104
Flash, ° F.	585	425	505	435	430
Pour, ° F.	40	35	50	25	35
Conradson carbon, %	0.55	...	...	...	Trace
Color, Robinson	12	17	14	18	....

[a] Products shown are bottoms oils obtained by fire and steam reduction of the hydrogenated product to the desired viscosity. The oils taken overhead during this reduction are lighter lubricating oils, gas oil, and gasoline. No finishing treatment has been applied. In two cases the reduced bottoms have been dewaxed.

[b] After dewaxing.

[c] Obtained as an overhead oil in reduction of the hydrogenated product to S. A. E. 40.

(3) The high-pressure final cooler was reduced in size.

(4) Low-sulfur natural gas available at Baton Rouge and not at Bayway permitted the elimination of equipment used in the removal of sulfur from refinery gas prior to reformation to hydrogen. This included a Koppers plant, and caustic and water-scrubbing equipment, as well as means for disposal of the Koppers plant foul gas. Also, the use of natural gas in the hydrogen furnace burners at Baton Rouge avoided the necessity of forced air blast equipment.

(5) The appearance of the plant was generally simplified and improved.

TABLE II. BURNING OILS PRODUCED IN COMMERCIAL-SCALE HYDROGENATION

	FEED STOCK	
	Refinery gas oil	West Texas gas oil
Gravity, ° A. P. I.	34.9	38.8
Refined oil viscosity at 60° F.	790[a]	430
Pensky-Martens flash, ° F.	80	...
Color	Straw	...
Sulfur, %	0.77	0.61
Initial boiling point, ° F.	210	284
10%, ° F.	444	400
50%, ° F.	515	446
90%, ° F.	594	516
Final boiling point, ° F.	657	614
	PRODUCT[b]	
	Burning oil	Burning oil
Gravity, ° A. P. I.	44.5	45.3
Refined oil viscosity at 60° F	405	400
Abel flash, ° F.	113	132
Color, Saybolt	+20	...
Sulfur, %	0.006	0.018
Initial boiling point, ° F.	310	346
10%, ° F.	364	380
50%, ° F.	435	420
90%, ° F.	513	476
Final boiling point, ° F.	552	541

[a] Extrapolated value.

[b] These inspections are on the burning oil as distilled from the hydrogenated product and without finishing treatment. In addition to the burning oil, the hydrogenated product normally contains 20 to 30 per cent gasoline.

RESULTS OF OPERATION OF LARGE-SCALE PLANTS

The operation of the two large-scale plants since their completion has demonstrated the workability of the process. Inasmuch as no coke is formed by the hydrogenation method, and since the catalysts employed are extremely rugged, the process is virtually continuous. In April, 1932, one of the units of the Bayway plant completed a run which had been in continuous progress without shutdown for one year. Another run is now in its eighth month of continuous operation in this plant. Similarly, at the Baton Rouge plant the most recent shutdown was at the completion of more than 10 months' operation. In this run and in the one mentioned for the Bayway plant, operation was suspended, since the catalyst had been in service for more than one year and required reworking. This catalyst is normally removed from the reaction chambers and restored to its original activity by chemical treatment.

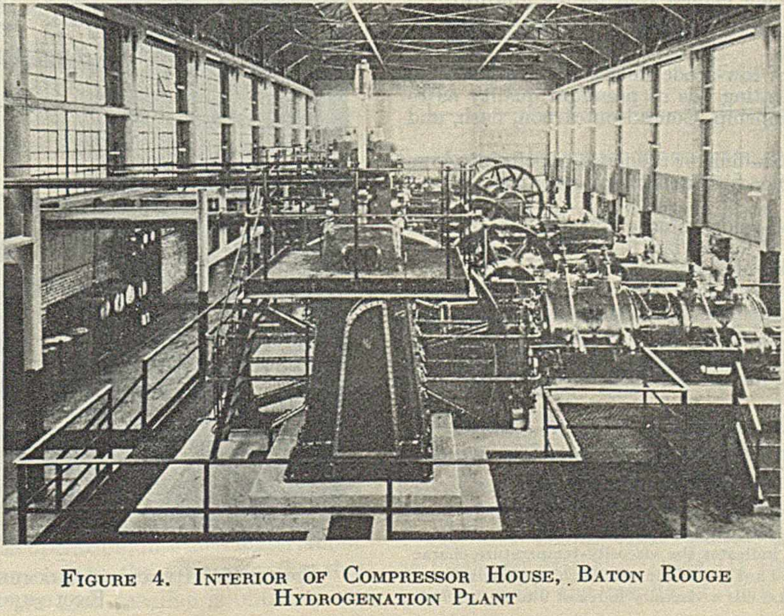

FIGURE 4. INTERIOR OF COMPRESSOR HOUSE, BATON ROUGE HYDROGENATION PLANT

In the production of hydrogen at the Bayway plant from refinery gas, as mentioned above, additional difficulty is incurred over the use of natural gas, in that it is necessary to remove approximately all traces of sulfur, as well as to limit the amount of higher hydrocarbons in the gas in order to avoid loss of catalyst activity in the first stage of the process. Two years' operation on this plant has shown the feasibility of continuous production of hydrogen of better than 96 per cent purity by this method and, in addition, has demonstrated that the metals used in the construction of the equipment are capable of withstanding the severe service to which they are subjected. No difficulty has been experienced from hydrogen attack or other types of corrosion of the high-pressure equipment, nor has heating and handling of the reacting materials under conditions of high temperature and pressure offered any obstacles in commercial operation. Although working with oil-hydrogen mixtures at high pressure and temperatures up to 1000° F., no lost-time accidents have occurred due in any way to the process.

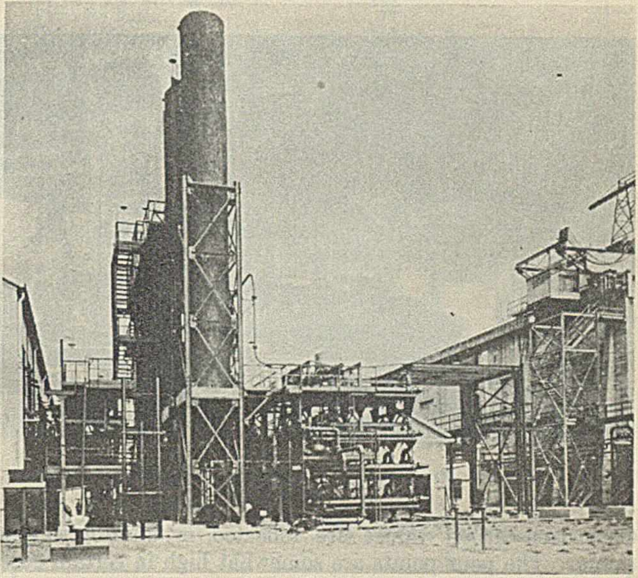

FIGURE 3. EQUIPMENT FOR REMOVAL OF CARBON DIOXIDE FROM HYDROGEN

Since their construction, the large-scale plants have found service in meeting variations in refinery demands and as such have produced high-quality motor oils, high A. P. I. gravity burning oils, gasoline, and neutral oils of quality comparable with those made from Pennsylvania crudes. For these purposes, distillates from Colombian, West Texas, East Texas, Midcontinent, and other crude sources have been charged to the plants. Considerable time has been spent in the production of motor oils, which have recently been placed on the market.

Table I shows representative lubricating oil products which have been obtained by commercial operation on several of these stocks. The inspections show the oils as obtained by laboratory work-up from the hydrogenated product without finishing treatment. Table I also demonstrates that high- and low-pour distillates have been handled having viscosities up to 144 seconds Saybolt at 210° F. These stocks have yielded products characterized by high A. P. I. gravity, high viscosity index,[1] and high flash points. Low Conradson-carbon values are reflected in uniformly good colors. The pour points are somewhat high in certain cases owing to inefficient laboratory dewaxing, and in two instances to the omission of dewaxing.

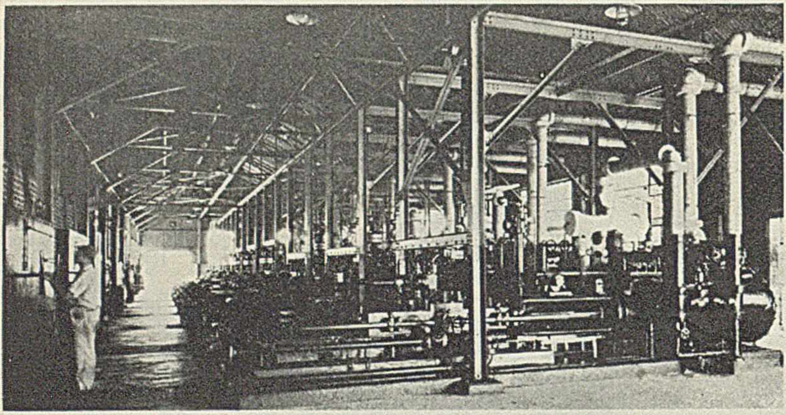

Figure 5. High-Pressure Feed Pumps

Table II shows inspections of burning oils produced by commercial hydrogenation of gas oil fractions. The products are low in sulfur and exhibit high A. P. I. gravity for their viscosity, thus indicating superior burning qualities. It is interesting to note in this connection that lamp tests of the commercial hydrogenated kerosenes have shown them to possess burning characteristics considerably superior to those indicated by their viscosity-gravity relationship.

All the hydrogenated products which have been produced commercially have been finished by the usual large-scale refinery methods. The amount of chemical treatment has been small in all cases, particularly in kerosene production where only a doctor treatment was required for finished burning oil.

TECHNOLOGICAL DEVELOPMENTS

A previous article (*2*) has shown five major adaptations of the petroleum hydrogenation process:

(1) The improvement of low-grade lubricating distillates to obtain high yields of lubricating oils of premium quality as to viscosity-temperature relationship, Conradson carbon, flash, and gravity.

(2) The conversion of paraffinic or aromatic gas oils into low-sulfur, gum and color stable, high-antiknock gasolines without production of coke or tar.

(3) The alteration of off-color, inferior burning oils or light gas oils to produce high A. P. I. gravity, low-sulfur, water-white kerosenes of superior burning characteristics.

(4) Conversion of heavy, high-sulfur, asphaltic crude oils and refinery residues into gasoline and distillates low in sulfur and free from asphalt, without concurrent formation of coke.

(5) The desulfurization, and color and gum stabilization of high-sulfur, badly gumming naphthas.

Recent work on item 2 has brought out new applications which are of sufficient importance to be classed as a major adaptation of the process:

(6) Manufacture of new and specialized products, such as high-flash safety aviation fuel of high-antiknock quality, and high-solvency naphthas for use as varnish and lacquer diluents, etc.

Development in the past two years has been limited chiefly to items 1, 2, and 6. However, the conversion of heavy crudes and tars (item 4) has been in continuous commercial operation in the plants of the I. G. Farbenindustrie in Germany during this time, as have other of the adaptations of the process.

Improvement of Low-Quality Lubricating Distillates

During the past two years new methods of catalyst manufacture have been developed, whereby it has been possible to obtain greater through-put, as well as greater yields and longer catalyst life. This latter feature is illustrated by the large-scale runs, mentioned previously, in which one year's service was obtained from the catalyst before reworking became necessary.

Lubricating distillates from a great number of crude sources have been investigated. Among these have been cuts from Colombian, Van Zandt, Reagan, Winkler, Burbank, Pecos, and Santa Fe Springs, as well as fractions from other East Texas, Midcontinent, Coastal, Californian, West Texas, and Venezuelan crudes. Intensive effort has been directed toward the interpretation of the results obtained by hydrogenation of different fractions of these crudes under various conditions of catalyst, temperature, time of contact, hydrogen pressure, etc.

Advance has been made toward the treatment of raw lubricating distillates of higher viscosity. Figure 7 shows results obtained in an operation of this kind upon a heavy

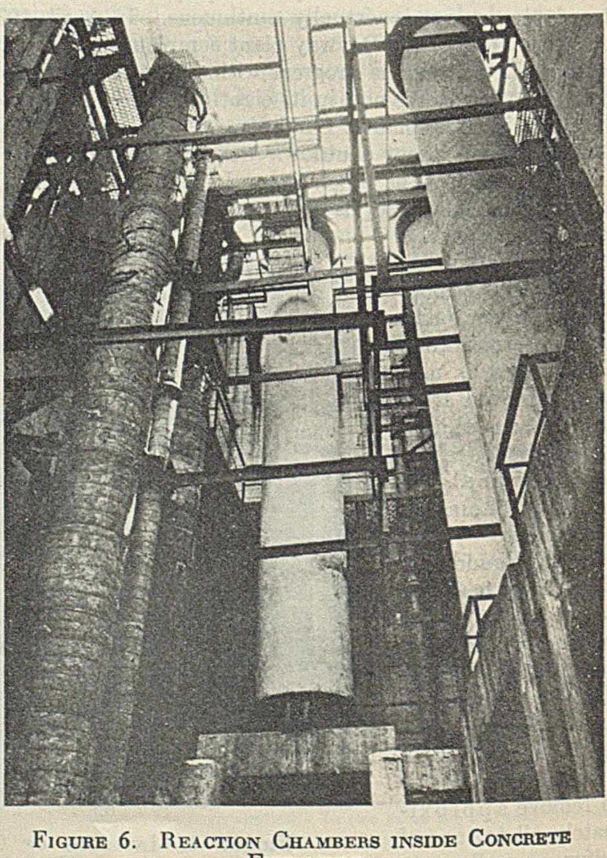

Figure 6. Reaction Chambers inside Concrete Enclosure

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[1] The term "viscosity index" was devised by Dean and Davis, *Chem. & Met. Eng.*, 36, 618 (1929), and indicates the viscosity-temperature characteristics of a lubricating oil. Thus paraffinic oils such as Pennsylvania have an index of 100, and Coastal oils a viscosity index of 0 to 20.

Midcontinent lubricating fraction. As is characteristic of the process, part of the feed has been converted to gasoline and gas oil, and the remainder to lubricating oil of somewhat lower viscosity but of much higher quality. In general, from 100 barrels of feed, 103 to 108 barrels of hydrogenated product are obtained, which in turn contain 60 to 85 barrels of lubricating oil, 10 to 35 barrels of gas oil, and 5 to 10 barrels of gasoline. Figure 8 shows products obtained by treatment of a West Texas lubricating fraction.

The hydrogenated lubricating oils are characterized by high viscosity index and high flash points, both of which qualities are found in the Pennsylvania type oils. The disadvantage of high Conradson-carbon content possessed by Pennsylvania oils, however, is not found in the hydrogenated products, thus accounting for their low carbon formation in actual service. Although not shown in Figures 7 and 8, from 80 to 90 per cent of the sulfur in the feed stock is eliminated by hydrogenation as hydrogen sulfide. Other alien elements, such as nitrogen and oxygen, are also removed as gaseous hydrides. Color is greatly improved, thus reflecting the low Conradson carbons characteristic of hydrogenated lubricants. These products have accordingly shown application in the manufacture of medicinal oils, white oils, and other products requiring high purity.

Numerous engine tests, both laboratory and field, which have been carried out on hydrogenated motor oils, have demonstrated them to be superior to the highest grade natural lubricants, as regards oil consumption, carbon formation, valve gumming, and engine wear, both for conditions of moderate and severe service. A description of some of these motor tests may be found in a paper by Haslam and Bauer (*1*).

FIGURE 7. PRODUCTS FROM TREATMENT OF MIDCONTINENT LUBRICATING FRACTION

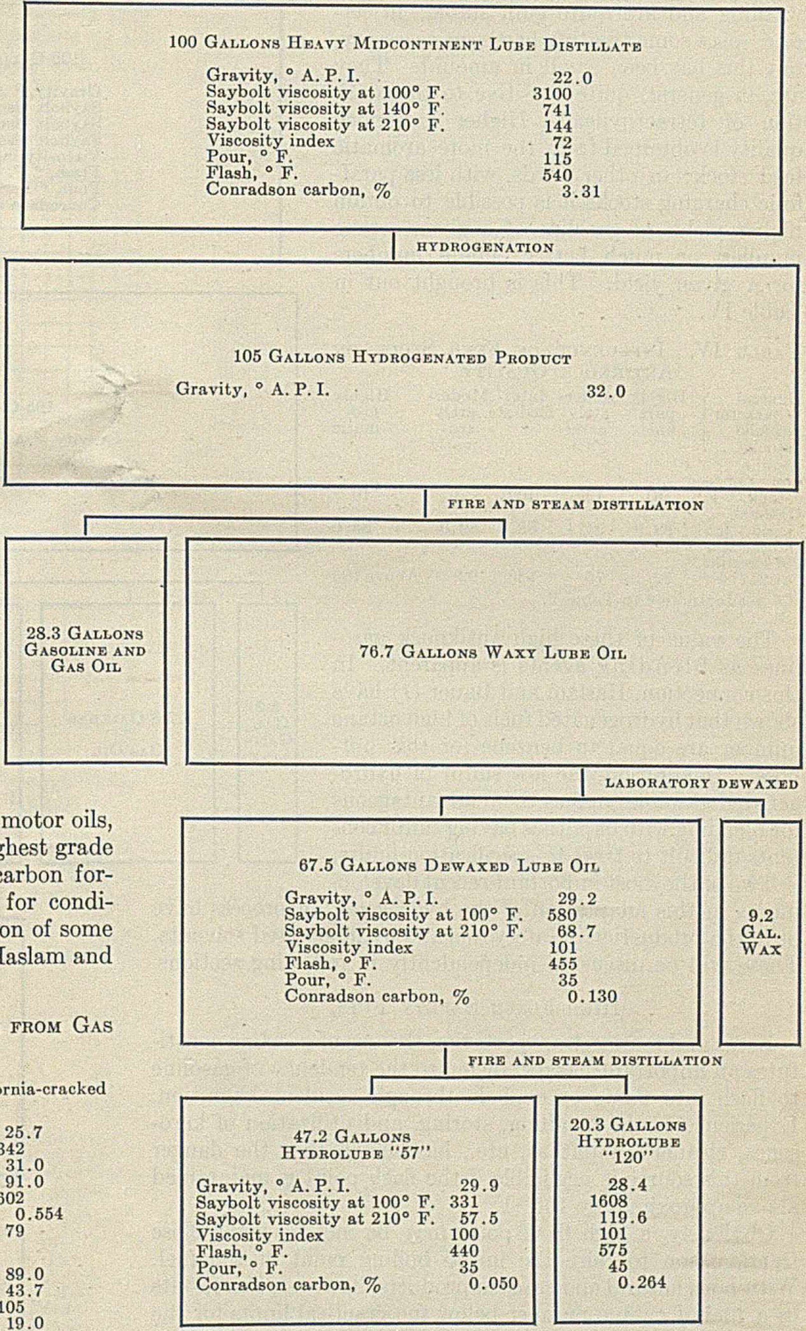


TABLE III. PRODUCTION OF ANTIKNOCK GASOLINE FROM GAS OILS

	Gas Oil Midcontinent	Gas Oil California-cracked
FEED STOCK		
Gravity, ° A. P. I.	37.8	25.7
Initial boiling point, ° F.	435	342
At 460° F., %	3.5	31.0
At 550° F., %	90.0	91.0
Final boiling point, ° F.	629	602
Sulfur, %	0.179	0.554
Aniline point, ° F.	159	79
HYDROGENATED PRODUCT[a]		
Yield, % by volume	86.5	89.0
Gravity, ° A. P. I.	56.4	43.7
Initial boiling point, ° F.	86	105
At 212° F., %	36.0	19.0
At 284° F., %	61.0	47.5
At 356° F., %	83.0	85.5
At 374° F., %	87.5	90.0
Final boiling point, ° F.	433	417
Octane number at 212° F.[b]	75.1	94
Dissolved gum, mg./100 cc.	3.6	2.8
Sulfur, %	0.022	0.017

[a] As received from hydrogenation unit.
[b] See footnote [a] to Table V.

PRODUCTION OF ANTIKNOCK GASOLINES

As pointed out in previous papers, the production of antiknock gasolines by hydrogenation, although carried out in the same equipment as the other adaptations of the process, differs from them, in that the extent of hydrogenation is limited so that stable but nonparaffinic products are formed. Sufficient hydrogenation is permitted to take place to avoid the formation of coke or tar. Two methods of operation have been employed: recycle operation, in which material not converted to gasoline is recycled to the operation (by this means a yield of 85 to 95 per cent gasoline is obtained on the charge, the remainder going to gas); once-through operation, whereby products above the gasoline boiling range are not returned to the reaction zone. The majority of work has been carried out on the recycle method of operation.

As with lubricating-oil hydrogenation, experimentation has been carried out with new and more active catalysts in order to obtain greater through-put and yields. The temperature of operation has been increased to higher levels with resulting improvements in conversion and antiknock quality.

The process has been found to be particularly applicable to aromatic, low aniline-point gas oils. Feed stocks which have been studied include straight-run and cracked gas oils from Midcontinent, California, West Texas, Coastal, East Texas, and Talang Akar crudes, as well as material such as Edeleanu extract. Table III shows two of these stocks together with the results of their hydrogenation.

The gasolines are low in sulfur and gum. They pass doctor and corrosion after lye washing and are quite gum stable; in certain cases some treating has been necessary, but this has been small in amount. They are, in general, quite sensitive to the addition of tetraethyllead. Higher antiknock quality is obtained from the more aromatic feed stock; in other words, with less paraffinic charging stocks it is possible to obtain higher yields of gasoline of a given octane number, or much better octane numbers for a given yield. This is brought out in Table IV.

TABLE IV. INFLUENCE OF FEED STOCK ON ANTIKNOCK QUALITY

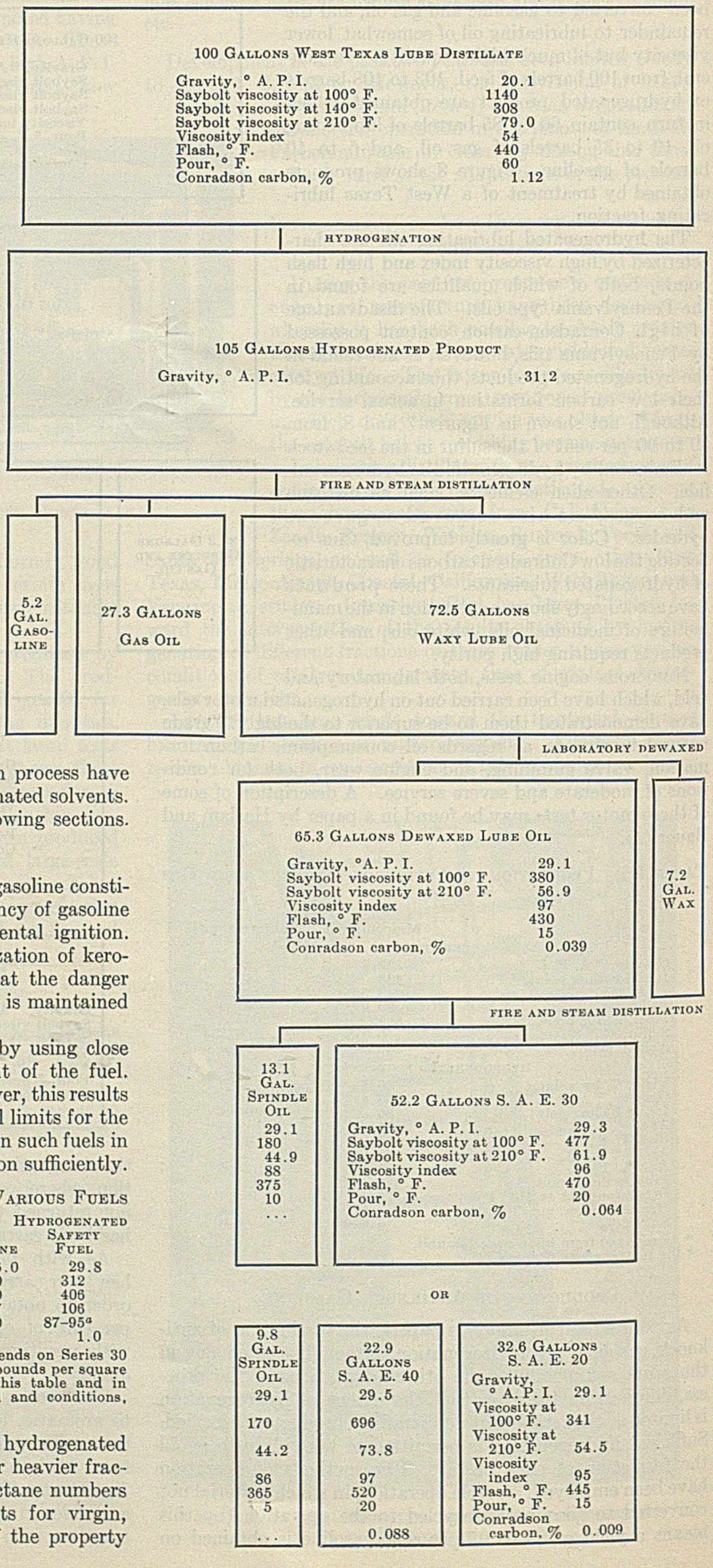
General character of feed stock	Highly paraffinic	Moderately paraffinic	Intermediate	Moderately aromatic	Highly aromatic
Aniline point of feed stock, ° F.	161	139	102	79	10
Gasoline yield, %	89.9	91.4	88.0	89.0	88.0
Octane No. of gasoline at 212° F.[a]	72	75	85	92	Above 100

[a] See footnote [a] to Table V.

The value of these high antiknock gasolines as blending agents is apparent. In this connection, Haslam and Bauer (*1*) have shown that hydrogenated fuels of high octane number are equal to benzene for this purpose. In addition, the low sulfur of hydrogenated gasolines makes them advantageous for blending with naphthas having sulfur contents difficult to treat to specification limits.

Two of the most important recent developments in this adaptation of the hydrogenation process have been the production of safety fuel and hydrogenated solvents. These will be discussed independently in following sections.

FIGURE 8. PRODUCTS FROM TREATMENT OF WEST TEXAS LUBRICATING FRACTION



HIGH-FLASH SAFETY FUEL

In air and marine transportation the use of gasoline constitutes an important hazard, owing to the tendency of gasoline to flash into flame or explode through accidental ignition. Experience in the handling, storing, and utilization of kerosenes, cleaner's naphthas, etc., has shown that the danger from this source is negligible if the flash point is maintained above approximately 105° F.

Obviously, a high flash point may be met by using close fractionation to raise the initial boiling point of the fuel. With both natural and cracked products, however, this results in a fuel of octane number below the practical limits for the Otto-cycle engine. The use of tetraethyllead in such fuels in permissible amounts does not improve detonation sufficiently.

TABLE V. COMPARISON OF SPECIFICATIONS OF VARIOUS FUELS

	Av. Commercial Gasoline	Kerosene	Hydrogenated Safety Fuel
Gravity, ° A. P. I.	59.0 to 68.0	46.0	29.8
Initial boiling point, ° F.	90 to 105	380	312
End point, ° F.	390 to 435	550	406
Abel flash, ° F.	−40 to −55	107	106
Octane number	65 to 75	Below 50	87–95[a]
Copper-dish gum, mg./100 cc.	5 to 7	....	1.0

[a] Determined against isoöctane and normal heptane blends on Series 30 engine, 300° F. jacket temperature, 600 r. p. m., 190 200 pounds per square inch compression pressure. Other octane numbers in this table and in Tables III and IV were obtained by the same method and conditions, except at the less severe jacket temperature of 212° F.

In contrast to this, it has been found that hydrogenated fuels have the best antiknock qualities in their heavier fractions. This is shown in Figure 9 (*1*) where octane numbers are plotted against various distillation points for virgin, cracked, and hydrogenated fuels. Because of the property of high octane number with high-boiling motor fuel fractions, hydrogenation yields a high-flash safety fuel of extremely good quality. This safety gasoline has already been placed on the market. Table V shows a comparison of the specifications of commercial gasoline and kerosene with those of hydrogenated safety fuel.

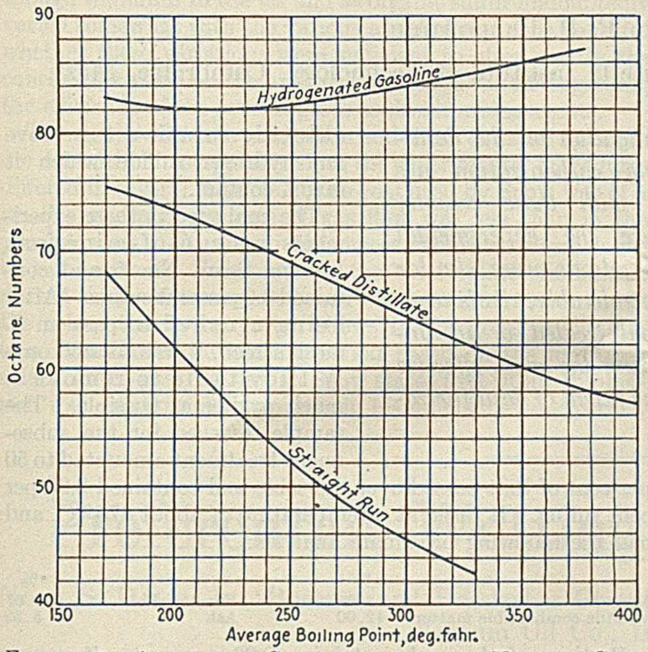


Figure 9. Antiknock Characteristics of Various Gasolines Plotted as Function of Boiling Range

In the production of high-flash fuel the hydrogenated product from the unit is distilled into two cuts. The bottoms fraction comprises the safety fuel, whereas the overhead cut represents a high-quality light aviation fuel. Table VI shows a typical example of the feed stock and the two products obtained.

Table VI. Production of High-Flash Safety Fuel

Feed Stock

Gravity, ° A. P. I.	25.5	Aniline point, ° F.	10
Sulfur, %	0.89	Initial boiling point, ° F.	348
Color, Saybolt	8	Final boiling point, ° F.	570

	Hydrogenated Products Light aviation fuel	 High-flash aviation fuel
Yield on feed, %	29.0	55.0
Gravity, ° A. P. I.	49.5	28.5
Sulfur, %	0.005	0.010
Abel flash, ° F.	...	107
Color, Saybolt	30	28
Color hold (1 hr. sunlight)	No drop	No drop
Copper-dish gum, mg./100 cc.	2.5	4.8
Doctor	Passes	Passes
Corrosion	Passes	Passes
Aniline point, ° F.	...	−20
Octane number at 300° F.[a]	83	93
Initial boiling point, ° F.	100	309
Final boiling point, ° F	335	411

[a] See footnote [a] to Table V.

The difference between the sum of the yields of the two products in Table VI and 100 per cent is represented by loss of feed to gas during the hydrogenation operation. The two products are characterized by high octane number, low sulfur and gum, and good color. Their high antiknock value makes them suitable for blending purposes to replace benzene and tetraethyllead.

Practical use of any high-flash fuel requires special attention for ease in starting. There are a number of solutions to this problem, most of which are in use at the present time. Among these are direct fuel atomization into the engine cylinder, provision for starting on gasoline, auxiliary vaporizing devices, etc. A more extensive discussion of hydrogenated safety fuels may be found by reference to Howard (*3*).

High-Solvency Naphthas

As in the production of safety fuel, solvents are obtained under hydrogenating conditions analogous to those in the manufacture of high octane-number gasoline. Low aniline-point straight-run, or cracked light-gas oils serve as the feed stock. The solvent power of naphthas so produced is much superior to that of ordinary petroleum solvents. Table VII compares a typical hydrogenated solvent with a petroleum and a coal-tar solvent of similar boiling range.

Table VII. Comparison of Various Solvents

	Solvent Naphtha Hydrogenated	 Normal petroleum	 Coal-tar
Gravity, ° A. P. I.	31.6	51.9	33.1
Color, Saybolt	25	30	22
Aniline point, ° F.	−19[b]	147	17
Sulfur, %	0.06	0.03	0.06
Initial boiling point, ° F.	293	311	302
Final boiling point, ° F.	412	413	378
Kauri butanol value[a]	77	30	72

[a] Standard testing method in the varnish and lacquer industry, denoting the amount of solvent naphtha which can be added to a standard Kauri gum solution without coagulation.
[b] Extrapolated value.

In solvents of the type shown in Table VII, high solvency is indicated by low A.P.I. gravity, low aniline point, and high Kauri butanol value. On this basis the hydrogenated solvent naphtha is decidedly superior to the petroleum solvent produced by ordinary refining methods, and in addition can be made better than coal-tar products as shown in Table VII.

In the production of solvents, the hydrogenated product from the unit is fractionated into a number of cuts of desired boiling range. The relative proportions of these fractions, as well as their distillation characteristics, may be controlled by adjustment of feed-stock boiling range. Table VIII shows three narrow-cut solvent naphthas obtained by fractionation of the hydrogenated product from a low aniline point, light-gas oil.

Table VIII. Hydrogenated Solvent Naphthas

Cut:	280–375° F.	320–400° F.	340–420° F.
Gravity, ° A. P. I.	34.7	28.7	25.6
Color, Saybolt	25	27	27
Aniline point, ° F.	−22[a]	−50[a]	−27[a]
Corrosion (copper)	Pass	Pass	Pass
Sulfur, %	0.02	0.03	0.02
Flash, ° F.	83	107	126
Kauri butanol value	74	78	80
Dimethyl sulfate value	100	100	100
Initial boiling point, ° F.	286	318	340
Final boiling point, ° F.	374	398	418

[a] Extrapolated values.

Commercial production is now under way for the establishment of a complete line of hydrogenated solvent naphthas. These materials find application as lacquer diluents, paint and varnish thinners, rubber solvents, and resin solvents, as well as in a number of special uses where a combination of high solvent power and controlled evaporation rate is essential. Tests have shown these high-solvency naphthas to be equal to toluene and xylene as solvents for most of the resins now on the market.

Acknowledgment

The authors wish to acknowledge their indebtedness to the operating personnel of the Bayway and Baton Rouge Hydrogenation Plants, as well as to the members of the hydrogenation laboratories of the Standard Oil Company of Louisiana, Standard Oil Company of New Jersey, and Humble Oil & Refining Company.

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Effect of Atmosphere on Desulfurization of Coal during Carbonization

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The results of an investigation on the desulfurization of coal during carbonization are presented and compared with those recently reported by Snow. Since the experimental methods of the two investigations were similar and the results differ considerably, it is concluded that the type of coal treated is an important factor in determining the most effective desulfurizing agent, and the extent of desulfurization.

A RECENT paper by Snow[1] reports the results of an extended investigation of the effect of various atmospheres on the elimination of sulfur from coal during carbonization. During the early part of 1928 some work on the same problem was carried out in this laboratory. The results were not published at that time because it was intended to study the problem further. This has not been possible, however, and although the data are admittedly incomplete, it seems best to present them at this time to supplement the work of Snow and to point out the fact that the various atmospheres may have decidedly different effects on different coals.

Experimental Procedure

The experimental work on this problem was carried out by R. A. Jack and G. A. K. Stachelhaus, using a method similar to that reported by Snow.

The desulfurization was accomplished by heating the coal at 600° C. in a stream of gas, its progress being followed by analyzing for the amount of hydrogen sulfide carried out in the gas.

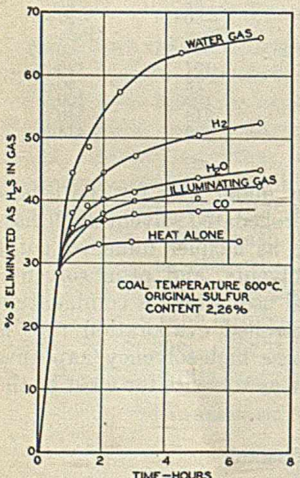

Figure 1. Progress of Sulfur Elimination during Heating Period

Heating was done in a nichrome-wound vertical-tube electric furnace. The tube was of glazed porcelain, 0.75 inch (0.9 cm.) in diameter and 20 inches (50.8 cm.) long. The charge was supported midway between the ends by a metallic screen which had been forced into position. An asbestos plug at the bottom end contained the delivery tube for the gas introduced into the furnace, and through a similar plug at the top a protected thermocouple was inserted to the center of the charge; a glass tube carried the gases from the furnace.

The furnace gases passed through a trap to remove tar and then bubbled through a train of wash bottles containing 2 per cent sodium hydroxide solution to absorb the hydrogen sulfide. Two trains were available so that the gas could be sent to one by the turn of a three-way cock, while the other could be removed for titration with standard iodine and renewal of the solution. When illuminating gas was used as a desulfurizing agent, it was first passed through cadmium chloride solution to remove any hydrogen sulfide which it might contain.

The coal used in these experiments was run-of-mine from Indiana Seam No. 5 and contained 3.9 per cent sulfur. After being crushed to pass an 8-mesh screen, it was treated on a Wilfley table to remove as much pyrites as possible. The sample reserved for the subsequent treatment amounted to 50 per cent of that passed over the table and contained 2.26 per cent sulfur. It fused at a temperature of about 475° C. and had the following proximate analysis:

	%		%
Moisture	2.01	Fixed carbon	50.67
Volatile combustible matter	42.00	Ash	5.32

Portions of the coal containing 2.26 per cent sulfur were charged into the electric furnace and heated at 600° C. The size of the charge varied from 20 to 30 grams, and the heating rate was such that the final temperature was reached in just one hour after heating began. The first runs were made to determine the effect of heat alone, when the only gases in contact with the coal, other than any residual air in the tube, were those resulting from its own decomposition. These tests were followed with runs in which various gases were passed through the coal during the entire heating period. The gas flow was kept constant at 3 cubic feet (0.08 cubic meter) per hour.

The effect of five gases—carbon monoxide, hydrogen, blue water gas, illuminating gas, and steam—was investigated. The progress of the sulfur elimination during the heating period, as indicated by the hydrogen sulfide content of the gas stream, is shown in Figure 1. The following is a summary of the results obtained giving as maximum sulfur elimination the values obtained after 7 hours of heating; the elimination after several hours was exceedingly slow:

Gas Used	S Eliminated as H_2S	Loss in Weight of Coal	Ratio % S to % Total Loss
	%	%	
Heat alone	33.5	28.5	1.18
Carbon monoxide	38.5	32.0	1.20
Illuminating	42.5	29.0	1.48
Steam	45.0	40.4	1.13
Hydrogen	52.5	34.2	1.56
Blue water	66.0	32.5	2.09

The values reported are for single runs with the exception of those for heat alone and for illuminating gas. For these two cases the reported values are averages of two runs made for check purposes. It was indicated by these check runs that the curves were reproducible within a 5 per cent range of sulfur removal.

Discussion of Results

The results show that all the gases were effective in removing sulfur as hydrogen sulfide. The exact extent of desulfurization was greater than that indicated, owing to some elimi-

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[1] Ind. Eng. Chem., 24, 903 (1932).

nated sulfur which went into tar and liquors, and to organic sulfur in the gas. Sulfur balances reported in the literature by others indicate that the sulfur appearing in these two products is usually less than 10 per cent of the total. Hence it is probable that the total elimination was not over 10 per cent greater than that appearing as hydrogen sulfide. Although the sulfur in the tar and as organic sulfur undoubtedly varied somewhat with the various atmospheres, it is doubtful whether these variations were sufficient to alter greatly the conclusions based on the hydrogen sulfide in the gas regarding the efficiency of the several gases as desulfurizing agents.

The results of this investigation and those reported by Snow are not entirely comparable since the experimental procedures differed in several respects. The coal used by Snow was of a smaller size and the rate of gas flow was less than in the present work. These two differences should counterbalance to some extent. Snow reports the total sulfur elimination after 4 hours of treatment based on the sulfur remaining in the coke; this investigation shows the progressive elimination over the entire heating period based on the hydrogen sulfide in the gas. Although Snow states that sulfur elimination was substantially complete in his 4-hour heating period, in this investigation sulfur continued to come off, in some cases even after 7 hours of treatment.

However, some general comparisons of the results may be made. The most striking difference is in the effect of water gas. Snow found the percentage sulfur elimination by a mixture of carbon monoxide and hydrogen to be intermediate between that produced by the two gases used separately. The present work shows a greater elimination with the mixture than with either of the separate constituents. Since the differences in both investigations are greater than the possibility of experimental error, it must be concluded that the different gases react differently with different coals. Snow's results show a generally higher percentage elimination. This is due partly to the sulfur in the tar and the organic sulfur which are not included in the present results, and it may be to some extent a result of the smaller size coal which he used; however, it is probably due in part to the different coals used. It is evident from the results of these two investigations that conclusions made from work on one coal cannot be applied with safety to a coal of different chemical composition.

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Preferential Wetting of Solids by Liquids

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When two immiscible liquids are brought into contact with a solid, it usually happens that one of the liquids wets the surface of the solid to the exclusion of the other liquid. This phenomenon of preferential wetting is encountered in many industrial processes—for example, in the flotation of ores, in the Trent process of cleaning coal, in the making of white lead by the Dutch process, etc. Preferential wetting determines to a considerable extent the behavior of solid particles at the interface of two immiscible liquids, and the ability of certain solids to emulsify pairs of liquids.

There has been a considerable amount of experimental work and a number of theoretical studies on interfacial surface tensions, spreading of liquids, behavior of solid particles at liquid interfaces, and other phases of the phenomenon of preferential wetting, etc., carried out by Brücke (*2*), Nuttall (*8*), Haskins (*5*), Des Courdes (cited by Rhumbler, *10*), Hofman (*6*), Stark (*11*), Rhumbler (*10*), Rheinders (*9*), Finkle, Draper, and Hillebrand (*3*), Freundlich (*4*), McMillen (*7*), and others. Bartell and his associates (*1*) have made many measurements of what is termed the "adhesion tension" between a liquid and a solid, a quantity which is involved directly in the phenomenon of preferential wetting, as will be shown.

Qualitative Study of Preferential Wetting

The displacement of one liquid by another from the surfaces of a powdered solid may be observed readily by the following procedure:

> Work 20 grams of the solid and either of the liquids together to form a soft putty; add the second liquid a few drops at a time, working it into the putty after each addition. If the solid is preferentially wet by the first liquid, it will be found that very little of the second liquid can be worked into the putty. If, however, the solid is preferentially wet by the second liquid, successive additions are readily worked into the putty. Presently the putty becomes somewhat crumbly and has about the same consistency as cottage cheese. Further additions of the second liquid then liberate relatively large amounts of the first liquid, until eventually practically all of the first liquid has been removed from the putty.
>
> Lesser quantities of the solid and of the liquids may be used if necessary, and, with a little experience, single drops of the liquids and correspondingly small amounts of the solid will suffice for observations which will determine which of two liquids preferentially wets a given solid.

The displacement of one liquid by another was observed in the manner indicated for twenty-five pairs of liquids, using in each case water as one of the liquids, and trying each pair of liquids on fifteen different solids. The results are given in Table I.

Quantitative Aspects of Preferential Wetting

In the ordinary capillary tube method of determining surface tension of a liquid,

$$r = \frac{2\gamma \cos \Theta}{hsg} \qquad (1)$$

where r = radius of tube
γ = surface tension of liquid against air
s = density of liquid
h = rise of liquid in tube
g = gravity constant
Θ = angle of contact between tube and liquid

It is obvious that, if a liquid for which the liquid-solid angle of contact is zero be used, the radius of the capillary tube may be determined from known or measured values of γ, h, s, and g. Having thus found r, the angle of contact for a second liquid may be determined from known values of r and g, and the known or measured values of γ, h, and s for the second liquid.

It is evident, then, that the angle of contact between the wall of a tube of any solid and the surface of any liquid may be determined, provided there may be found one liquid for which the liquid-solid angle of contact is zero. If the radius of the capillary tube can be determined by direct measurement, the necessity of finding a liquid of zero angle of liquid-solid contact is, of course, avoided.

Table I. Water *vs.* Organic Liquids in Preferential Wetting

Liquid	Sulfur	$CaCO_3$ Ppt.	ZnO	$PbCO_3$	Sphalerite	Pyrolusite	Hematite	Malachite	Galena	Smithsonite	Covellite	Realgar	Cerussite	Stibnite	Pyrite
Xylene	O[a]	W	W	O	W	W	W	W	O	OW	O	O	O	O	O
Toluene	O	W	W	W	W	W	W	W	WO	W	O	O	W	O	O
Aniline	O	W	W	WO	OW	W	W	W	O	O	O	O	OW	O	O
Turpentine	O	W	W	O	W	W	W	W	OW	OW	OW	O	WO	O	WO
Chloroform	O	W	W	W	W	W	W	W	WO	W	WO	O	W	O	OW
Nitrobenzene	O	W	W	W	W	W	W	W	OW	W	OW	O	OW	O	OW
Amyl alcohol	O	W	W	WO	O	W	W	W	O	O	O	O	O	O	O
Cottonseed oil	O	W	W	O	WO	W	W	W	OW	OW	OW	O	WO	O	O
Linseed oil	O	O	O	O	O	O	O	O	O	O	O	O	OW	O	O
Paraffin oil	O	W	W	WO	W	W	W	W	OW	OW	OW	O	OW	O	O
Mineral oil	O	OW	W	W	W	W	W	W	O	OW	OW	O	O	O	O
Lard oil	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Rosin oil	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Olive oil	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Oleic acid	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Corn oil	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Oil of sesame	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Sperm oil	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Castor oil	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Coconut oil	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Ethyl acetate	O	W	W	W	W	W	W	W	O	O	O	O	O	O	O
Dimethylaniline	O	W	W	OW	O	WO	OW	WO	O	O	O	O	O	O	O
Furfural	O	W	W	WO	O	W	W	W	O	O	O	O	O	O	O
Benzylaldehyde	O	OW	O	O	O	WO	WO	O	O	O	O	O	O	O	O
Tung oil	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O

[a] W, decided preference for water. O, decided preference for organic liquid. WO, slight preference for water. OW, slight preference for organic liquid.

In studies of preferential wetting, it is seldom practical to use the solid in the form of a capillary tube. Moreover, the pressure p, which must be measured, may be too small to be determined accurately if capillary tubes as large as ordinarily used in surface tension measurements are employed. In many cases it is possible to grind the solid to a powder and pack it, a little at a time, into a strong metal tube of, say, 1 inch (2.54 cm.) diameter, using heavy packing pressures after each addition of the powder. The pores of the cylinder of solid so obtained form, in effect, a series of capillary tubes, of which the average radius may be measured by the indirect method outlined above. This method of using a powdered and compressed solid in place of a capillary tube has been developed particularly by Bartell and his associates. The metal tube containing the packed powder, together with its immediate attachments, is usually designated as a Bartell cell. Actual use of the cell in making adhesion tension measurements will be mentioned below. For the present it will be assumed that the cell is, in effect, the equivalent of a capillary tube of very small radius.

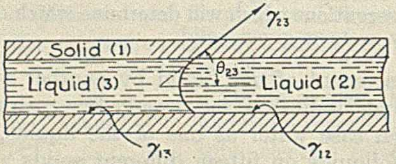

Figure 1. Two Liquids in Capillary Tube

Freundlich has defined the adhesion tension, B_{12}, of a solid 1 with reference to liquid 2 as:

$$B_{12} = \gamma_1 - \gamma_{12} \tag{2}$$

where γ_1 = surface tension of solid against air
γ_{12} = interfacial tension of solid 1 against liquid 2

It may readily be shown that:

$$\gamma_1 - \gamma_{12} = \gamma_2 \cos \Theta_{12} = B_{12} \tag{3}$$

where γ_2 = surface tension of liquid 2 against air
$\cos \Theta_{12}$ = angle of contact of solid 1 with liquid 2

It would appear, therefore, that the adhesion tension of a liquid for a solid could be determined by simply measuring the density of the liquid and its rise in a capillary tube of known radius. For liquids which have contact angles considerably greater than zero, this method apparently gives acceptable results. For a liquid which gives a zero or very small angle of contact with a solid, however, it has been argued by Bartell and others that the adhesion tension, B_{12} or $\gamma_1 - \gamma_{12}$, is not correctly measured by the quantity $\gamma_2 \cos \Theta_{12}$. The tendency of the liquid to spread on the solid does reduce the angle of contact to zero, but the tendency to spread may actually be much larger than just enough to reduce the angle of contact to zero; i. e., the adhesion tension is not necessarily limited to an upper value of γ_2, as required by Equation 3. For liquids of high spreading power, Bartell has proposed the equation:

$$B_{12} = \gamma_1 - \gamma_{12} = K\gamma_2 \tag{4}$$

Experimental evidence for the argument advanced by Bartell may be presented as follows: Choose two immiscible liquids, one of which (liquid 2) has greater than zero angle of contact and the other (liquid 3) of zero contact angle against the wall of the tube of solid. Measure the quantities $\gamma_2 \cos \Theta_{12}$ and $\gamma_3 \cos \Theta_{13}$ by the usual capillary rise method as suggested above.

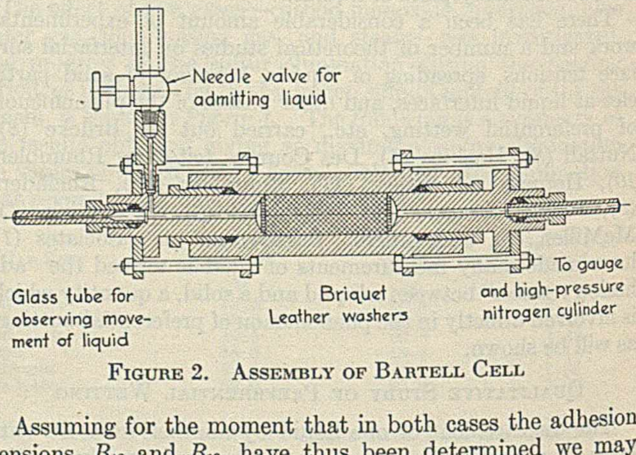

Figure 2. Assembly of Bartell Cell

Assuming for the moment that in both cases the adhesion tensions, B_{12} and B_{13}, have thus been determined we may write:

$$B_{12} = \gamma_1 - \gamma_{12} = \gamma_2 \cos \Theta_{12} \tag{3}$$

$$B_{13} = \gamma_1 - \gamma_{13} = \gamma_3 \cos \Theta_{13} \tag{5}$$

Subtracting,

$$B_{13} - B_{12} = \gamma_{12} - \gamma_{13} \tag{6}$$

Consider now that both liquids are in the tube, forming a liquid-liquid interface as shown in Figure 1. Again it may readily be shown that:

$$\gamma_{13} - \gamma_{12} = \gamma_{23} \cos \Theta_{23} \tag{7}$$

By measuring the force necessary to prevent the liquids from moving along the tube, the quantity $\gamma_{23} \cos \Theta_{23}$ may be directly evaluated.

From Equations 6 and 7 we have:

$$B_{12} - B_{13} = \gamma_{23} \cos \Theta_{23} \qquad (8)$$

in which all three terms have been measured directly. It will be found, however, that the experimental values do not satisfy Equation 8, indicating, presumably, that one of the terms has been incorrectly evaluated. If, as suggested, the simple procedure of measuring rise in a capillary tube is not applicable as a means of obtaining the adhesion tension of a liquid of zero (or very small) liquid-solid contact angle, then obviously the procedure outlined above permits evaluating this adhesion tension by directly measuring B_{12} and $\gamma_{23} \cos \Theta_{23}$, and then solving Equation 8 for B_{13}. For liquids of small contact angles it will actually be found that the values of B_{13} so determined are indeed much larger than $\gamma_2 \cos \Theta_{13}$.

It will be noted from Figure 1 and Equation 7 that the force per unit of capillary area required to prevent one liquid from displacing another in contact with a solid is measured by $\gamma_{13} - \gamma_{12}$—i. e., by the difference of the interfacial surface tensions of each liquid against the solid; it is also measured by $\gamma_{23} \cos \Theta_{23}$—i. e., the interfacial tension of one liquid against the other—times the cosine which the interface makes with the solid. Presumably the same argument—that adhesion tension is not necessarily limited to a maximum value equal to the surface tension—would also apply here; i. e., the method is applicable only when the angle of contact of the liquid-liquid interface, Θ_{23}, is considerably greater than zero.

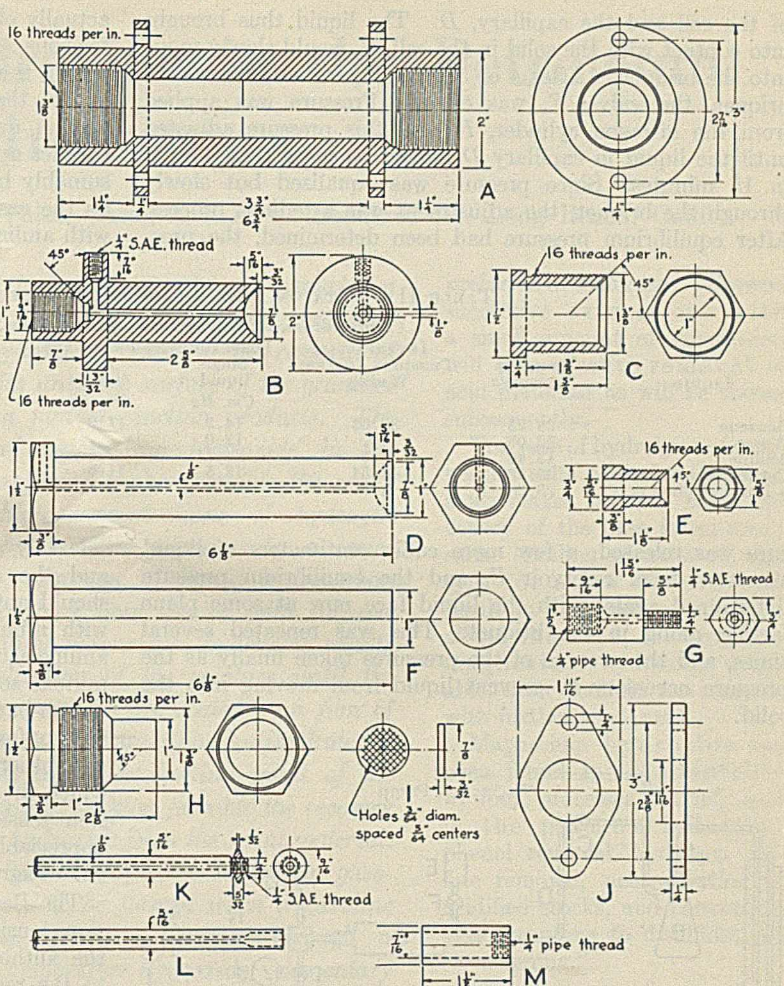

FIGURE 3. DETAILS OF PARTS OF BARTELL CELL

A, body (one required); *B*, plunger (two required, one with side outlet as shown); *C*, packing gland (two required); *D*, plunger for impregnating briquet with liquid (one required); *E*, packing gland (two required); *F*, packing plunger (one required); *G*, bushing for attaching reservoir (one required); *H*, packing plug (one required); *I*, retaining disks (two required); *J*, compression collar (two required); *K*, capillary connecting tube (one required); *L*, glass capillary tube (one required); *M*, coupling for reservoir (one required).

Experiments with Bartell Cell

This cell has been described by Bartell in various publications. Figure 2 shows an assembly of the cell; Figure 3, a dimensioned drawing of the parts of the cell; and Figure 4, an assembly of the cell and auxiliary apparatus for carrying out measurements. The cell actually used in securing the few data given below was constructed principally of brass. The authors believe it would be better, however, to use only steel, in which case the body of the cell and the plungers could be case-hardened, and the bore and plungers ground and polished.

In Figure 4, manometer *A* served to test the cell and connections for leaks; manometer *M* and gages *J* and *H* were so arranged as to cover a considerable range of pressure, so that the actual pressure could be read more accurately by using whichever of the three was the best suited for the purpose. Cell *G* and parts immediately adjacent thereto were enclosed in an air thermostat.

Flowers of sulfur were chosen as solid 1 to be studied and benzene (liquid 2) as the liquid by which to measure the pore size (average radius of capillaries), it being assumed that benzene has a zero angle of contact with sulfur. The angles of contact against sulfur were then determined for water (liquid 3), aniline (liquid 4), carbon tetrachloride (liquid 5), and *n*-butyl alcohol (liquid 6), by measuring the pressure necessary to prevent each of these liquids from moving through the compressed sulfur cylinder in the Bartell cell. Likewise the pressure required to prevent movement of the liquid-liquid interface in contact with the solid was measured for each of the organic liquids against water.

For packing the flowers of sulfur in the cell, the following procedure was followed: Referring to Figure 3, the plug, *H*, was screwed into the cell cylinder, *A*. This was set in a hydraulic press; 1.5 grams of sulfur were placed in the cell; the packing plunger, *F*, was inserted; and a pressure of 6000 pounds per square inch (421.8 kg. per sq. cm.) was applied on the plunger. The plunger was then withdrawn, another 1.5 grams of sulfur added, the plunger replaced, and the pressing repeated. This operation was repeated until 70 grams of sulfur had been added, giving a briquet about 3.5 inches (8.9 cm.) long. Packing in all cases was with the dry solid. It was found by experience that dry packing must be used if the pore size was to be duplicated with any degree of accuracy.

After the sulfur had been packed in the tube, the plug and packing plunger were laid aside, and the cell parts assembled as shown in Figure 2. Finally the cell was made a part, *G*, of the set-up shown in Figure 4. In making a determination, the system was first evacuated and tested for leaks by observing the manometer, *A* (Figure 4). The pressure in the system was then adjusted to 2 or 3 cm. of mercury, and the cock, *C*, closed. The liquid to be studied was then allowed to flow from the reservoir, *E*, into the end of the cell and the capillary, *D*. The liquid thus brought into contact with the solid in the cell, *G*, would slowly move into the briquet. After 4 or 5 cc. of liquid had entered the briquet, the valve, *F*, was closed. Pressure was applied from the nitrogen cylinder, *P*, and this pressure adjusted until the liquid in capillary *D* moved no more than 1 mm. in 15 minutes. Since pressure was equalized but slowly through the briquet, the adjustment was a tedious process. After equilibrium pressure had been determined, the pressure was released, a few more cubic centimeters of liquid admitted from reservoir *E*, and the equilibrium pressure determined again, with the liquid face now at some plane farther along in the briquet. This was repeated several times, and the average of the pressures taken finally as the pressure necessary to prevent liquid from moving into the solid.

TABLE II. DATA ON WETTING OF SOLID SULFUR BY VARIOUS LIQUIDS

(Temperature, 25° C.; average capillary radius, 2.98×10^{-4} cm.)

LIQUID	SURFACE TENSIONS	INTERFACIAL TENSIONS AGAINST WATER	DISPLACEMENT PRESSURES Single liquid	DISPLACEMENT PRESSURES Two liquids	COS Θ SINGLE LIQUID	COS Θ INTERFACE WITH WATER	γ COS Θ SINGLE LIQUID	ADHESION TENSIONS BY EQUATION 8
			Cm. Hg	*Cm. Hg*				
Benzene	28.25	38.63	14.2	17.3	1.000	0.993	28.3	58.3
Water	72.08	...	12.0	...	0.331	...	23.9	..
Aniline	43.40	6.0	21.7	2.5	0.994	0.829	43.1	28.9
Carbon tetrachloride	26.12	44.54	12.5	11.6	0.951	0.518	24.1	47.0
n-Butyl alcohol	23.38	1.5	7.7	0.41	0.655	0.546	13.3	24.7

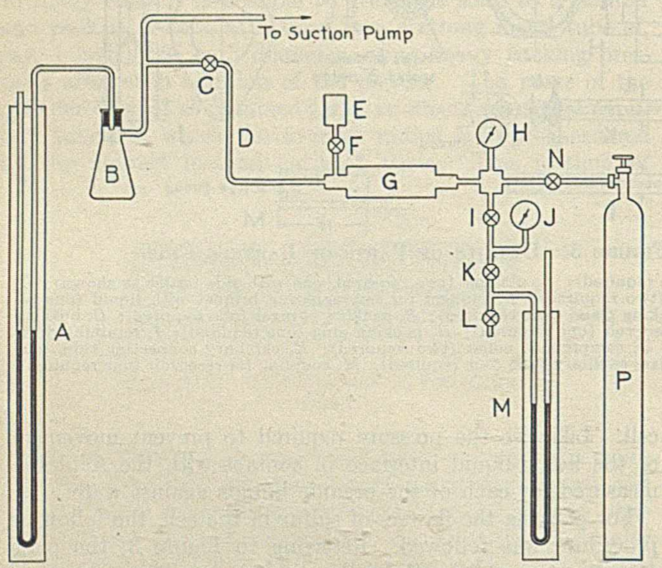

FIGURE 4. ASSEMBLY OF APPARATUS FOR DETERMINATION OF ADHESION TENSIONS

A, mercury manometer; *B*, safety flask; *C*, cock; *D*, capillary glass tube; *E*, reservoir for liquid; *F*, needle valve; *G*, Bartell cell; *H* and *J*, Bourdon gages; *I*, *K*, *L*, *N*, needle valves; *M*, mercury manometer; *P*, nitrogen cylinder.

Where two liquids were to be brought into contact in the briquet, the briquet was packed dry (as indicated above) until all except the last 0.25 inch (0.635 cm.) had been formed. Water was then forced into the briquet under gentle pressure until all air was displaced. The last 0.25 inch (0.635 cm.) of the briquet was packed with sulfur completely wet by the organic liquid to be used. In this manner a liquid-liquid interface free from air was formed in the briquet. After the cell and auxiliary apparatus were assembled as described, the organic liquid was placed in the reservoir and the pressure determinations carried out as outlined.

The data for water and the four organic liquids are summarized in Table II.

The displacement pressures given in Table II are those actually observed. If the values of $\gamma \cos \Theta$ and of adhesion tensions calculated from these observed pressures are correct in the sense that they may be checked by other investigators, then there are some inconsistencies for which there are no evident explanations. For liquids with angles of contact approaching zero, the adhesion tensions should presumably be always greater than $\gamma \cos \Theta$; this was found to be the case with benzene and carbon tetrachloride but not with aniline. Again, for liquids with angles of contact considerably greater than zero, it is not apparent why $\gamma \cos \Theta$ and the adhesion tension as determined by Equation 8 should not be the same; this was found not to be the case with *n*-butyl alcohol. Possibly the solubility of sulfur in aniline causes the discrepancy; also it may be that the slight mutual solubility of water and aniline, and that of water and *n*-butyl alcohol, cause both the discrepancies noted. It is unfortunate that, in all the published papers of Bartell and others, there is apparently only a single instance in which the data permit calculation of both $\gamma \cos \Theta$ and adhesion tension by Equation 8 for liquids of contact angles appreciably greater than zero. In this single case the two values agree closely.

The Bartell cell method of determining $\gamma \cos \Theta$ or adhesion tensions is, at best, exceedingly tedious. Moreover, the authors were unable to check Bartell's statements as to the reproducibility of results. After several months of practice, results have been checked with the same briquet within about 5 per cent, and with different briquets within about 8 per cent maximum variation for a single liquid. Where two liquids were used, the maximum variation was sometimes as much as 15 per cent.

In several of Bartell's papers there will be found the tacit assumption that wet and dry briquetting with the same packing pressures will give the same pore size. The present authors found this to be far from true; and, incidentally, this assumption runs contrary to all practical experience in briquetting solids.

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RECEIVED May 18, 1932. The experimental data of this paper are taken from a dissertation presented to the Graduate School of Yale University by N. S. Davis, Jr., in candidacy for the Ph.D. degree.

Magnesium Hydroxide in the Petroleum Industry

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Passage of hydrocarbon mixtures containing phenols and hydrogen sulfide over granular magnesium hydroxide results in the removal of these impurities until the surface of the granules is coated by a film of reaction products. The employment of magnesium hydroxide in the form of a suspension makes possible the ready removal of high concentrations of hydrogen sulfide from hydrocarbon mixtures by a series of extractions. Passage of liquid hydrocarbon mixtures which have been treated with sulfuric acid over granular magnesium hydroxide results in the neutralization of the mixture until the surfaces of the granules are coated by a film of reaction products. Magnesium sulfhydrate is readily hydrolyzed at the boiling point of the suspended solution, making possible the recovery of magnesium hydroxide from the spent material. Basic magnesium mercaptides, soluble in gasoline, are believed to be formed when a gasoline containing mercaptans is passed through a column of dry magnesium hydroxide; elementary sulfur reacts with these compounds, converting them to disulfides. Magnesium hydroxide spent in the sweetening process can be regenerated by boiling with water, boiling with sodium hydroxide, washing twice with water, and drying.

THE use of alkali in the petroleum industry is principally confined to the treatment of large volumes of gas or liquid containing small percentages of undesirable acid impurities. The application of a base in solid granular form, over which the liquid or gas undergoing treatment may pass, offers the possibility of furnishing a long operating cycle with a minimum of handling expense. The adaptability of magnesium hydroxide to such work has been studied.

Mined as the mineral brucite, magnesium hydroxide has a hardness of 2.5 on Moh's scale. Magnesium hydroxide may also be prepared by hydroxylation of magnesium oxide, prepared by calcination of magnesite. The oxide employed for the purpose should contain 90 to 95 per cent magnesium oxide, show less than 3 per cent ignition loss, contain less than 2.5 per cent insoluble matter, and should not be "dead burnt," since ready hydration is desired. The hydration of granular magnesium oxide furnishes a nonfriable hydroxide mechanically satisfactory as tower packing.

Brucite is found in commercial quantities at Luning, Nev., and Chewelah, Wash. Seaton (*5*) has recently discussed Pacific Coast magnesite deposits.

The salts formed by the reaction of magnesium hydroxide with weak acids are subject to hydrolysis to a marked degree, owing to the slight solubility of the base. In employing a tower packed with magnesium hydroxide to remove weak acids from liquid or gaseous petroleum products, the magnesium salts formed are deposited progressively on the surface of the base and thus the acids are removed as passage through the tower occurs, until, after contact with a large number of successive surfaces, the amount of free acid becomes small to the banishing point. Thus, even though the process of salt formations is never complete, the removal of successive increments of acids as salts insoluble in hydrocarbons results in eventual neutralization of essentially all free acid.

If the concentration of the weak acids is appreciably large, it is conceivable that the use of a solid base may not represent the most economical method of application; that is, the surface of the magnesium hydroxide will become coated with a film of reaction products so rapidly that the time of use will be too short for effective plant operation. The use of magnesium hydroxide as a thin suspension is to be preferred in such cases. Several successive extractions with a small amount of suspension will give effective removal of acid materials as will be shown subsequently.

The ease of hydrolysis of magnesium salts of volatile weak acids makes possible ready recovery of the base from such salts. Boiling of salts of this type for a few minutes will result in expulsion of virtually all of the acid, leaving the magnesium hydroxide available, after cooling, for reaction with further weak acid.

Magnesium hydroxide has been found to be adaptable to four processes carried out in the petroleum industry: phenol removal, hydrogen sulfide removal, neutralization of acidified stocks, and conversion of mercaptans to disulfides, or "sweetening."

PHENOL REMOVAL

The presence of phenols and allied substances may be detected by means of ferric chloride (*4*). Shaking of 300 cc. of a cracked gasoline with 3 cc. of ferric chloride produced a pronounced change in color of the reagent. Another 300-cc. sample of this gasoline was shaken with two 3-cc. portions of a suspension of magnesium hydroxide in water (approximately 25 per cent by weight magnesium hydroxide ground to pass 100-mesh screen) and filtered to remove any trace of emulsified material. The resulting material gave a negative phenol test.

A portion of the suspension with which the gasoline had been agitated was acidified with hydrochloric acid and tested for phenols. A pronounced color change with ferric chloride was observed. The balance of the suspension was boiled gently for a few minutes, cooled, acidified, and, when tested, gave a slight positive phenol test.

A portion of the same gasoline was treated with granular magnesium hydroxide in a laboratory column. The column employed consisted of a glass tube, 1.2 × 90 cm., and contained 125 grams of dry magnesium hydroxide. The gasoline was introduced at the bottom of the column at the rate of 5 cc. per minute under sufficient head to force it upward through the packing. The efflux material was free from phenols. In no instance have phenols been detected in gasolines which have been thus treated. The presence of other undesirable compounds in treated products has proved the vitiation of the base by surface films of reaction products,

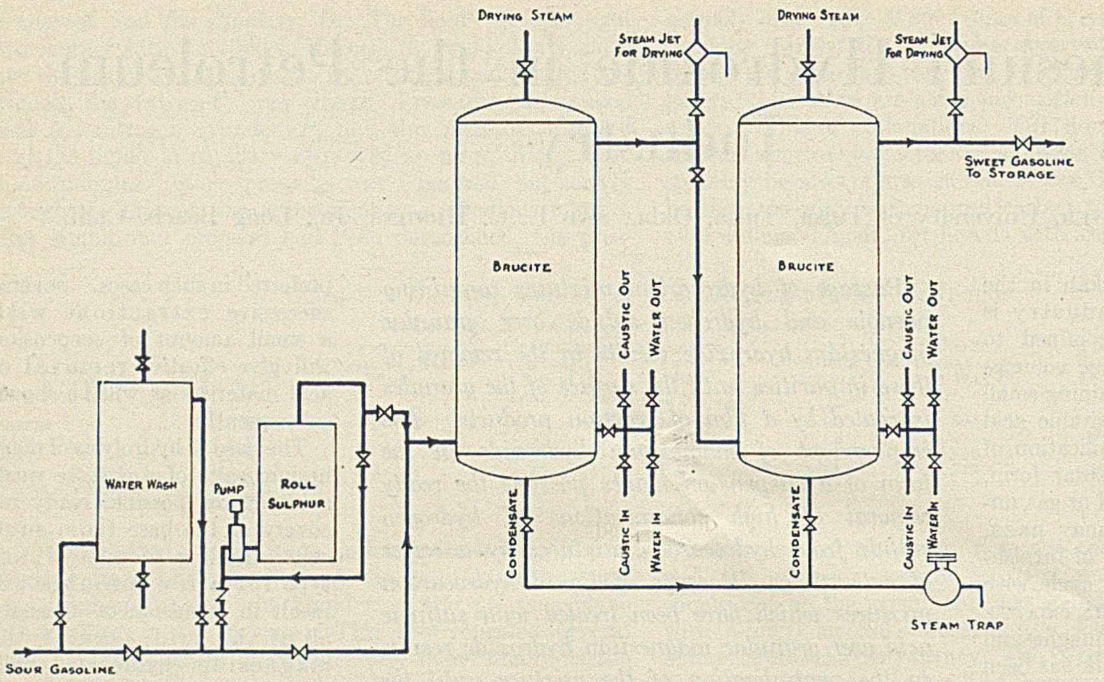


FIGURE 1. FLOW SHEET OF MAGNESIUM HYDROXIDE SWEETENING UNIT

but phenol removal has always been substantially complete.

REMOVAL OF HYDROGEN SULFIDE

The presence of hydrogen sulfide in hydrocarbon mixtures may be followed readily with lead acetate. Work has been done with still gas, natural gas, gasoline, and crude oil, to determine the effectiveness of hydrogen sulfide removal from these materials by magnesium hydroxide.

In the presence of water at atmospheric temperature the following equilibrium (7) exists:

$$2H_2S + Mg(OH)_2 \rightleftharpoons Mg(HS)_2 + 2H_2O \quad (1)$$

Since hydrogen sulfide is feebly dissociated and magnesium hydroxide is very slightly soluble, the equilibrium should lie appreciably to the left at ordinary temperatures. At elevated temperatures in open containers the high vapor pressure of hydrogen sulfide from aqueous solutions should result in ready shift of the equilibrium to the left, owing to loss of hydrogen sulfide from the solution as rapidly as hydrolysis occurs. At atmospheric temperature, several successive extractions should be required to remove substantially all of the hydrogen sulfide from gaseous or liquid hydrocarbons.

Gasoline rich in hydrogen sulfide was passed through a tower similar to that employed for phenol removal. When the rate was low, the efflux gasoline was substantially free of hydrogen sulfide. Upon accelerating the process greatly, hydrogen sulfide was markedly present in the efflux. The tower, when filled with gasoline containing hydrogen sulfide at all levels, was allowed to stand overnight, after which the efflux from the tower showed a slight but definite hydrogen sulfide content. This finding is in accord with the expectation that successive extraction by increments occurs if sufficient time is allowed for equilibrium to be established at each successive level of the packing. So little time was allowed for reaction that the gasoline at the uppermost level contained substantially all of its original hydrogen sulfide content. Upon standing, equilibrium was established and the slight hydrogen sulfide content found was due to the appreciable hydrolysis of magnesium sulfhydrate [$Mg(SH)_2$]. Gasoline was again started through the apparatus at a moderate rate. An efflux free from hydrogen sulfide was obtained after running a few minutes, as was anticipated.

Municipal natural gas was "loaded" with hydrogen sulfide by passage through a flask containing sodium sulfide on to which dilute acid was slowly dropped. The gas, rich in hydrogen sulfide, was then passed through a magnesium hydroxide column. A slight back pressure was maintained by bubbling the efflux gas through a few inches of water. The gas when bubbled through lead acetate (in place of the efflux water bubbler) gave no precipitate at a fairly rapid rate.

Crude oil from the Pecos field in West Texas, rich in hydrogen sulfide, was passed through a column of magnesium hydroxide, resulting in the removal of the hydrogen sulfide from this material.

Owing to the difficulty of maintaining a fixed percentage of hydrogen sulfide in materials employed in prolonged laboratory runs, the qualitative laboratory findings were extended to a more exact basis in semiplant-scale apparatus. All runs were made at or near the maximum rate at which complete hydrogen sulfide removal was possible. In only one run was the magnesium hydroxide exhausted for hydrogen sulfide removal at the conclusion of the run. The results obtained are shown in Table I.

An inspection of run 2 in Table I indicates that the length of operation for removal of hydrogen sulfide from materials extremely rich in this substance would probably be prohibitively short in commercial operation before hydrolysis and

TABLE I. HYDROGEN SULFIDE REMOVAL BY DRY GRANULAR MAGNESIUM HYDROXIDE[a]

RUN	MATERIAL	H_2S CONTENT		WEIGHT OF $Mg(OH)_2$		TIME	VOLUME TREATED		RATE PER HOUR	
		Mg./liter	*Grams/gal. or cu. ft.*	*Kg.*	*Lb.*	*Hours*	*Liters*	*Gal. or cu. ft.*	*Liters/metric ton*	*Gal. or cu. ft./ton*
1	Still gas[b]	5.3	245	27.2	60	24	4,750	174	728	241
2	Still gas[b]	3.2	148	27.2	60	77	44,453	1632	2125	707
3	Gasoline[c]	8	0.53	7.5	16.5	145	2,017	533	2240	448
4	Gasoline[c]	8	0.53	7.5	16.5	113	3,085	815	3720	873

[a] Magnesium hydroxide exhausted at rate maintained when run ceased.
[b] Gas volumes: liters at 1 atm. and 0° C.; or cubic feet at 1 atm. and 60° F.
[c] Gasoline volumes in liters or gallons.

rejuvenation of the surface of magnesium hydroxide granules would be necessary. The application of magnesium hydroxide in a finely divided suspension in water appears to offer a more economical method of treatment for products heavily laden with hydrogen sulfide.

In order to gain some information about the rate of extraction of hydrogen sulfide by magnesium hydroxide suspended in water, the following experiments were performed (a 5 per cent by weight suspension was employed throughout):

Gasoline samples were "loaded" with hydrogen sulfide and were then hand-shaken intermittently with magnesium hydroxide suspension for 30 minutes in each extraction. This mixing was probably not as thorough as that obtained in a short time with a well-designed mechanical mixer. The samples were allowed to stand until separation of the two layers was complete, before draining the water layer. In employing 10 per cent of the suspension by volume, no trouble with emulsions was encountered. When employing 100 per cent of the suspension, an emulsion persistent for some minutes was obtained. The hydrogen sulfide content of samples was obtained by shaking an aliquot with three washings of 2 per cent sodium hydroxide, pouring the sodium hydroxide slowly, with stirring, into a funnel immersed in a solution containing sufficient hydrochloric acid to neutralize the sodium hydroxide, to which a measured amount of standard iodine solution had been added. The excess iodine was then titrated with standard thiosulfate solution. The results obtained are summarized in Table II.

Gas samples were enriched in hydrogen sulfide by passing natural gas at constant rate through a flask containing sodium sulfide on to which acid of known normality was dropped at a constant rate. The approximate hydrogen sulfide content of the gas could then be calculated. The validity of this method was checked by passing a known volume of gas thus enriched through sodium hydroxide solution and analyzing as outlined above. The calculated hydrogen sulfide content was 111 mg. per liter, whereas the analysis showed a content of 115 mg. per liter. Rates of gas flow and hydrogen chloride addition were kept constant for 4 minutes, after which the gas was bubbled at a constant rate through two Geissler-type potash bulbs in series, each containing approximately 20 cc. of magnesium hydroxide suspension. The washed gas was tested for hydrogen sulfide content by bubbling through lead acetate. At the first indication of hydrogen sulfide the run was concluded. A blank was run with water in place of the suspension. The rates obtained would obviously be greater if countercurrent movement of the suspension were employed. The results obtained are given in Table III.

The ease of hydrolysis of magnesium sulfhydrate at the boiling point of the suspension was studied quantitatively. Spent suspension from gas extraction was employed. It was boiled gently for 2 minutes and analyzed. The original spent suspension contained 1.91 grams of hydrogen sulfide per liter, and, after hydrolysis, 0.357 gram per liter or a decrease of 81.2 per cent. The hydrolyzed suspension was used in hydrogen sulfide extraction from gas. As anticipated, the resulting gas was low in hydrogen sulfide content, but not completely free from it. The results obtained are included in Table III.

The results obtained with magnesium hydroxide suspension show that this material is adaptable to rapid removal of large amounts of hydrogen sulfide from liquid and gaseous hydrocarbons, and further that regeneration of the base may readily be accomplished. The cost of heating the suspension to bring about hydrolysis should not be excessive if well-designed heat exchange equipment is employed in conjunction with continuous operation.

ACID NEUTRALIZATION

Granular magnesium hydroxide is readily applicable for neutralizing acidified stocks. Many distillates require acid treatment before the final stages of refinement. The stock is desludged and washed with water immediately after the acid treatment and then neutralized. Solid granular magnesium hydroxide is effectively used for this purpose. The product of the reaction is magnesium sulfate ($MgSO_4 \cdot 7H_2O$) which is readily soluble in water so that, upon revivification of the packed tower, this material is removed by washing, leaving the surface of the magnesium hydroxide exposed again for neutralizing.

MERCAPTAN ALTERATION

In the course of experimental work on hydrogen sulfide removal with granular magnesium hydroxide, it was observed

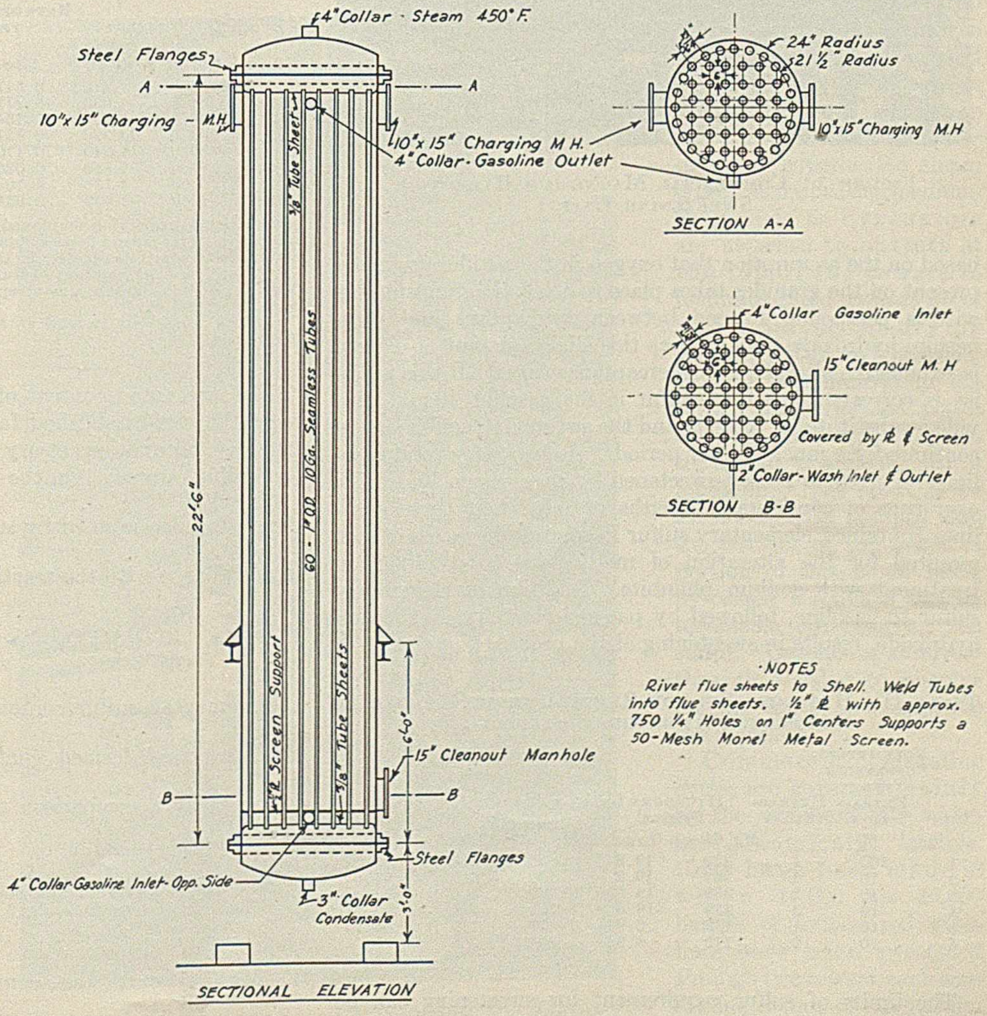


FIGURE 2. DETAIL OF DRYING EQUIPMENT

in some instances that the treated material was "sweet to doctor;" that is, it failed to yield a precipitate of lead sulfide when shaken with sodium plumbite and sulfur by the method outlined by the Bureau of Mines (*1*). Further investigation showed that this sweetening took place, in most instances, only for a short time after the start of passage of gasoline through the column. The explanation of this behavior is based on the assumption that oxygen in the air film originally present on the granules takes place in a reaction, presumably with a compound formed between mercaptans and magnesium hydroxide. As soon as this slight amount of oxygen is exhausted, alteration of mercaptans ceases. If this premise is correct, solution of sulfur in the gasoline should provide a substitute for oxygen, and the sweetening action should continue for a much greater period. A check of several gasolines reported to be self-sweetened by magnesium hydroxide over runs of considerable lengths revealed that these gasolines contained elementary sulfur in solution in excess of that required for the alteration of mercaptans to disulfides in treatment with sodium plumbite. Addition of elementary sulfur to gasoline, followed by passage over dry magnesium hydroxide, results in sweetening of the product.

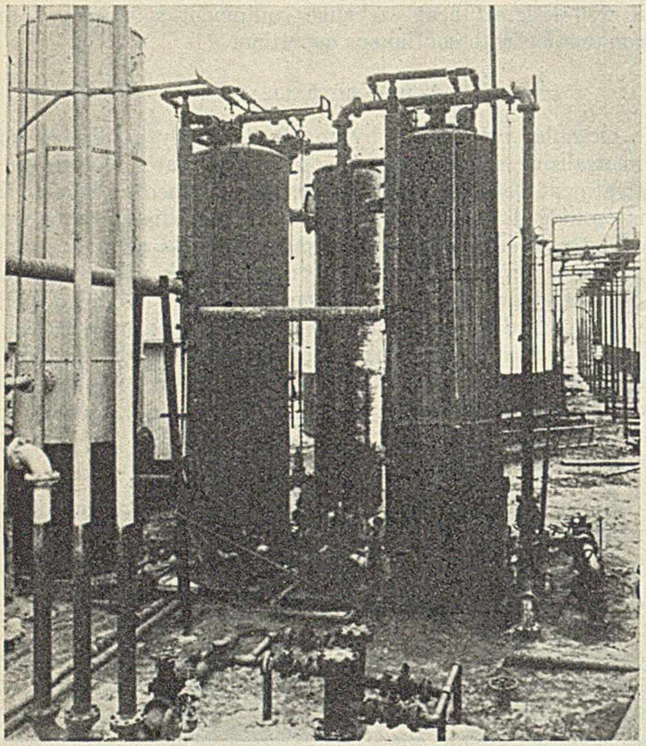


FIGURE 3. COMMERCIAL MAGNESIUM HYDROXIDE SWEETENING UNIT

TABLE II. HYDROGEN SULFIDE REMOVAL FROM GASOLINE BY MAGNESIUM HYDROXIDE SUSPENSION

RUN	VOLUMETRIC SUSPENSION PER EXTRACTION	EXTRACTIONS	HYDROGEN SULFIDE CONTENT Original		Final		H_2S REMOVAL
	%		*Mg./liter*	*G./gal.*	*Mg./liter*	*G./gal*	%
1	100	1	339	19.8	36	2.1	89.5
2	10	1	339	19.8	146	8.5	56.8
3	10	2	339	19.8	26	1.5	92.4
4	10	3	339	19.8	Nil	Nil	99
5	10	1	119	6.95	17	1.0	85.7
6	10	2	119	6.95	Nil	Nil	99

The limits of sulfur requirement for sweetening can be carefully defined. If too much sulfur is employed, a treated product, corrosive to copper in accordance with a Bureau of Mines specification (*2*), results. If too little sulfur is employed, the sweetening reaction is not complete. The sulfur content of the gasoline is essentially unchanged when the proper balance is struck between corrosiveness and "sourness." Since Ott and Reid (*3*) have shown that a gasoline-soluble basic lead mercaptide is one of the important intermediates in plumbite sweetening, it seemed logical to search for a corresponding magnesium compound. Two gasolines, rich in mercaptans, were empirically sweetened with magnesium hydroxide by addition of sulfur by increments until the delicate balance between incomplete mercaptan alteration and corrosive product had been established. Untreated samples of these gasolines were shaken with finely divided dry magnesium hydroxide. After a period of shaking, the characteristic mercaptan odor was not noticeable. The gasolines, at this stage, when treated with sodium plumbite and sulfur, gave a heavy precipitate of lead sulfide. Measured quantities of the gasolines thus treated were filtered and shaken with measured volumes of standard sulfuric acid. After shaking a few minutes, the characteristic mercaptan odor was again noticeable in the gasoline. The sulfuric acid was back-titrated with sodium hydroxide. A considerable titer of sulfuric acid had been consumed in each case. The aqueous layer contained magnesium ion.

TABLE III. HYDROGEN SULFIDE REMOVAL FROM GAS BY MAGNESIUM HYDROXIDE SUSPENSION[a]

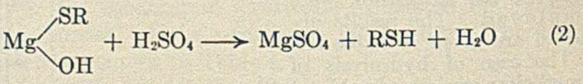
RUN	H_2S CONTENT		RATE OF THROUGH-PUT PER MINUTE		TIME	GAS Per liter suspension per hour	Per gallon suspension per hour
	Mg./liter	*G./100 cu. ft.*	*Liters*	*Cu. ft.*	*Minutes*	*Liters*	*Cu. ft.*
1	5.0	210	0.547	0.0197	4	54.7	7.31
2	24.5	1,030	0.277	0.00995	4	27.7	3.70
3	93.5	3,930	0.164	0.0059	4	16.4	2.19
4	267.0	11,290	0.121	0.0043	4	12.1	1.62
5	39.0	1,640	0.110	0.0039	24	66.0	8.82
6	187.0	7,850	0.0364	0.0013	50	45.5	6.07
7[b]	27.0	1,130	0.103	0.0037	17	43.8	5.85
8[c]	40.0	1,690	0.084	0.0031	2	..	..

[a] 40 cc. of suspension employed in all runs. Assuming same rate of removal in countercurrent flow as obtained with suspension, stationary; suspension to be changed completely in time interval of run.

[b] Hydrolyzed suspension; efflux gas last 3 minutes of run contained MgH_2S per liter. In all runs except 7 and 8 efflux gas was free of H_2S over duration of run.

[c] Water employed instead of suspension; efflux very rich in H_2S at end of run.

The mercaptan content of the gasolines can be calculated from the well-established fact (*7*, *8*) that one atom of elementary sulfur is necessary for each two atoms of mercaptan sulfur present. On the assumption that the magnesium compound decomposed by sulfuric acid is $\mathrm{Mg}\begin{matrix}\diagup \mathrm{SR}\\ \diagdown \mathrm{OH}\end{matrix}$ reacting in accordance with the reaction:



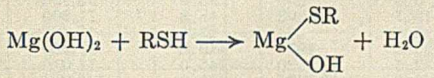
$$\mathrm{Mg}\begin{matrix}\diagup \mathrm{SR}\\ \diagdown \mathrm{OH}\end{matrix} + H_2SO_4 \longrightarrow MgSO_4 + RSH + H_2O \qquad (2)$$

the mercaptan sulfur content can also be calculated. That the compound formed conforms to the formula $\mathrm{Mg}\begin{matrix}\diagup \mathrm{SR}\\ \diagdown \mathrm{OH}\end{matrix}$ is shown by a comparison of the two calculations:

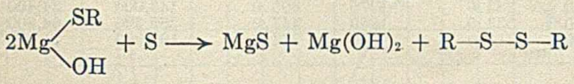
	MG MERCAPTAN S PER LITER Sample 1	Sample 2
Calculated from S requirement	334	177
Calculated from Equation 2	326	184

If $\mathrm{Mg}\begin{matrix}\diagup \mathrm{SR}\\ \diagdown \mathrm{SR}\end{matrix}$ were the compound present, the calculated mercaptan sulfur content from titration would be approximately double the value calculated from the sulfur requirement.

Disregarding intermediate mechanism, the alteration of mercaptans to disulfides may be postulated to occur as follows:



$$Mg(OH)_2 + RSH \longrightarrow Mg\begin{matrix} \diagup SR \\ \diagdown OH \end{matrix} + H_2O \quad (3)$$



$$2Mg\begin{matrix} \diagup SR \\ \diagdown OH \end{matrix} + S \longrightarrow MgS + Mg(OH)_2 + R{-}S{-}S{-}R \quad (4)$$

The identification of magnesium sulfide as a product of the reaction has not been made. If magnesium sulfide is present as a product of the sweetening reaction, it exists in a thin film on the surface of the granules. On withdrawal of gasoline with subsequent intrusion of air, the thin film of magnesium sulfide in contact with air would be expected to undergo rapid oxidation to magnesium sulfate, among other possibilities. The presence of sulfate ion in the hydrogen chloride in the solution obtained from magnesium hydroxide which has been employed in sweetening, is readily demonstrable. A blank run on the original magnesium hydroxide gives a faint sulfate test as compared with that obtained from magnesium hydroxide after use.

The intermediate mechanism of magnesium hydroxide sweetening is not established. Shaking of a gasoline solution of the basic mercaptide with sulfur does not cause sweetening, even after prolonged contact. Contact with the surface of magnesium hydroxide is evidently necessary for completion of the reaction. The presence of water prevents the formation of the mercaptide almost entirely, driving Equilibrium 3 extremely far to the left.

The rapidity of mercaptan alteration in the process is dependent both upon the mercaptan content and the molecular weight of the mercaptans—the activity of mercaptans as acids decreases as the number of carbon atoms in the molecule increases. As the sweetening reaction progresses, the film of magnesium sulfide blankets an ever increasing portion of the magnesium hydroxide surface, so that the rate of sweetening decreases as the through-put of gasoline increases.

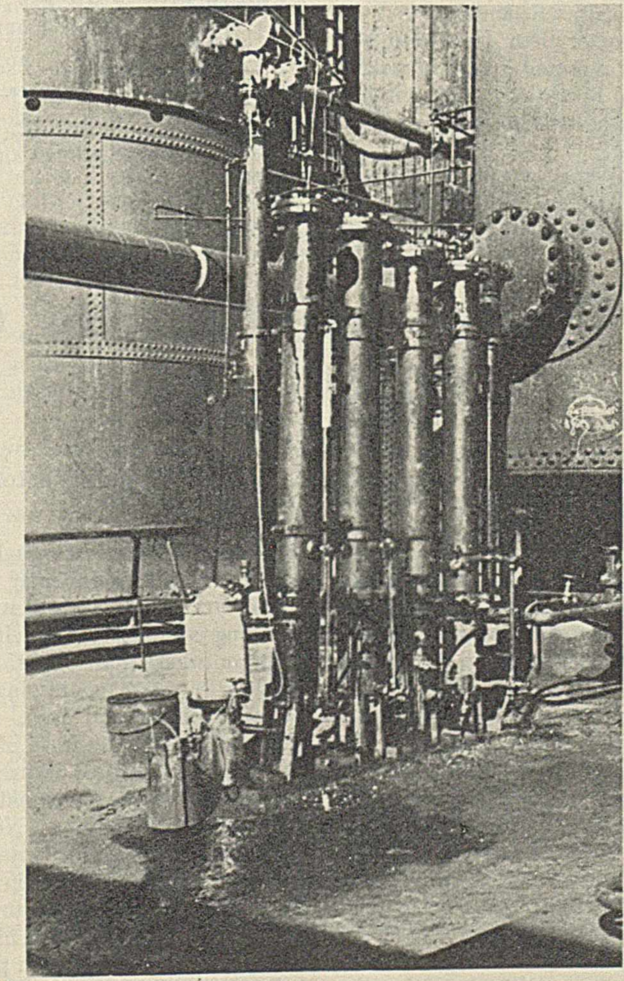


FIGURE 4. SEMIPLANT-SCALE MAGNESIUM HYDROXIDE TOWERS

REGENERATION OF MAGNESIUM HYDROXIDE

Eventually the rate becomes so slow that regeneration of the magnesium hydroxide surface becomes desirable. The hydrolysis of magnesium sulfide by boiling water should result in ready restoration of magnesium hydroxide. A sample of spent magnesium hydroxide was thus boiled, followed by thorough drying. The resulting material did not behave as well as before treatment. An analysis of the base revealed the presence of approximately 2 per cent silica and a trace of nonvolatile acid materials. If either or both of these materials were present on the surface of the magnesium hydroxide, they should be removed by boiling with sodium hydroxide. Boiling of the spent magnesium hydroxide with 2 per cent sodium hydroxide, followed by washing with water and drying, furnishes a product as active as when first employed in sweetening.

Experiments have indicated that analogous results can be obtained when using magnesium oxide as a base, instead of magnesium hydroxide, in the sweetening process. This feature has no particular significance because of the fact that, when the material is spent, revivification with boiling water is necessary, which will eventually result in the complete hydroxylation of the oxide. Violent ebullition, with the possibility of disastrous results, may take place in revivifying the oxide because of heat evolved.

COMMERCIAL OPERATIONS

On the basis of these findings, sweetening has been carried out in repeated cycles in the laboratory, and on semi-commercial and commercial scale. Gasoline containing the requisite amount of sulfur in solution is passed through one or more columns containing dry magnesium hydroxide. The capacity of the columns and the through-put are fixed by the concentration and nature of the mercaptans.

Commercially, two towers, 4 feet in diameter and 20 feet high, are connected in series. They are equipped with drying coils having a surface of about 25 square feet per ton of brucite. Saturated or superheated steam is used as the heating medium. Steam jets or evacuators are attached to outlets at the top of the towers to facilitate rapid removal of vapor during the drying period after revivification. Brucite is contained in the towers on perforated plates or screens above the bottom to curtail channeling to a minimum. The stock to be sweetened is pumped into the bottom of the tower, a portion of this stock being by-passed through a smaller receptacle containing roll sulfur. Gasoline is admitted through a valve to dissolve enough sulfur to complete the reaction.

Commercial operating cycles are governed mainly by the minimum rate which is economically feasible. Runs have been made in which 14,000 to 20,000 barrels of sour mixed gasolines have been sweetened through two towers, each containing 8 tons of magnesium hydroxide before revivifica-

TABLE IV. GASOLINE SWEETENING WITH MAGNESIUM HYDROXIDE

RUN	MERCAPTAN S CONTENT		WEIGHT OF $Mg(OH)_2$		TIMES REVIVIFIED	TIME	THROUGH-PUT		RATE PER HOUR		VOLUME	
	Mg./liter	*Lb./1000 gallons*	*Kg.*	*Lb.*		*Hours*	*Liters*	*Gallons*	*Liters/metric ton*	*Gal./ton*	*Liters/metric ton*	*Gal./ton*
1	77	0.64	0.950	2.08	1	25.2	22.7	6.0	950	228.0	23,900	5,500
2	72	0.60	0.984	2.16	0	354.0	70.8	18.7	203	48.8	71,800	17,300
3	168	1.40	1.100	2.42	0	48.0	19.2	5.08	364	87.5	17,400	4,200
4	72	0.06	0.900	1.98	2	52.0	87.2	23.0	1870	449.0	97,200	23,400
5	326	2.72	0.860	1.89	3	10.8	9.5	2.5	1020	245.0	11,010	2,520
6	14.4	0.12	7.48	16.5	1	113.0	1073.0	283.0	1270	305.0	143,000	34,400
7	14.4	0.12	7.48	16.5	2	145.0	2020.0	533.0	1860	447.0	269,500	64,800
8	14.4	0.12	7.48	16.0	4	111.0	800.0	211.0	965	232.0	107,000	25,800

tion was necessary. When the minimum rate cited above is reached and the efflux becomes sour, the gasoline in the columns is displaced with water, and the base is boiled with the water and then with 2 per cent sodium hydroxide and two washings with water, after which the washed material is dried *in situ* and is ready for another cycle.

Table IV lists a number of sweetening runs. In some of these, large through-put has been sacrificed for rapid rate. Runs 1 and 3 are typical of this type. Run 2 resulted in a good yield with a gasoline quite high in mercaptans, while a reasonably rapid rate was maintained. It is difficult to account for the fact that run 7 is apparently badly out of line.

The loss in sodium hydroxide per cycle has been found to be 40 mg. of sodium hydroxide per kilogram of magnesium hydroxide by analysis of the sodium hydroxide wash plus the first water wash, which is normally stored because of the appreciable alkali content. This analysis was compared with that of the original solution.

The loss in weight of magnesium hydroxide is slight. In laboratory operations the loss usually encountered is 1 to 2 per cent per cycle. No loss greater than 4 per cent has been obtained, and one laboratory reported a gain in weight of 0.375 per cent. In commercial operations, one unit has put through 75,000 barrels without the addition of any makeup magnesium hydroxide.

Figure 1 shows a flow sheet of the sweetening process. Figure 2 shows the details of drying equipments in use in commercial towers. Figure 3 is a photograph of a commercial magnesium hydroxide sweetening unit in operation in the Midcontinent territory. Figure 4 shows a system of four towers in semiplant-scale sweetening and hydrogen sulfide removal.

ACKNOWLEDGMENT

The writers wish to express their thanks to the numerous oil companies in the Midcontinent territory who have furnished the samples of sour and unrefined distillates employed in this work.

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Freezing Points of Mixtures of Oleum and Nitric Acid

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THERE was almost no available information on the freezing points of high acidity mixtures of nitric and sulfuric acids until an article by Holmes, Hutchison, and Zieber (*2*) appeared in 1931. An earlier paper by Holmes in 1920 (*1*) gave data on acid mixtures only up to 103 per cent total acidity. Their work has been supplemented here by experiment and with a curve built on higher total acidities.

As oleum of about 50 per cent free sulfur trioxide (111.25 per cent of 100 per cent sulfuric acid) is delivered from the plant, 5 to 7 per cent of nitric acid is added to depress the freezing point sufficiently to handle and store the product safely. No attempt was made in these experiments to limit the amount of nitric acid added, since it was assumed that larger amounts would necessarily cause further depression.

In the manufacture of nitric acid this same mixture of oleum and antifreeze is charged to circulating tanks where it is gradually built up to 70 per cent nitric acid by receiving the distillate from the plant. During the process this acid is constantly circulated through cooling coils. It was in these coils that the first difficulty caused by frozen acid occurred. These freezes reoccurred and were relieved each time by breaking coil joints and melting out frozen acid with water. This continued from year to year until the situation became acute when a tank containing 27.5 per cent nitric acid and 81 per cent sulfuric acid froze. It was with great difficulty that this tank was finally freed of the frozen acid.

Work of a practical nature was immediately started which resulted in the development, in 1930, of a plant freezing-point curve (Figure 1). No attempt was made to secure pure acid or to control total acidities, but all the samples were prepared in the plant in the ordinary course of operation by mixing together 110.5 to 111 per cent sulfuric acid and approximately 96 per cent nitric acid, which contained from 0.1 to 2.0 per cent nitrogen peroxide as well as ferric sulfate.

In the mixtures, beginning with 13 per cent nitric acid, definite compounds of nitric and sulfuric acid were found

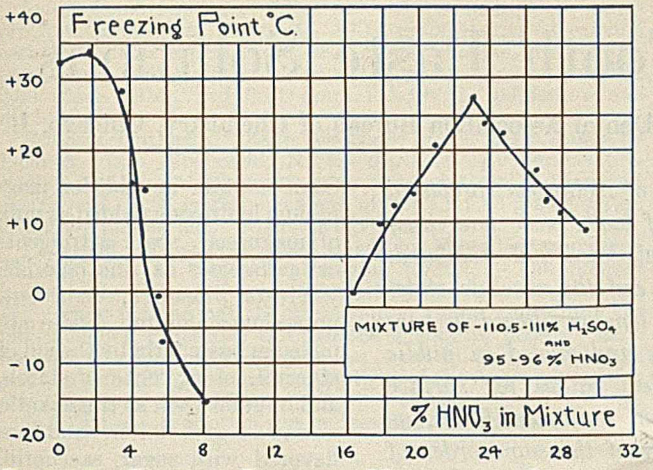

Figure 1. Freezing Points of Mixtures of Oleum and Nitric Acid

which were solid above 30° C. These crystallized out on standing and formed a hard mass which filled the lower part of the container. Analysis of these crystals was as follows:

	%		%	
H_2SO_4	88.75	≈	72.46	SO_3
HNO_3	25.12		21.50	N_2O_5
N_2O_4	0.08		6.04	H_2O
	113.95		100.00	

The nearest calculated compound to this is $N_2O_5\,(SO_3)_4\,H_2O$:

	Theoretical	Observed
N_2O_5	24.21	21.50
SO_3	71.75	72.46
H_2O	4.04	6.07

This compound, known as Solid or Export Mixed Acid, has a specific gravity of 2.18 and a melting point of 93° to 104° C. according to Schultze (*3*).

The method and apparatus (Figure 2) used in determining the freezing points are not materially different from those described in Holmes's paper (*2*). Mixtures of solid carbon dioxide, ether, and alcohol were found most convenient for low-temperature freezing points. By this means a temperature of −70° C. was obtained. In determining the freezing points, the samples of mixed acids were inoculated with crystals of the same acid composition as the one under test.

Table I. Analyses and Freezing Point Determinations of Mixtures of Sulfuric and Nitric Acids

Sample	H_2SO_4	HNO_3	N_2O_4	Total Acidity	Freezing Point
	%	%	%	%	° C.
1	108.48	1.56	0.08	110.12	33.0
2	106.63	3.22	0.12	109.67	27.9
3	104.94	4.47	0.19	109.06	15.0
4	104.43	4.96	0.32	109.71	14.0
5	104.50	4.96	0.32	109.78	14.5[a]
6	103.73	5.37	0.28	109.38	− 0.5
7	103.42	5.87	0.21	109.50	− 7.0
8	100.57	8.19	0.32	109.08	−16.0
9	88.67	16.43	1.81	106.91	− 0.5
10	87.35	18.10	1.50	106.95	10.0
11	86.50	18.42	1.93	106.85	12.0
12	86.62	19.43	0.76	106.81	14.0
13	84.97	20.61	0.91	106.49	20.5
14	83.38	22.74	0.94	107.06	28.0
15	81.88	23.75	1.03	106.66	23.0
16	80.00	24.54	1.00	105.54	22.0
17	80.06	24.64	1.01	105.71	22.0[b]
18	77.71	26.63	0.81	105.15	17.0
19	77.18	27.26	0.86	105.30	14.8
20	76.09	28.40	0.85	105.34	11.0
21	74.83	29.47	0.89	105.13	9.0

[a] Same acid as sample 4.
[b] Same acid as sample 16; freezing points determined 3 months apart.

An outstanding characteristic of nitric-sulfuric mixtures, of total acidities from 106 to 109 per cent, is the amount of supercooling they will take without freezing—at least on small laboratory samples. This property increases directly with the increase in content of oxides of nitrogen. Table I does not list the many mixtures of nitric acid percentages ranging from 6 to 16, especially those from 8 to 13 per cent, which were reduced to a temperature as low as −70° C., but which supercooled to such an extent that no freezing point could be obtained. No positive way (using carbon dioxide as a cooling agent) is known to the authors which will make such mixtures freeze. Possibly either repeated inoculations over the nitric acid range, or long standing at extremely low temperature might be successful.

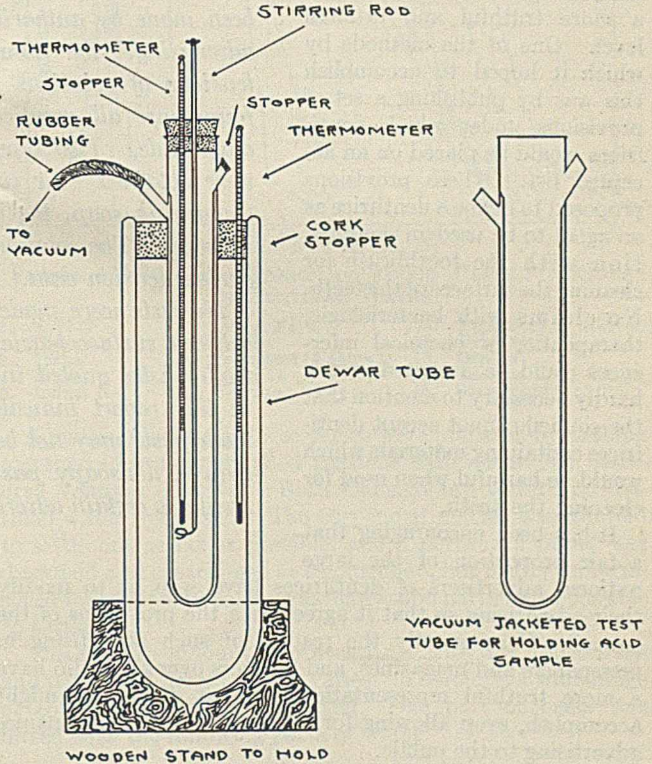

Figure 2. Freezing Point Apparatus

Investigation will be continued on freezing points of high total acidity, maintaining the total acidity constant over a wide range of nitric acid concentrations, and devoting special attention to those fuming sulfuric acid mixtures which are found in plant operation, and whose freezing points are difficult to determine because of supercooling.

Literature Cited

(1) Holmes, J. Ind. Eng. Chem., 12, 781 (1920).
(2) Holmes, Hutchison, and Zieber, *Ibid.*, 23, 1102 (1931).
(3) Schultze, U. S. Patent 1,047,567 (Dec. 7, 1912).

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Correction

In the paper by A. L. Ward, C. W Jordan, and W. H. Fulweiler on "Gum Deposits in Gas Distribution Systems. I. Liquid-Phase Gum," Ind. Eng. Chem., 24, 969 (1932), the following corrections should be noted:

Page 972, column 1, line 31, the phrase, "when gas free from naphthalene and saturated with styrene vapor is passed through saturated picric acid," should be added to the sentence, "In addition, styrene. . . . . .does not form a picrate."

Page 976, Table V, Samples 9 and 10, "Refined" should read "Reformed;" Sample 10, "86%" should read "86% Reformed Oil Gas."

Surface Tension of Tooth Paste Solutions

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The surface tension of solutions prepared from fourteen samples of tooth paste have been measured and the data tabulated and correlated. The results do not bear out the absolute statement of the low surface tension alleged to have been made by authorities and quoted in public advertising; the numerical values for surface tensions of solutions from soap dentifrices, as found, are all practically of the same order of magnitude. Two types of surface tension data were obtained—one corresponding to the pastes containing soap, the other to pastes containing no soap. The solutions of all give relatively low surface-tension data.

No tests were made to determine the relation between surface tension and cleansing power of tooth pastes quoted in advertisements. Nothing in this report indicates that a soap-containing tooth paste may not be as useful or more useful than a nonsoapy paste. The relation of these results to certain advertising is discussed.

Early in 1930 the American Dental Association through a recently organized Council on Dental Therapeutics, undertook to place the advertising of the dentifrice on a more truthful and rational level. One of the methods by which it hoped to accomplish this was by publishing a set of provisions under which dentifrices would be placed on an accepted list. These provisions proposed to define a dentifrice as an agent to be used in conjunction with the toothbrush for cleaning the surfaces of the teeth. No claims with bacteriologic, therapeutic, or chemical inferences could be accepted. It is hardly necessary to mention that the council cannot accept dentifrices containing materials which would be harmful when used for cleaning the teeth.

It has been encouraging that a fair proportion of the large national advertisers of dentifrices have seen fit to modify their advertising so that it agrees with the provisions of the council. Consequently the readers of such advertising in newspapers and magazines, and listeners over the radio have a more truthful representation of what dentifrices might accomplish, even allowing for the puffery that accompanies advertising to the public.

It was unfortunate, therefore, that photographs and signed testimonials appeared in newspapers and magazines, claiming that the low surface tension of one dentifrice made it superior to the others as a cleaning agent, basing this distinction on the one characteristic. These signed testimonials were accompanied by photographs of men described as distinguished scientists, world renowned, unquestionable leaders in science, public figures of unimpeachable authority, etc., together with quotations of their records from "Who's Who" and "American Men of Science." The signed statements were to the effect that they had examined a number of tooth pastes and that they had found one of them to possess the lowest surface tension. They concluded, without citing factual evidence, that the tooth paste of the company which employed them possessed "the greatest cleansing action." On general grounds it could be assumed that any soap-containing dentifrices would have a low surface tension.

These advertisements attracted the attention of this bureau and the writers awaited published reports in scientific journals upon which these statements might be based. Inasmuch as these factual data did not appear, examination was undertaken here to determine the surface tension of "solutions" prepared from tooth pastes.

EXPERIMENTAL PROCEDURE

Tooth pastes in general contain as abrasive either calcium carbonate or some form of calcium phosphate (tricalcium phosphate, calcium pyrophosphate, or dicalcium phosphate). Some contain in addition magnesium hydroxide (added as milk of magnesia), soap, astringents or germicides as zinc chloride, various phenols, orris root, potassium chlorate. These are mixed in paste form by the aid of glycerol, of glycerite of starch, and of gums such as tragacanth, karaya, and water, and are flavored with sugar, saccharin, and volatile oils. This general statement is not exhaustive, as an examination of the patents issued for dentifrices in the past two decades would show. Probably no other class of products better illustrates the extent to which the abuses of the patent situation have been carried. It reflects credit neither to the intelligence of the patentors nor to the patent system.

Fourteen dentifrices were used in the tests. Ten of these account, in general, for the more widely advertised products in this class. Others were introduced as samples became available. The samples were all original unopened packages. Data on the composition of the tooth pastes investigated have been gathered from the manufacturer, from the technical and advertising literature, and from other sources.

S. T. 37 Tooth Paste. This tooth paste (made by Sharp & Dohme, Inc., Philadelphia) is based apparently on the work of Feirer and Leonard (*6*) who examined several tooth pastes consisting essentially of gelatin, chalk, and glycerol, with sodium bicarbonate and butyl- and hexylresorcinol. They claimed that such a paste, containing 1 per cent of sodium bicarbonate and 0.16 per cent of hexylresorcinol in 20 per cent aqueous solution, destroyed all of the common pathogenic bacteria in 15 seconds. From the data reported below, it is apparent that the name "S. T. 37 Tooth Paste" does not accurately define the composition of the product on the market. Furthermore, the council does not accept dentifrices for which bacteriologic claims are made.

Colgate's Ribbon Dental Cream.[1] Each 100 grams of this paste (made by Colgate-Palmolive-Peet Company, Chicago) contains 28.0 grams glycerol, 5.0 grams soap (vegetable), 35.7 grams calcium carbonate, 7.6 grams precipitated chalk, 2.1 grams sodium benzoate, 0.9 gram aromatics, 6.5 grams corn starch, and 14.2 grams water.

Ipana Tooth Paste. Preliminary unpublished investigations indicate that Ipana (made by Bristol-Myers Company, New York) contains 18.8 per cent glycerol, 38.5 per cent calcium carbonate, 29.1 per cent water, approximately 6 per cent soap, β-naphthol, and a plant material which has not yet been fully investigated.

Forhan's. This tooth paste (made by the Forhan Company, New York) was found to contain approximately 0.2 per cent of zinc chloride (*2*), 5 per cent soap, and 46.0 per cent calcium carbonate. The manufacturers refused to divulge the formula.

Iodent Tooth Paste No. 1.[1] This paste (made by Iodent Chemical Company, Detroit) is composed of 55 grams precipitated calcium carbonate, 6 grams soap, 34 grams glycerol, 1.25 grams petrolatum, 0.25 gram saccharin, 1.0 gram oil of peppermint, 2.26 grams water, and 0.24 gram iodides (as potassium and calcium) (*3*).

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[1] Acceptable to the Council on Dental Therapeutics

Iodent Tooth Paste No. 2.[1] The composition is 30.14 grams precipitated calcium carbonate, 30.14 grams prepared calcium carbonate, 7.23 grams soap, 28.9 grams glycerol, 1.51 grams petrolatum, 0.30 grams saccharin, 1.20 grams oil of peppermint, 0.30 gram water, and 0.24 gram iodides (as potassium and calcium) (*3*).

Pebeco Tooth Paste.[1] Each 100 grams of this paste (made by Lehn & Fink, Bloomfield, N. J.) contains 19.98 grams precipitated chalk, 41.62 grams potassium chlorate, 2.15 grams stearic acid, 14.87 grams sugar and glycerol, 19.13 grams water, 0.72 gram binder, and 1.53 grams flavoring (*4*).

Pepsodent. This tooth paste (made by Pepsodent Company, Chicago) has an avowedly changing formula. The product has been the subject of several articles by Gies and collaborators (*8*). They pointed out the unwarranted claims concerning the film-removing properties through the agency of pepsin. Each formula was inferred to be the last word in dental science, a position difficult to reconcile in the light of the firm's advertising and changes of composition.

In 1920 the composition was represented as follows:

	%
Pepsin	0.81
Acid calcium phosphate	1.04
Calcium chloride	0.44
Precipitated tricalcium phosphate	51.99
Glycerol, alcohol, water, flavoring, etc.	45.72

In 1926 the formula was given as:

	%
Pepsin	0.621
Acid calcium phosphate	0.512
Acid calcium tartrate	0.190
Calcium chloride	0.237
Benzoic acid	0.094
Mitigated calcium phosphate Tricalcium phosphate Anhydrous calcium sulfate	59.400
Glycerol, water, flavoring, etc.	38.946

It is worthy to note the plethora of figures in this and the succeeding formula. One naturally wonders if this is the result of "laboratory analysis" or "lead pencil analysis" from the "mixing formula."

Pepsodent Tooth Paste is now advertised as having the following composition:

	%
Special calcium phosphate	59.400
Benzoic acid	0.100
Tragacanth gum	0.600
Karaya gum	1.200
Calcium chloride	0.237
Glycerol, water, flavor	38.463

The exact chemical nature of the "special" calcium phosphate is not stated in any advertising literature that has come to the attention of the authors. Preliminary investigations indicate it to be related to brushite ($CaHPO_4 \cdot 2H_2O$).

Listerine Tooth Paste. This paste (made by Lambert Pharmacal Company, St. Louis) is admittedly secret in composition. Qualitative tests indicate the abrasive portion to consist of calcium sulfate and tricalcium phosphate. Soap was not found.

Kolynos Dental Cream. This paste (made by the Kolynos Company, New Haven, Conn.) was stated by the manufacturers to have the following composition: 18.87 per cent alcohol, 0.21 per cent thymol, 0.35 per cent saccharin, 1.30 per cent oil of eucalyptus, 1.42 per cent oil of peppermint, 0.22 per cent benzoic acid, 28.63 per cent glycerol, 20.00 per cent soap, 29.01 per cent chalk (*5*).

Dr. West's Tooth Paste. This paste (made by The Western Company, Chicago) has the following formula, according to the manufacturer: 39.71 per cent calcium carbonate (Sturge), 0.76 per cent carbonate of magnesia, 1.51 per cent soap (imported castile), 17.80 per cent milk of magnesia, 2.50 per cent silica, 2.50 per cent simple sirup, 30.54 per cent glycerite of starch, 3.75 per cent mineral oil, 0.06 per cent gum tragacanth, 0.07 per cent saccharin, 0.78 per cent flavoring oils, 0.02 per cent color solution.

Orphos Tooth Paste. This paste (made by Orphos Inc., New York) on qualitative examination was found to contain calcium sulfate and tricalcium phosphate as the abrasive portion.

Lactona Dentifrice. The specimen of Lactona (made by Lactona Company, Chicago) used for the surface tension test had, according to the manufacturer, the following formula: 41 to 45 per cent glycerol, 42 to 38 per cent tricalcium phosphate, 3.0 per cent galactonic lactone, 9.0 per cent water, 0.3 per cent malic acid, 3.7 per cent alcohol, 0.37 per cent gum tragacanth or karaya, 0.6 per cent sodium chloride and flavoring.

Specimens for the test were obtained by squeezing portions of the paste from the tubes and weighing by difference. Cursory visual examination indicated that the pastes were uniform as to homogeneity, with the exception of Iodent Tooth Pastes Nos. 1 and 2. On squeezing from the tubes, the latter yielded a strip of paste with a layer of liquid surrounding it.

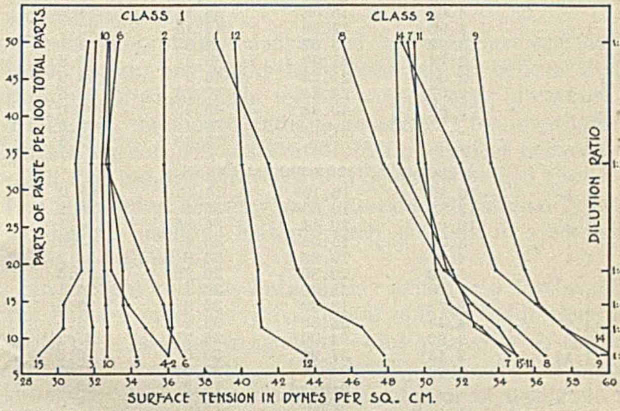

FIGURE 1. SURFACE TENSION OF TOOTH PASTE SOLUTIONS IN DISTILLED WATER

1. S. T. 37
2. Colgate's
3. Ipana
4. Forhan's
5. Iodent No. 1
6. Iodent No. 2.
7. Pebeco
8. Pepsodent (A aplgc 2)
9. Listerine
10. Kolynos
11. Pepsodent (A aplgc 4)
12. Dr. West's
13. Orphos
14. Lactona
15. Soap solution (5 %)

Aqueous solutions of these pastes were prepared by shaking together accurately weighed portions with accurately measured volumes of water. Both Chicago tap water and distilled water were used. The suspended matter was allowed to settle out as far as possible, and a portion of liquid was drawn off and centrifuged at a controlled, but nearly uniform, speed for a half hour to cause as many solid particles as possible to settle.

The relative amount of water used with the toothbrush and paste by different people varies. Therefore, a wide range of concentrations was employed. One part of paste was mixed with the following parts of water:

Parts	*% by weight*	*Parts*	*% by weight*	*Parts*	*% by weight*
1	50	4	20	8	11$^1/_9$
2	33$^1/_3$	6	14$^2/_7$	12	7$^9/_{13}$

Five cubic centimeters of the centrifuged liquid were transferred to a clean watch glass, and the surface tension of the solution determined by means of a tensiometer, of the DuNoüy type. A comprehensive treatment of the methods for measuring surface tension is included in articles by Ferguson, DuNoüy, and Klopsteg (*7*).

Constant readings could usually be obtained by waiting for one minute after placing the solution in the dish, and one minute between readings.

The usual precautions for cleaning the glassware used were observed. The instrument was standardized by the absolute method, and checked with boiled distilled water cooled to 22° C., as a reference liquid. Measurements were made at prevailing room temperature (25° C.).

The surface tension values for a 5.0 per cent solution of soap (U. S. P.) were determined for comparison.

The results obtained are shown in Table I.

Figure 1 and Figure 2 show the surface tension values of solutions in relation to concentration in distilled and tap water, respectively. All the plotted points were connected by straight lines rather than by attempting to draw curves.

DISCUSSION OF RESULTS

It may be seen from the graphs that the values for surface tension obtained for the solutions of the tooth pastes examined

Table I. Data on Tooth Pastes

Dilution Ratio	Paste *Grams*	Water *Cc.*	Surface Tension *Dynes/sq. cm.*	Temp. *° C.*
		S. T. 37 TOOTH PASTE		
1:1	16.78	16.78[a]	38.6	22.5
	19.33	19.33[b]	38.3	24.5
1:2	10.30	20.60	41.55	22.5
	9.00	18.00	40.55	24.4
1:4	4.08	16.32	43.05	22.5
	4.02	16.08	44.45	24.7
1:6	2.93	17.58	44.15	22.5
	3.92	23.52	44.95	24.7
1:8	2.74	21.92	46.5	23.8
	2.66	21.28	45.9	24.9
1:12	2.07	24.84	47.75	23.8
	3.54	42.48	46.45	25.0
..	...	Distilled	73.4	22.5
..	...	Tap	73.95	22.5
		COLGATE'S RIBBON DENTAL CREAM		
1:1	16.19	16.19[a]	35.75	25.0
	12.85	12.85[b]	35.6	26.1
1:2	10.07	20.14	35.85	26.1
	8.33	16.66	35.9	25.6
1:4	4.97	19.88	36.0	26.2
	5.20	20.80	35.75	26.5
1:6	3.70	22.20	36.1	26.1
	2.72	16.32	35.8	26.6
1:8	4.44	35.52	36.2	26.5
	3.00	24.00	35.7	27.2
1:12	3.16	37.92	36.0	26.2
	2.88	34.56	35.0	27.3
..	...	Distilled	74.2	23.0
..	...	Tap	75.5	26.5
		IPANA TOOTH PASTE		
1:1	12.18	12.18[a]	32.0	23.6
	12.36	12.36[b]	32.0	24.0
1:2	7.88	15.76	31.8	23.2
	9.74	19.48	31.8	24.0
1:4	6.47	25.88	31.85	23.2
	4.29	17.16	31.75	24.5
1:6	4.10	24.60	31.7	23.2
	3.28	19.68	31.75	24.6
1:8	3.27	26.16	31.9	23.3
	3.76	30.08	31.85	24.6
1:12	3.64	43.68	31.85	23.5
	3.30	39.60	31.75	24.4
..	...	Distilled	72.55	23.5
..	...	Tap	73.0	24.4
		FORHAN'S		
1:1	14.06	14.06[a]	32.75	24.5
	15.86	15.86[b]	32.3	24.7
1:2	9.81	19.62	32.75	24.7
	7.55	15.10	32.35	25.1
1:4	3.82	15.28	32.95	24.7
	5.63	22.52	32.5	24.9
1:6	4.14	24.84	33.8	24.8
	3.67	22.02	32.6	24.9
1:8	2.48	19.84	34.8	24.8
	2.70	21.60	33.0	24.5
1:12	2.38	28.56	36.0	24.8
	2.59	31.08	33.4	24.1
..	...	Distilled	72.9	24.5
..	...	Tap	72.9	24.5
		IODENT TOOTH PASTE NO. 1		
1:1	14.68	14.68[a]	32.8	23.2
	20.83	20.83[b]	33.0	24.0
1:2	11.23	22.46	32.75	23.4
	8.08	16.16	31.9	24.5
1:4	7.86	31.44	33.5	23.2
	6.34	25.36	31.8	24.5
1:6	3.29	19.74	33.7	22.0
	5.01	30.06	32.0	24.5
1:8	3.26	26.08	33.9	22.2
	3.92	31.36	32.8	25.2
1:12	3.07	36.84	34.35	22.1
	2.02	24.24	33.0	25.5
..	...	Distilled	72.85	22.3
..	...	Tap	72.9	24.9
		IODENT TOOTH PASTE NO. 2		
1:1	28.03	28.03[a]	33.3	22.5
	16.16	16.16[b]	33.2	22.0
1:2	8.96	17.92	32.65	22.2
	9.56	19.12	32.5	21.8
1:4	5.13	20.52	34.9	21.8
	8.62	34.48	34.0	21.4
1:6	4.73	28.38	35.85	21.5
	6.76	40.56	35.1	22.0
1:8	2.14	17.12	36.05	21.5
	2.39	19.12	33.5	22.7
1:12	2.94	35.28	36.8	21.9
	2.73	32.76	33.7	22.7
..	...	Distilled	72.9	22.4
..	...	Tap	73.3	22.8
		PEBECO TOOTH PASTE		
1:1	14.30	14.30[a]	49.0	25.5
	15.65	15.65[b]	50.0	26.5
1:2	9.41	18.82	50.0	25.4
	9.66	19.32	50.2	26.2
1:4	6.30	25.20	50.6	25.2
	5.18	20.72	50.7	26.5
1:6	5.12	30.72	51.25	25.0
	3.50	21.00	51.05	26.4
1:8	3.25	26.00	53.0	25.6
	3.01	24.08	52.3	25.0
1:12	2.62	31.44	54.65	25.7
	2.49	29.88	54.15	26.6
..	...	Distilled	72.9	25.5
..	...	Tap	73.1	25.8
		PEPSODENT (A APLGC 2)		
1:1	15.15	15.15[a]	45.45	24.0
	19.27	19.27[b]	45.8	24.0
1:2	9.21	18.42	47.65	24.0
	9.17	18.34	48.8	24.0
1:4	4.64	18.56	50.9	24.0
	4.18	16.72	51.55	24.0
1:6	5.43	32.58	53.5	24.0
	3.00	18.00	52.6	23.8
1:8	4.97	39.76	54.9	24.3
	2.99	23.92	54.4	23.6
1:12	2.74	32.88	56.55	24.4
	3.72	44.64	56.95	23.5
..	...	Distilled	73.0	24.2
..	...	Tap	72.85	23.4
		LISTERINE TOOTH PASTE		
1:1	15.77	15.77[a]	52.7	28.2
	12.76	12.76[b]	50.65	28.8
1:2	9.65	19.30	53.6	28.1
	7.11	14.22	54.5	28.5
1:4	6.69	26.76	55.8	27.2
	4.26	17.04	55.4	28.0
1:6	3.85	23.10	56.5	29.5
	3.73	22.38	56.2	28.0
1:8	2.69	21.52	57.8	28.8
	3.12	24.96	59.75	28.5
1:12	2.91	34.92	59.4	28.0
	1.74	20.88	61.25	29.2
..	...	Distilled	71.4	28.9
..	...	Tap	71.55	28.8
		KOLYNOS DENTAL CREAM		
1:1	16.18	16.18[a]	32.7	27.2
	15.33	15.33[b]	33.0	27.0
1:2	8.24	16.48	32.4	28.0
	8.26	16.52	32.9	26.8
1:4	3.40	13.60	32.55	26.5
	4.42	17.68	32.55	27.2
1:6	2.77	16.62	32.65	27.4
	3.80	22.80	32.1	27.0
1:8	1.97	15.76	32.75	28.2
	2.12	16.96	32.25	28.0
1:12	1.35	16.20	32.7	27.5
	2.90	34.80	32.0	27.1
..	...	Distilled	71.85	27.5
..	...	Tap	72.3	27.0
		PEPSODENT (A APLGC 4)		
1:1	13.65	13.65[a]	49.4	26.0
	15.70	15.70[b]	49.45	27.0
1:2	6.06	12.12	49.6	26.7
	7.19	14.38	49.8	27.2
1:4	3.46	13.84	51.2	27.0
	5.16	20.64	52.55	26.8
1:6	3.70	22.20	52.5	27.1
	4.09	24.54	53.7	26.8
1:8	2.99	23.92	54.0	26.6
	4.00	32.00	54.0	27.6
1:12	2.52	30.24	55.0	26.0
	1.76	21.12	55.95	27.0
..	...	Distilled	71.9	27.0
..	...	Tap	71.75	27.0
		DR. WEST'S TOOTH PASTE		
1:1	13.88	13.88[a]	39.6	23.8
	13.64	13.64[b]	38.95	24.7
1:2	9.19	18.38	40.0	24.5
	7.62	15.24	39.1	24.6
1:4	4.60	18.40	40.85	24.6
	5.52	22.08	39.95	24.5
1:6	3.11	18.66	41.0	24.6
	2.99	17.94	42.0	24.2
1:8	3.04	24.32	41.1	24.7
	3.57	28.56	49.55	24.0
1:12	2.70	32.40	43.5	25.3
	3.05	36.60	55.0	24.0
..	...	Distilled	72.95	24.9
..	...	Tap	72.9	23.0

[a] Distilled water. [b] Tap water.

fall into two main groups: (1) the surface tension is relatively low and is practically constant for the range of concentrations investigated; (2) the surface tension is of a relatively higher value and increases with decreasing concentration. The difference, however, is relatively not great. Tests were not made for an advertised milk of magnesia tooth paste.

The surface tensions of solutions of class 1 tooth pastes are essentially of the same order of magnitude as would be obtained from a solution of soap (U. S. P.) Indeed, all of the tooth pastes belonging to class 1 contain soap in various amounts up to 25 per cent. Those dentifrices which were examined and which fall in class 1 are: Colgate's, Ipana, Forhan's, Iodent No. 1, Iodent No. 2, and Kolynos.

TABLE I. (*Concluded*)

DILUTION RATIO	PASTE *Grams*	WATER *Cc.*	SURFACE TENSION *Dynes/sq. cm.*	TEMP. *° C.*
		ORPHOS TOOTH PASTE		
1:1	16.77	16.77[a]	48.4	28.0
	18.95	18.95[b]	48.7	28.1
1:2	11.38	22.76	48.6	28.0
	6.30	12.60	49.65	28.2
1:4	7.11	28.44	51.5	28.0
	4.05	16.20	51.0	28.1
1:6	4.15	28.50	52.3	28.0
	4.75	24.90	52.5	28.2
1:8	4.87	27.84	52.75	28.2
	3.48	38.94	53.0	28.1
1:12	5.05	60.60	55.0	28.0
	4.25	51.00	54.8	28.1
..	...	Distilled	72.0	28.1
..	...	Tap	71.9	28.2
		LACTONA DENTIFRICE		
1:1	14.48	14.48[a]	48.7	26.6
	14.24	14.24[b]	48.0	25.7
1:2	10.36	20.72	51.9	26.8
	12.78	25.56	54.0	25.9
1:4	5.63	22.52	54.25	26.8
	4.88	19.52	55.35	26.2
1:6	4.26	25.56	56.4	27.0
	4.04	24.24	57.5	26.0
1:8	3.31	26.48	57.75	26.0
	5.11	40.88	58.5	26.0
1:12	3.91	46.92	60.25	26.0
	4.76	57.12	60.85	26.0
..	...	Distilled	71.6	26.8
..	...	Tap	72.2	25.8
		5 PER CENT SOAP SOLUTION		
1:1	10.0	10.0[a]	31.6	27.6
	10.0	10.0[b]	30.8	27.7
1:2	5.0	10.0	31.0	27.7
	5.0	10.0	29.5	27.5
1:4	5.0	20.0	31.3	27.2
	5.0	20.0	29.0	27.8
1:6	5.0	30.0	30.3	27.8
	5.0	30.0	27.5	28.0
1:8	5.0	40.0	30.25	27.9
	5.0	40.0	27.75	27.5
1:12	5.0	60.0	29.0	27.8
	5.0	60.0	27.55	27.8
..	...	Distilled	71.5	27.8
..	...	Tap	71.0	28.0

[a] Distilled water.
[b] Tap water.

The relative values of the surface tension of solutions of dentifrices other than those containing soap depend on the concentrations used. For example, it can be readily appreciated that a paste whose solution shows a lower surface tension at one concentration may not show the same surface tension at a different concentration. This is merely cited to show how misleading unqualified statements of "research" work may be when they are examined critically. The reader of statements of "surface tension" not supported by factual evidence or exact statements is not in a position to know whether a 1:12 or 1:1 concentration was used. The writer of advertising copy for the public might protest that the public does not want to be bothered by details, but in the last analysis it is the details that make a claim valid or invalid.

Class 2 includes the following pastes: Pebeco, Pepsodent (A aplgc 2), Listerine, Pepsodent (A aplgc 4), Orphos, and Lactona. These pastes are known not to contain soap. Their solutions have surface tensions higher than those containing soap, and the surface tension increases with dilution.

The exact amount of soluble substances present in each protocol cannot be stated from the examination made. The soluble constituents are, in general, glycerol with small amounts of essential oil used in flavoring, small amounts of sugar or saccharin, soluble salts, and any of the many substances compounded in tooth pastes.

Two pastes yield figures between the soap-containing and the soap-free dentifrices. These are S. T. 37 and Dr. West's. Judging from the form of the curve, Dr. West's is more like the paste of class 1, whereas S. T. 37 is more like the paste of class 2. Dr. West's Tooth Paste is stated to contain 1.5 per cent soap.

The question has been raised as to what conclusion may be drawn from the reported data which would aid the user in forming an opinion as to the cleansing power of a tooth paste. In the opinion of the authors the answer would be that no sound conclusion may be drawn from such data unless actual figures about the cleansing power were given and then correlated with surface tension data. This apparently was not done by the experts quoted in the advertising, and it is hardly necessary to point out that at the present time there is no standard by which to measure the cleansing power of a dentifrice on teeth.

From the prominence given the "lower surface tension" of tooth pastes, one might have been led to believe that a thorough brushing of the teeth is unnecessary. Just work up a lather in the mouth and the penetrating foam with its low surface tension will penetrate into the crevices between the teeth and remove every particle of debris lodged there! If this is the case, one may well question the rationality of including an insoluble material such as chalk in a soap-containing tooth paste.

In the last analysis, until further evidence is forthcoming, the balance of conservative dental opinion holds that, if a tooth paste is effective at all, it is due primarily to the friction between the teeth and the brush; the aid of other substances in dentifrices is only secondary or of negligible importance. It was an appreciation of this that led the Council on Dental Therapeutics to define a dentifrice as a preparation which might aid the toothbrush in cleaning the teeth.

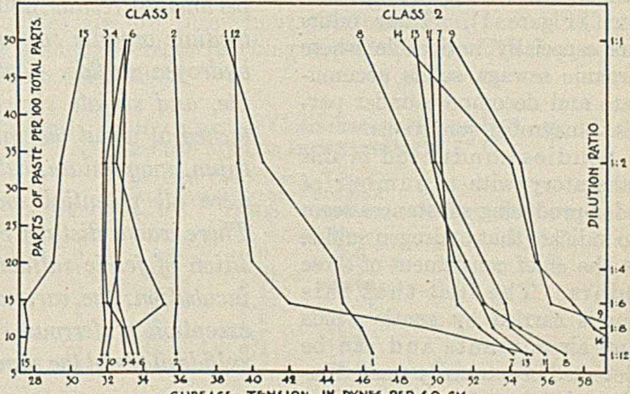

FIGURE 2. SURFACE TENSION OF TOOTH PASTE SOLUTIONS IN TAP WATER

The data reported are given at their face value. There has been nothing at stake but the desire to represent scientific data as obtained, and also the hope that such an effort as this might dissuade other distinguished scientists from rushing into newspaper advertising which imposes on the public confidence in the chemical profession. It is almost trite to state that in the long run such misrepresentation will not react to the efforts which chemists and other scientists are making to bring worthwhile scientific information to the public.

In conclusion it should be pointed out that nothing in this report indicates which tooth paste is best. Experimental information to permit one to draw even a relatively fair conclusion on this point is sorely lacking. Unfortunately, most studies on the properties of tooth pastes, like this one, have been undertaken to knock down the "scientific straw men" created by dentifrice advertising. The investigations on standards for dentifrices and dentifrice abrasives are being continued. When consumers, by the force of their purchasing power, make manufacturers appreciate that the sole function of the dentifrice is to aid the toothbrush in cleaning the surfaces of the teeth, actual experimental data submitted to, and acceptable to unbiased authorities will possibly take the place of "scientific straw men" in advertising.

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RECEIVED May 26, 1932.

Studies on Hydrogen Sulfide Formation in Sewage

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Incubation of domestic sewage under anaërobic conditions shows the presence of a very small proportion of combined sulfides as compared with volatile sulfide (hydrogen sulfide) throughout the course of decomposition. Two distinct peaks of sulfide formation are characteristic of the decomposition (slight changes in pH values). Experimental results point to the presence of intermediate organic sulfur compounds as sources of hydrogen sulfide. Additions of thiosulfate, sulfite, and sulfate showed that all forms were attacked at about the same rate. Sodium, ammonium, magnesium, calcium, and ferrous sulfates were all potential sources of hydrogen sulfide. There was a distinct retardation in the decomposition of ferric sulfate. During the first day of incubation, the various sulfates added (with the exception of ferrous sulfate) produced hydrogen sulfide at about the same rate as the control.

ODORS are often a serious problem in the vicinity of sewage plants where growth of the community necessitates the construction of dwellings adjacent to these plants. Complaints have also been heard from dwellers near sewer lines, catch-basins, pumping stations, etc. (Figure 1). These odors are especially noticeable where organic sewage solids accumulate and decompose under partial anaërobic conditions.

Studies conducted in this laboratory with a number of odor-producing substances seem to indicate that hydrogen sulfide is the chief constituent of these odors. The fact that this gas is carried by gentle winds and air currents and can be detected in extremely small dilutions in the atmosphere often accounts for the nuisances created (Figure 2). Bach (*2*) states that bad odors in sewage are due to sulfur compounds and not to nitrogenous compounds. Inorganic sulfur preponderates over organic sulfur to a great extent in raw sewage. Buswell (*3*) found that raw sewage rarely contained over 1.0 p. p. m. of organic sulfur, whereas inorganic sulfur in some cases was as high as 90 p. p. m. In one case organic sulfur was registered as a trace and inorganic sulfur 92.8 p. p. m. It appeared, therefore, that the decomposition of sulfates should be given the most important consideration in any study of the production of hydrogen sulfide from sewage.

There are four sources of sulfur in sewage—namely:

1. Sulfur in inorganic combination as sulfates, thiosulfates, etc., present in the water supply of the community.
2. Sulfur in inorganic combinations as sulfates, thiosulfates, etc., present in the ground or surface waters which find their way by infiltration into the sewer.
3. Sulfur in inorganic combinations, proteins, etc., or as inorganic sulfates from human excreta.
4. Sulfur in organic or inorganic combination present in industrial wastes.

Of these four sources, in general those from water supplies and due to infiltration are probably the most important. Infiltration water is often very high in sulfate content. Sulfur entering from human excreta is negligible in comparison with the other sources, whereas sulfur in industrial waste is found in special cases.

Owing to the greater hardness of the water supplies, the sulfate content of sewage in the West and Middle West is usually high compared to that found in the eastern United States. Analysis of the raw sewage at the Plainfield, N. J., disposal plant showed 70 p. p. m. of sulfate.

There is a variation in the type of sulfur compound predominating in different domestic wastes, whether it be calcium, magnesium, sodium, or ferrous sulfate, etc. The inorganic sulfur may be present to some extent as thiosulfate, sulfite, etc.

The different salts apparently give rise to different quantities of hydrogen sulfide when subjected to the same conditions. Rudolfs (*4*) found a wide variation in the amount of hydrogen sulfide formed from sulfates when they were added to fresh sewage sludge and subsequently incubated under anaërobic conditions. His results showed sulfide formation to diminish in order of the following arrangement: Ammonium, magnesium, calcium, copper, sulfate, sulfuric acid, sodium, aluminum, zinc, and ferrous sulfate.

An attempt has been made to study the availability of these various sulfur compounds as potential sources of hydrogen sulfide. Studies have been made on the effect of pH, temperature, seeding, strength of sewage, concentration of sulfates, certain pure compounds, and control substances as chlorine, iron salts, etc., on the formation of hydrogen sulfide in sewage. The results of this work will be published later.

METHODS

Sewage used in these experiments was taken from the influent channel of the Plainfield, N. J., sewage disposal plant after it had passed through the Reinsch Wurl screen. It was taken at 11 A. M. as representative of sewage of average daily composition. This sewage is domestic, averaging 220 p. p. m. suspended solids. It is approximately six hours old when it reaches the plant. However, the sewer leading to the plant was designed to give a rapid flow with little collection of solids in it. All samples were incubated in 500-cc. stoppered bottles.

Two methods were employed to determine hydrogen sulfide.

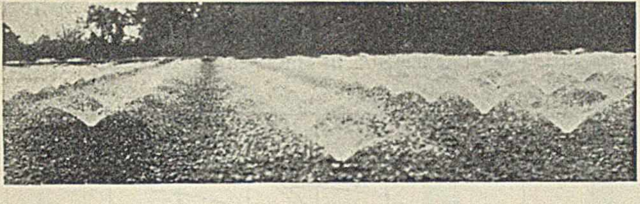

Figure 1. Trickling Filters, Frequently Sources of Odor

The one method, that of Almy (*1*), modified by Buswell (*3*) for sewage analysis, was used when the hydrogen sulfide content did not exceed one or two p. p. m. The other method employed was the one in which hydrogen sulfide is allowed to react with standardized iodine solution. In both cases the hydrogen sulfide was driven out of the sewage by carbon dioxide to remove the interfering substances. This was accomplished by constructing an aërator from large-bore glass tubing. An alundum filter disk was fastened in the lower end of the tube. Carbon dioxide, led into the cylindrical chamber under this plate through a tube, diffused through the plate, giving an even flow of fine bubbles up through the whole of the liquid. A tube at the top of the aërator led the gases off to a ten-bulb absorption tube where hydrogen sulfide was absorbed in either zinc acetate solution or allowed to react with standard iodine solution, depending on the method used.

In determining total sulfides, concentrated hydrochloric acid was added to the sample being aërated; this accelerated the removal of hydrogen sulfide from the liquid and also decomposed the combined sulfides. One-half hour to one-hour aëration, depending on the amount of sulfide present, sufficed to drive out the sulfides from the sample. When hydrochloric acid was not added, as would be the case where only volatile sulfide or free hydrogen sulfide was determined, longer aëration periods were required. Even then it could not be ascertained that all the hydrogen sulfide was removed, although the amount remaining would be negligible. This would tend to make the determinations of combined sulfide slightly higher than they were actually.

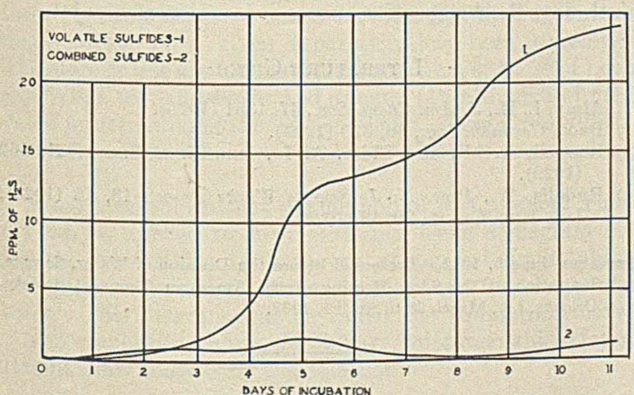

Figure 3. Production of Volatile and Combined Sulfides from Sewage

Sulfates were determined gravimetrically by precipitation with barium chloride after iron and color were removed.

The pH was determined colorimetrically using bromothymol blue, giving a pH range of 6.0 to 7.6 which served for all determinations, comparisons being made with a standard LaMotte block comparator set.

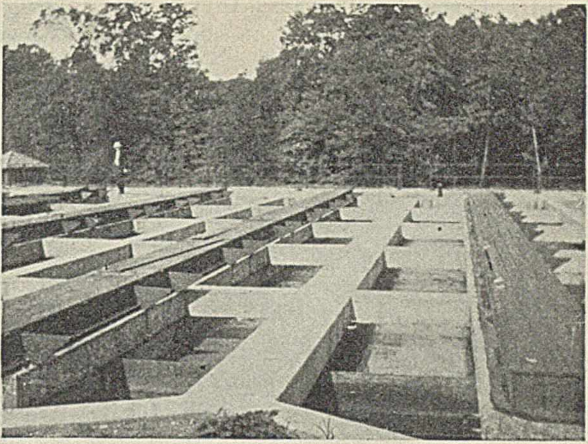

Figure 2. Imhoff Tanks Produce Hydrogen Sulfide

Results

Comparison of Combined to Free Hydrogen Sulfide and pH. Bottles were filled with sewage, stoppered and placed in an incubator set at 37.5° C. Daily, or at such times as was deemed necessary, a bottle was removed from the incubator and a determination made of free sulfide, combined sulfide, and pH. Sulfates were determined at the beginning and at the end of the experiment. The results of these determinations are given in Table I and partially plotted in Figure 3. The curves illustrate the small amount of combined sulfide in relation to free sulfide during incubation. Combined sulfides are low throughout the incubation period. There is a slight increase reaching a peak on the fifth day, after which they fall off.

Table I. Comparison of Combined to Free H_2S and pH in Sewage during Incubation (37.5° C.)

Days	Volatile Sulfide as H_2S	Combined Sulfide as H_2S	Total Sulfide as H_2S	pH	Sulfates
	P. p. m.	*P. p. m.*	*P. p. m.*		*P. p. m.*
0	0.0	0.0	0.0	7.5	76.6
1	0.1	0.24	0.34	7.1	
2	0.53	0.47	1.00	7.1	
4	2.65	0.59	3.24	7.0	
5	13.2	1.9	15.1		
6	12.8	0.7	13.5	7.2	
7	13.3	0.4	13.7		
11	24.0	1.2	25.2	7.2	17.1

Volatile sulfide is seen to increase very slowly up to the fourth day, when there is a rapid rise in sulfide production. During the next two or three days there is a definite retardation, after which comes another period of rapid production. The reason for the slow formation of hydrogen sulfide during the first few days evidently lies in the fact that the sample was taken in cold weather when the temperature of the sewage was very low. Such a low temperature would not be favorable to the growth or multiplication of sulfate-reducing organisms in the sewage and in the deposits in the sewer from which seeding could take place, and some time was required for these sulfate reducers to multiply sufficiently to produce a measurable quantity of hydrogen sulfide.

Changes in pH were small except at the beginning and end of incubation. On the first day there was a lowering in pH value from 7.5 to 7.1, and at the end there was a rise from a minimum of 7.0 to a maximum of 7.2. The drop in pH could hardly be considered a factor in the retardation of sulfide formation during the first few days.

Decomposition of Sulfate, Thiosulfate, and Sulfite. Formation of sulfides from thiosulfate, sulfate, and sulfite was studied by adding to different portions of a sewage sample 30 p. p. m. of sulfur in the form of the above compounds. A portion of the sample to which no sulfate had been added was used as a control. The incubator was maintained at 26° C. Results are given in Table II, and hydrogen sulfide production plotted in Figure 4.

TABLE II. EFFECT OF DIFFERENT TYPE SULFUR COMPOUNDS

Days of Incubation	—Control—		Na_2SO_4 Added, 30 p. p. m. as S		$Na_2S_2O_3$ Added, 30 p. p. m. as S		Na_2SO_3 Added, 30 p. p. m. as S	
	Total sulfides	pH	Total sulfides	pH	Total sulfides	pH	Total sulfides	pH
	P. p. m.		*P. p. m.*		*P. p. m.*		*P. p. m.*	
1	6.0	7.1	4.7	7.2	13.9	7.2	8.0	7.3
2	17.3	7.0	13.1	7.0	29.1	6.9	18.3	7.1
3	18.1	7.0	23.0	6.9	33.2	6.9	23.2	6.8
4								
5	32.8	7.0	40.5	6.9	56.3	6.9		
6							45.6	7.0
7	26.2	6.9	58.2	6.9	59.0	6.9		
8							57.7	6.9
9	30.3	6.8						
10			57.5	7.0	54.8	6.9	54.3	7.0

Thiosulfate was the most readily decomposed, the production of sulfides rising above that from the control, sulfite-, and sulfate-containing sewage from the beginning of the incubation period. Since there is a greater ratio of sulfur to oxygen in thiosulfate than in the other compounds, this would be expected. For every unit of oxygen from these sulfur compounds made available for stabilization of the organic material, more sulfur would be reduced in the thiosulfate sample than in the other salt-containing liquids.

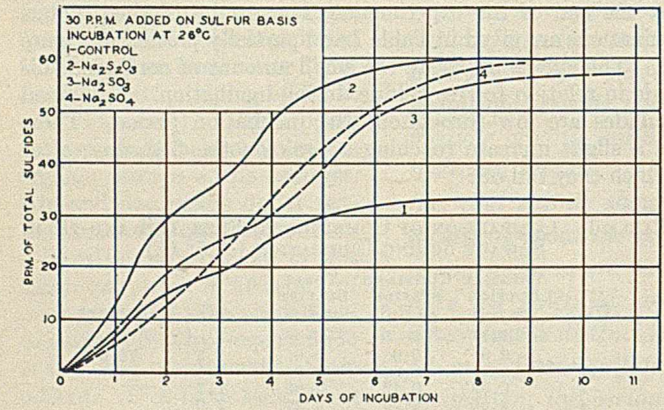

FIGURE 4. EFFECT OF SULFUR COMBINED WITH SODIUM ON HYDROGEN SULFIDE PRODUCTION

The sulfite-containing sewage yielded more sulfides during the first few days, after which there was a slight retardation below that of the sewage to which sulfate had been added. The sulfite at the concentration added did not seem to retard the biological action, judging from the standpoint of sulfide formation.

DECOMPOSITION OF SULFATES WITH DIFFERENT CATIONS. The decomposition of sodium, ammonium, calcium, magnesium, and ferrous sulfates was studied by adding 150 p. p. m. of SO_4^{--} each of these salts to portions of a sewage sample and incubating them in bottles. Incubation was carried out at 32° C. Results are plotted in Figure 5.

A distinct retardation in sulfide production from ferric sulfate was noticeable from the beginning. The remaining sulfates followed the control during the first few hours of incubation. Sodium sulfate seemed to be the most rapidly decomposed compound during the first few days. Magnesium sulfate was decomposed at the slightly slower rate than sodium sulfate, and ammonium sulfate yielded smaller amounts of hydrogen sulfide than magnesium sulfate during the first eight days. Calcium sulfate did not decompose much more rapidly than ferrous sulfate, although the retardation was not noticeable during the first four days as was the case with the iron salt. Since calcium sulfate is not very soluble in water, this could be expected.

It is significant that during the first day of incubation all the sulfates except that of iron decomposed at very nearly the same rate. Two peaks in sulfide production are very distinct for each incubation. This is indicative of a two-stage decomposition or stabilization of the organic material.

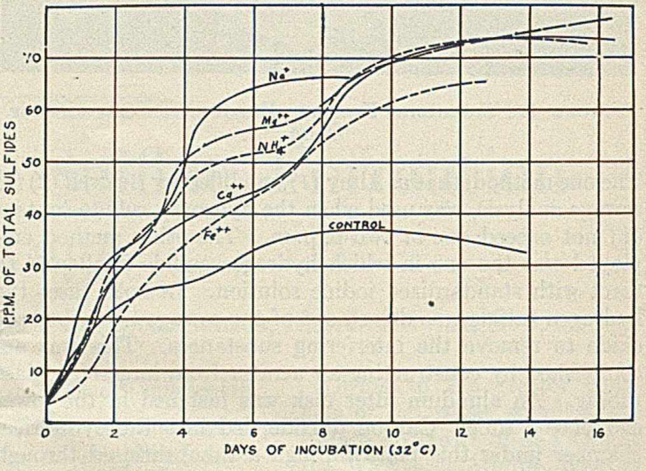

FIGURE 5. HYDROGEN SULFIDE FORMATION FROM SEWAGE TO WHICH VARIOUS SULFUR-CONTAINING COMPOUNDS WERE ADDED

Although the sewage is maintained under anaërobic conditions, the decomposition of sulfates brings about an oxidation of the organic material. Thus for every p. p. m. of hydrogen sulfide produced in the sewage, there is necessarily available approximately 2 p. p. m. of oxygen for oxidation of the organic material. The energy produced by the oxidation of the organic material is therefore in excess of that required to reduce the sulfates. There must be present, then, during the first few days of incubation organic material readily attacked and available for oxidation, causing a rapid rise in the rate of hydrogen sulfide production, after which there is a slowing up of activity until the more resistant material is available for attack. Although some of the sulfates decompose less rapidly than others, they are all potential sources of hydrogen sulfide. It is interesting to note that sodium, magnesium, ammonium, and calcium sulfates decomposed to the same extent on the ninth day, their respective curves converging at a point.

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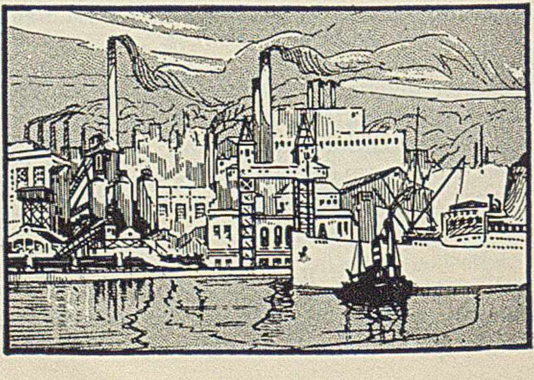
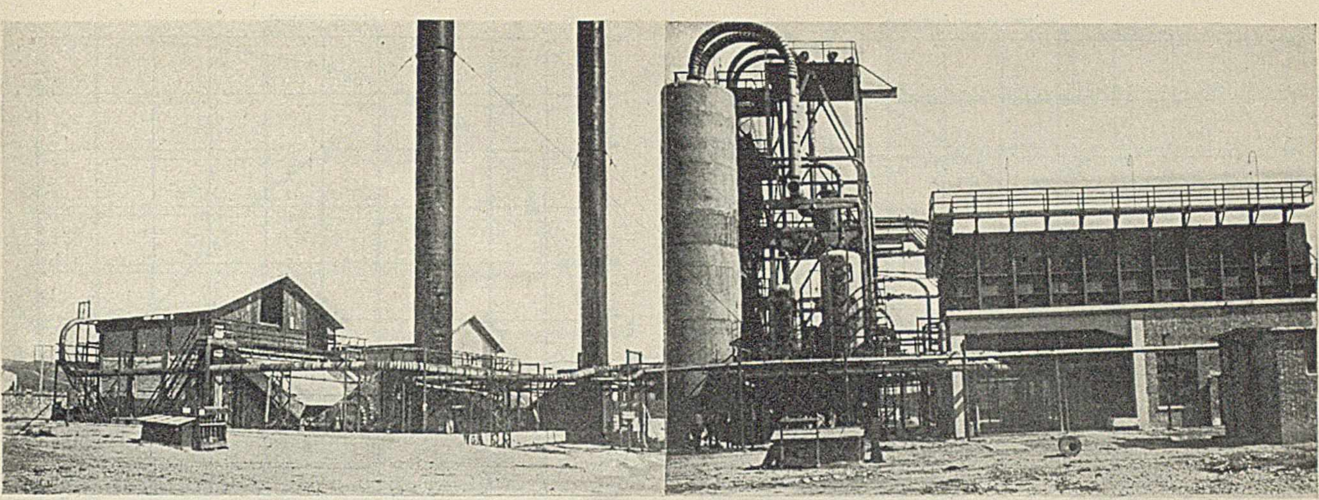
RECEIVED June 6, 1932. Presented before the Division of Water, Sewage, and Sanitation at the 83rd Meeting of the American Chemical Society, New Orleans, La., March 28 to April 1, 1932.





Topping Unit (25,000-Barrel) at Grozny, U. S. S. R.

Vapor-Liquid Equilibrium Curves of Petroleum Fractions[1]

S. N. Obryadchakoff, Grozny, U. S. S. R.

In calculating the performance of a rectifying column used for the separation of binary mixtures, it is necessary to know the relationship between compositions of liquid and vapor phases in equilibrium over the range of conditions existing in the column. This relationship may be expressed as a mathematical formula or it may be used in the form of a diagram. In the latter case a graphical method may be used for determining the number of plates, the heat consumption, and other requirements for a desired separation.

When dealing with ternary mixtures, the mathematical calculations become complicated, and with complex mixtures like petroleum no exact method for working out the requirements of a given separation has been developed. The more or less approximate methods, such as those of Lewis and Wilde (*5*), and Lewis and Smoley (*4*), although of great value in determining the efficiency of a column, are difficult to use for solving the usual problems of a petroleum refinery unit.

It has been shown that the method of McCabe and Thiele (*6*) can be applied to such problems, using a diagram giving the relationship between the vapor and liquid phases in equilibrium which is similar to that used for binary mixtures. This diagram will be called the equilibrium curve.

The equilibrium curve for binary mixtures which follow Raoult's law is given by the equation:

$$y = \frac{qx}{1 + (q - 1)x} \tag{1}$$

where y = mole fraction of light material in vapor phase
x = mole fraction of light material in liquid phase
q = ratio of vapor pressure of light material to that of heavy material at equilibrium temperature

This equation may be used for binary mixtures of materials which deviate slightly from Raoult's law, in which case a correction factor would be applied to q. (This correction factor would be the same as that determined by Brown (*1*) for naphtha.) However, most binary mixtures met with in practice do not follow Raoult's law closely enough to allow the use of this equation, and it is necessary to construct the equilibrium curve from experimental data. The composition of vapor and liquid in equilibrium are actually determined by any one of several methods and the results plotted. It will be noted that the equation does not contain any factor depending on temperature and that q is assumed to be constant over the range dealt with. Actually q varies slightly with temperature, but the variation is too small to make any difference in most engineering calculations, and q can be considered constant over the range of temperature from top to bottom of a fractionating tower. All the experimental methods of determining the curve involve the production of a vapor and a liquid which are in equilibrium at a certain pressure and temperature, and each pressure and temperature condition gives one set of samples only and one point on the equilibrium curve. To get other points, the pressure or the temperature must be varied, and usually the temperature is varied. Assuming that the pressure is constant, the liquid and vapor compositions and the temperature are all dependent variables, any two of which may be plotted against each other. The three curves that may be obtained are shown in Figure 1. Curves *A* and *B* were formerly much used in assembling distillation data, and curve *C*, which is obtained by eliminating the temperature from *A* and *B*, is the equilibrium curve used by McCabe and Thiele.

Curves for Complex Mixtures

In constructing the equilibrium curve for a complex mixture, the same procedure is followed as in the case of a binary mixture. The mixture is partially vaporized under equilibrium conditions at a given pressure and temperature, and samples of the vapor and liquid phases obtained. These two samples are then analyzed by distillation methods, but instead of getting a single percentage for each analysis, the compositions of the samples must be represented by curves. Vaporizations may be made at various tempera-

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[1] Rewritten and additional data furnished by W. A. Peters, Jr., E. B. Badger & Sons Co., 271 Madison Ave., New York, N. Y.

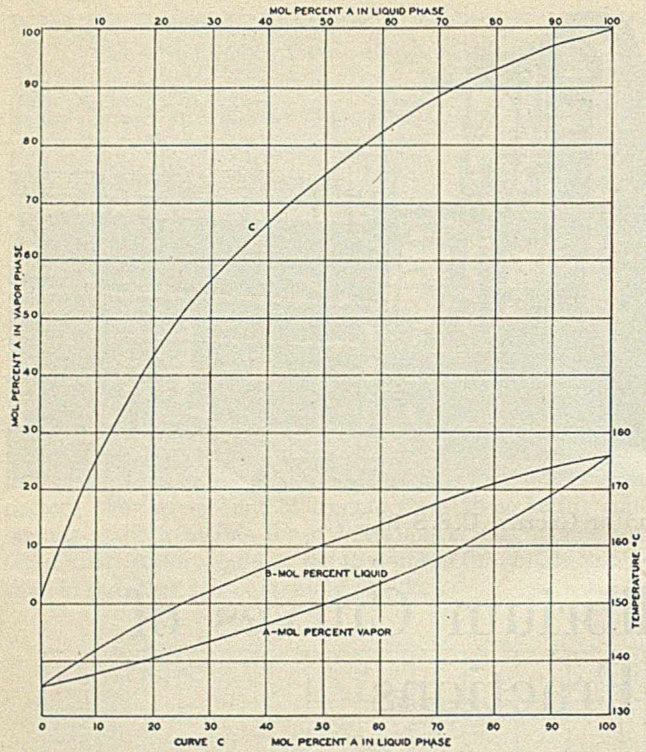

Figure 1. Typical Vapor Liquid Equilibrium Curve for Binary Mixture

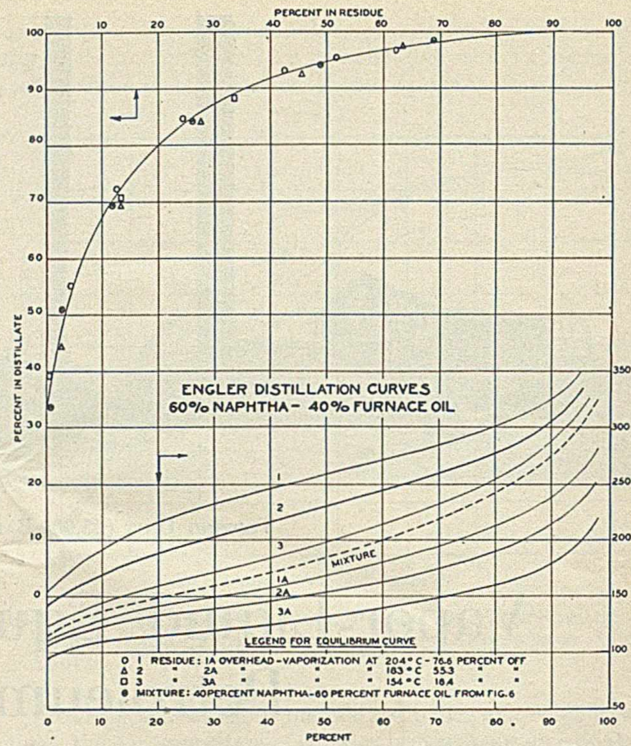

Figure 2. Equilibrium Curve for Naphtha and Furnace Oil Mixture with Engler Distillation Curves

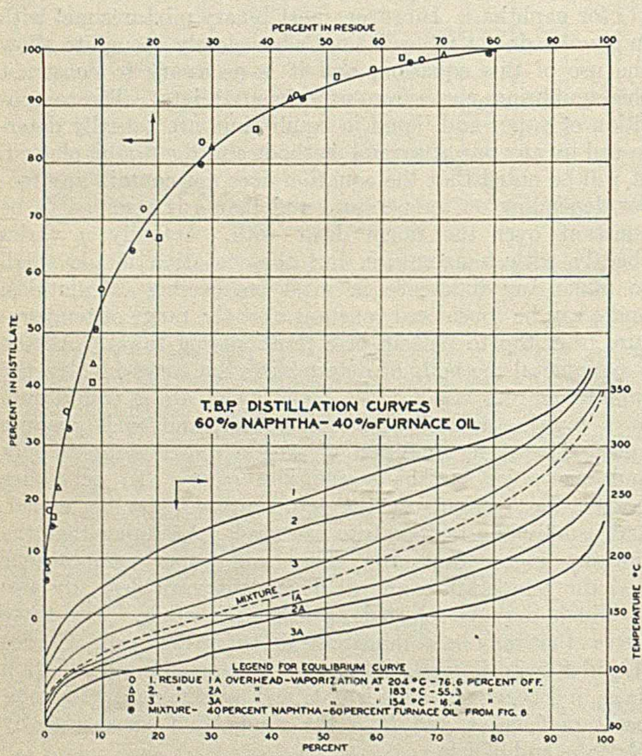

Figure 3. Equilibrium Curve for Naphtha and Furnace Oil Mixtures, with T. B. P. Distillation Curves

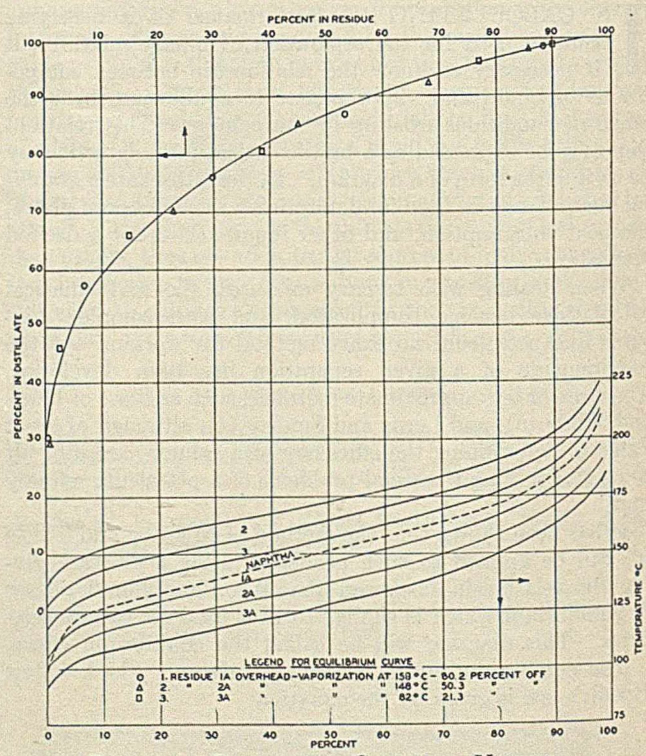

Figure 4. Equilibrium Curve for Naphtha

tures and a series of curves obtained. Such a series of curves is shown for a mixture of petroleum hydrocarbons in Figure 2. Although any pair of these curves look like curves *A* and *B* in Figure 1, they are not the same. A plot of the analyses of the complex mixture similar to that of the binary mixture would require three dimensions, and the equilibrium curve would also have to be in three dimensions and would be useless for engineering calculations. However, in separating such a mixture of complex hydrocarbons, the ultimate components are usually of no practical interest, but only the materials boiling above and below a certain temperature. Furthermore, these materials are not usually analyzed by a method that would give more than a very approximate determination of the ultimate constituents. The distillation curves of Figure 2 were determined by the A. S. T. M. method. If, for example, the mixture of Figure 2 were to be separated into two cuts, one containing all the material

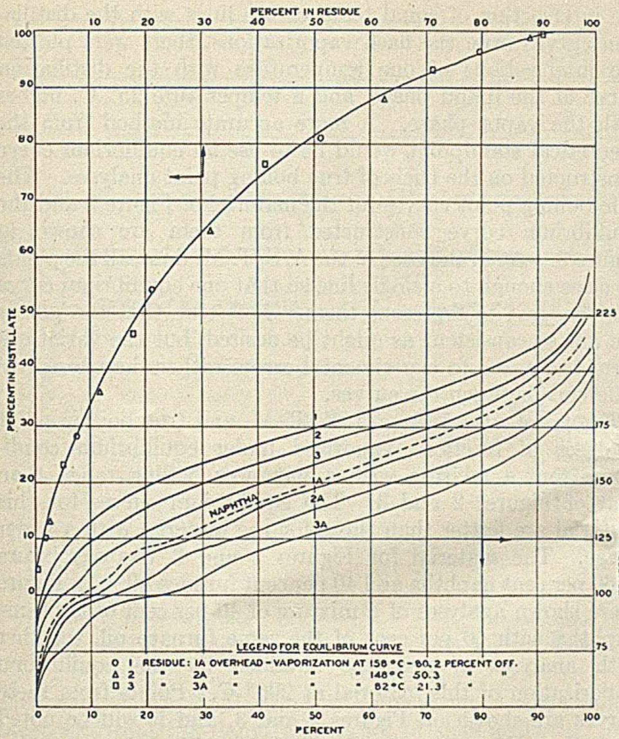

Figure 5. Equilibrium Curve for Naphtha, T. B. P. Distillation Basis

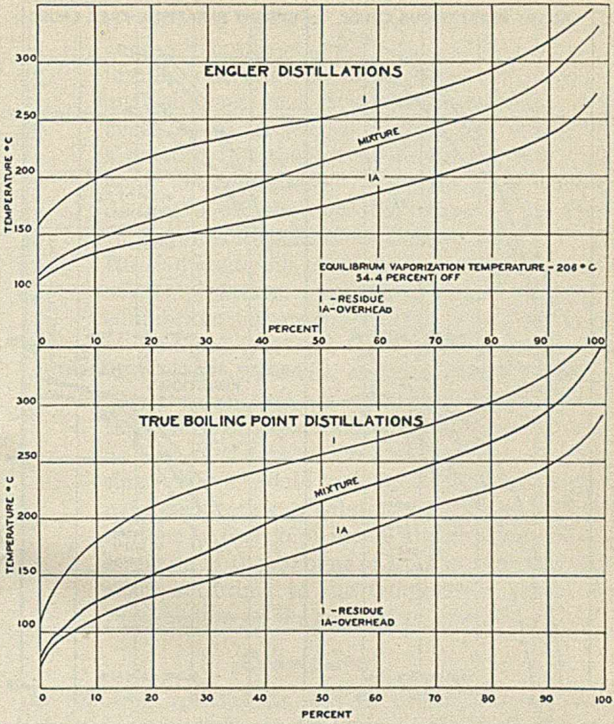

Figure 6. Distillation of Products from Equilibrium Vaporization, 40 Per Cent Naphtha–60 Per Cent Furnace Oil

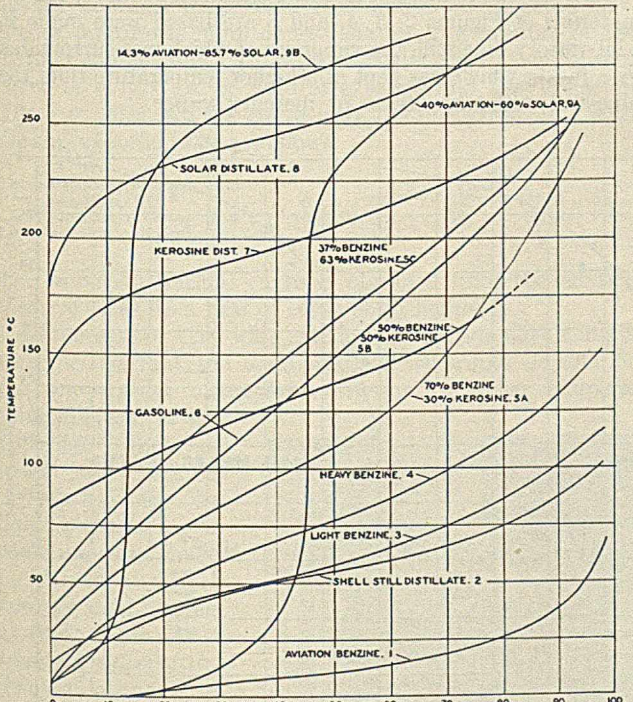

Figure 7. Engler Distillation Curves for Grozny Refinery Products

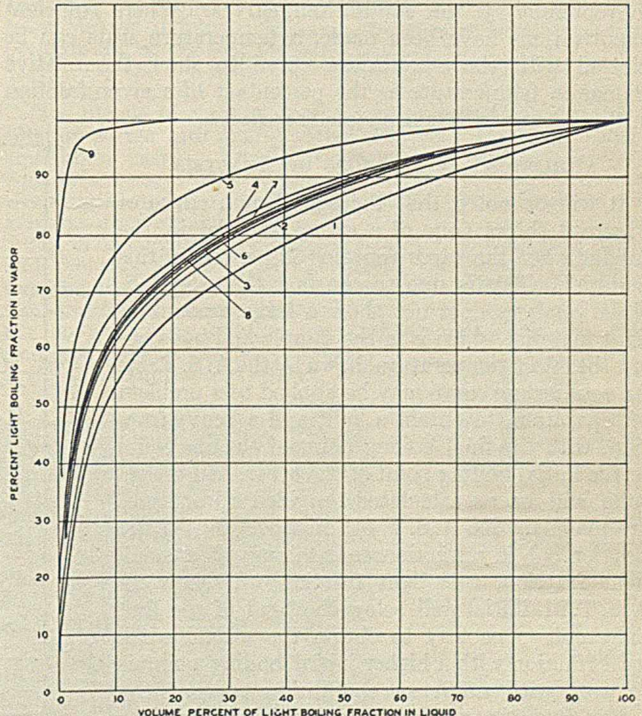

Figure 8. Equilibrium Curves for Materials in Figure 7

boiling above 200° C. and the other containing all the material boiling below 200° C., by A. S. T. M. distillation, an equilibrium curve might be constructed considering the mixture as containing only two components and the procedure would be exactly the same as in the case of a binary mixture. The three sets of curves of Figure 2 would give three points on the equilibrium curve. If more points were required more vaporizations under different conditions of temperature or pressure must be made. But other curves can be constructed by eliminating the temperature between any pair of distillation curves. These curves give the relation between the amount of material boiling above and below any temperature in the vapors and similar materials in the liquid from any one equilibrium vaporization. In the upper part of Figure 2 are plotted various points determined from the distillation curves to make up the dif-

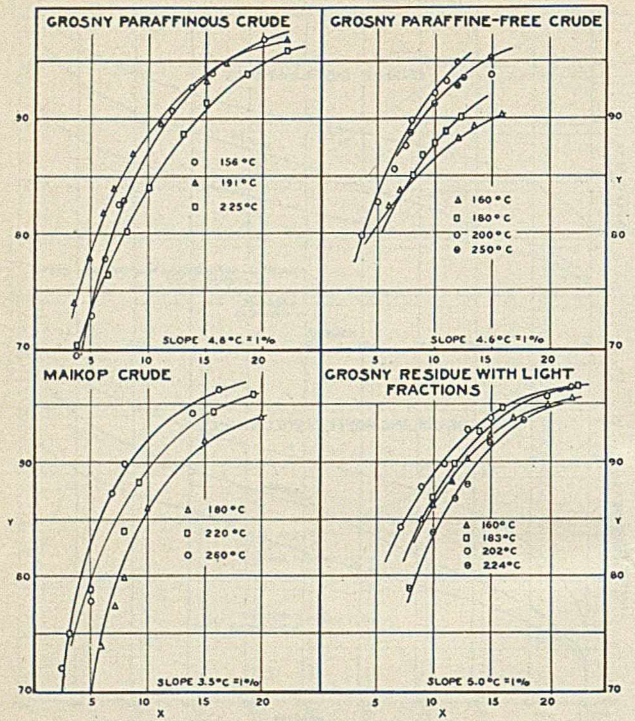

FIGURE 9. EQUILIBRIUM CURVES FOR RUSSIAN CRUDES, ENGLER DISTILLATION BASIS

ferent equilibrium curves, and it is seen that all the points lie close enough together so that a single line can be used to represent all the equilibrium curves. Where sufficient vaporizations have been made, a temperature scale can be plotted with the equilibrium curve to show the relative change in temperature as the percentage of a given fraction in the vapor and liquid phases is varied.

VARIATIONS IN METHODS OF ANALYSIS

It will be noted that the equilibrium curve of Figure 2 shows none of a given material in the residue when the vapor contains 32 per cent of this material. This is due to the fact that the A. S. T. M. analysis does not show a large amount of light material which is in the sample and boils below the initial temperature shown by the A. S. T. M. An equilibrium curve may be applied to a problem of separation, to obtain a light and a heavy fraction, with the final boiling point of the one equal to the initial boiling point of the other, and the results will be as calculated provided all analyses are made by the A. S. T. M. method. But if the heavier cut is refractionated, taking off a small light fraction, this light fraction will show an A. S. T. M. initial well below the final of the first light cut. One way to obtain the second small light fraction with a higher initial boiling point is to work with a different equilibrium curve.

For example, a crude may be separated into a gasoline with an end boiling point of 160° C. and a residue with an initial of 160° C. both by Engler analysis. The equilibrium curve on which the separation was based would also be calculated from A. S. T. M. analyses as described above. If now the residue is further fractionated, it will give a naphtha with an initial boiling point of about 135° C. by A. S. T. M. analysis. But if the first separation is made to give a residue with an initial of 185° C., the naphtha from this residue would have an initial of 160° C. An equilibrium curve, to give such results, would be obtained if, instead of plotting the intersection of equal temperature lines with the distillation curves from the flash vaporizations, there were plotted the intersections of one temperature with the distillation curve of the liquid phase, and a temperature 25° C. higher with the vapor phase. A more accurate method from the theoretical standpoint would be to use an equilibrium curve constructed on the basis of true boiling point analyses. The true boiling point curves for the material of Figure 2 and the equilibrium curve constructed from them are shown in Figure 3. As in the case of the A. S. T. M. data, all the points lie close enough to a single line so that one equilibrium curve may be used to represent them. It is true that the points are not so consistent as might be desired, but the variations seem to be due to experimental errors rather than to a real difference between the curves.

Figures 4 and 5 show A. S. T. M. and true boiling point analyses of fractions vaporized under equilibrium conditions from a mixture with a narrower boiling range than that of Figures 2 and 3. The equilibrium curves for this material are flatter than those for the material with a wider range. The material for Figures 2 and 3 was a mixture of 60 per cent naphtha and 40 per cent furnace oil. In Figure 6 are shown analyses of a mixture of 40 per cent of the same naphtha with 60 per cent of the same furnace oil, together with analyses of fractions obtained by the equilibrium vaporization of this material at 206° C. Points from these curves are shown on Figures 2 and 3, and it will be noted that they lie close enough to the equilibrium curve for the 60–40 mixture so that the same curve may be used for both.

The vaporizations on which the equilibrium curves for the materials of Figures 2, 3, 4, and 5 are based were made in a laboratory pipe still, the vaporizer of which was surrounded by a jacket which was kept at a higher temperature than the pipe-still outlet by steam or mercury vapor.

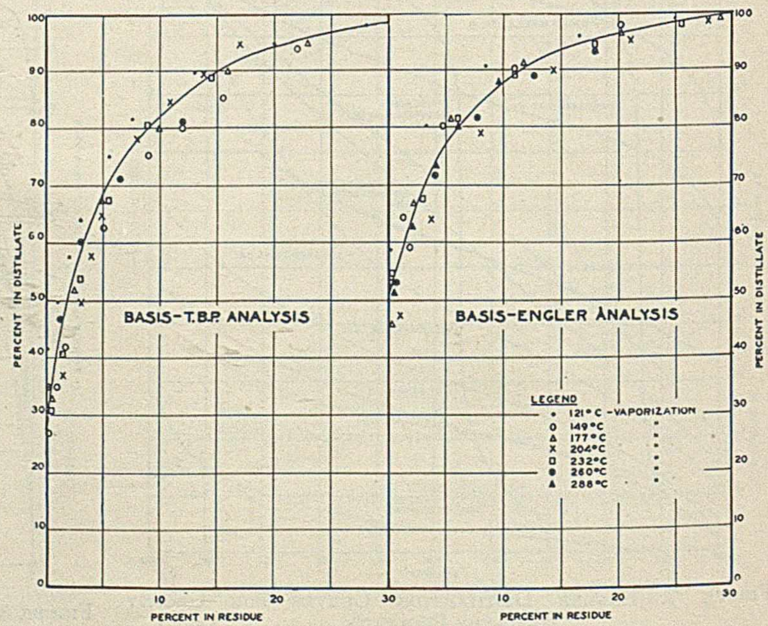

FIGURE 10. EQUILIBRIUM CURVES FOR MIDCONTINENT CRUDE

Figure 7 shows the Engler boiling ranges for various distilled products and mixtures determined in the laboratory at Grozny, and Figure 8 shows the equilibrium curves for these products. The equilibrium curves for the materials of Figure 7 were determined by the analyses of fractions obtained by equilibrium vaporization of the samples in an apparatus similar to that used by Leslie and Good (*3*). Similar results have been obtained by L. I. Hackatoroff, A. N.

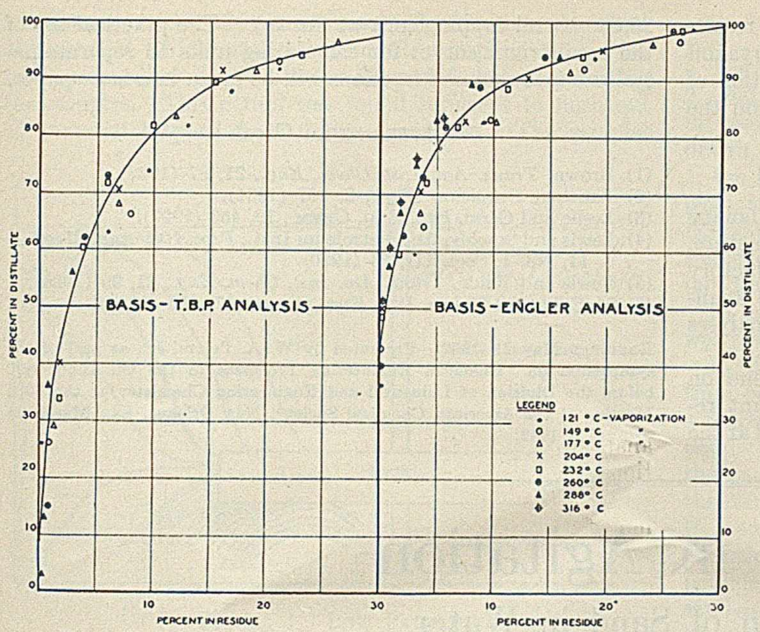

Figure 11. Equilibrium Curves for Cabin Creek Crude

Sachanen, and N. A. Hiathintoff, using samples taken simultaneously from the liquid and vapor of shell stills.

Where the fraction under consideration is a mixture of two cuts with widely different boiling ranges, it is necessary to make a separate equilibrium vaporization for each point on the equilibrium curve. This would be expected since such a mixture is more or less similar to a mixture of two distinct components. Curve 9 of Figure 8 is the equilibrium curve of a mixture of natural gasoline and heavy gas oil. The five points on the curve were obtained from five equilibrium vaporizations as follows:

Temperature of equilibrium vaporization, ° C.	67.4	90.2	133.6	163.8	185.0
Light fraction in vapor, %	100	99	96	85.5	86
Light fraction in liquid, %	19	12	3.5	1.5	0.5

The same equilibrium curve is obtained from the mixture of curve 9a as from that of curve 9b in Figure 7.

In the case of very wide fractions and crude oils, it might be expected that the equilibrium curve would depend on the temperature of vaporization, for at higher temperatures materials are vaporized which, at lower temperatures, were only in the liquid phase so far as could be determined by the methods of analysis used. Thus at higher temperatures the slope of the distillation curve of the material entering into the process is actually steeper than at lower temperatures. At still higher temperatures, where the light fractions practically disappear from the liquid phase, the effective slope of the material actually entering into the process will again be smaller and the equilibrium curve will not be so steep. Such shifts in the equilibrium curve should depend on the method of analysis used, and it would be expected that a curve based on Engler distillations would show a greater shift than those based on true boiling point determinations. The data so far available do not show the expected effect at all clearly. In Figure 9 are shown equilibrium curves for four Russian crude oils based on vaporizations at various temperatures. In Figures 10 and 11 are given equilibrium curves constructed from the analyses of Midcontinent and Cabin Creek crudes which were given by Fancher and Leslie and Good (*2*, *3*). The Russian data are somewhat more consistent than those of Leslie and Good or Fancher, but in no case is the variation great enough so that a single curve would not be accurate enough for most engineering calculations. Further work must be done on this point before any determination can be made of the amount of shift in the equilibrium curve according to the temperature of the flash vaporization or the method of analysis.

Operating Force for Topping Unit at Grozny

Conclusions

The following conclusions may be drawn from an examination and comparison of the curves given in Figures 2 to 11:

(1) Fractions which have distillation curves with equal slopes will have the same equilibrium curves. The values given for the slope of the distillation curves are arbitrarily taken as the difference between the temperatures of the 20 per cent and 80 per cent points divided by 60.

(2) The fraction with the greatest slope will have the steepest equilibrium curve.

(3) Blends of various proportions of materials giving distillation curves with approximately the same slope have similar equilibrium curves. This is important for it indicates that one equilibrium curve can be used for any one section of a fractionating tower, such, for example, as the section between the kerosene draw off and the top.

(4) The equilibrium curve for fractions with a small slope, and probably for all materials within the limits of accuracy required for engineering calculations, does not depend on the temperature at which the equilibrium vaporization is made, nor on where the dividing temperature, separating the light from the heavy material, is taken.

(5) The equilibrium curves, especially when based on true boiling point analyses, are similar in form to curves plotted from Equation 1.

These conclusions suggest the possibility of constructing empirical equilibrium curves for petroleum mixtures by assigning values to q in Equation 1. A. M. Tregoobov has assumed that

$$q = \left(\frac{t_b}{t_a}\right)^{10}$$

where t_b and t_a are taken as the absolute initial boiling points of the heavy and light fractions, respectively. It is obvious that this assumption would only give satisfactory results in certain special cases. Obryadchakoff and Hohryakoff give the following relation for q, based on an inspection of many equilibrium curves determined experimentally on the basis of Engler distillations:

$$q = 1.8 \times 1.022^{d}$$

where d is the difference in ° C. between the average boiling points of the two fractions to be obtained from the mixture.

Curves constructed from the equation may be satisfactory for preliminary calculations, but until more data are available, it would be best to base the curve on actual analyses where it is to be used for designing equipment.

The justification for using this method must depend on how well the calculated results check with actual plant results. The author checked the results herein described at the 25,000-barrel topping unit at Grozny. The practical use of the equilibrium curves for calculating units to separate petroleum into required fractions will be given in a later paper.

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Studies in Agitation

Suspension of Sand in Water

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Mixing, although one of the most frequently used unit operations in chemical engineering, remains from a standpoint of stirrer design and performance one of the least studied and one of the least known processes. It has been shown (*1*, *2*, *3*) that the common paddle agitator is an efficient stirring device when used to mix a solution of an electrolyte with water, or for dissolving a soluble material in a solvent. However, there seem to be no data on the mixing or suspending of an insoluble solid in a liquid by means of a paddle agitator. It is the purpose of this paper to present evidence on such a case.

Since mixing had been found to take place completely within 2 or 3 minutes when used on electrolytes (*3*), it was decided that for these experiments screened sand and water would be used. This would eliminate the variable of changing surface area (*2*), and, it was hoped, would slow down the rate of mixing sufficiently to enable a study of the comparative value of various agitators to be made. However, as will be shown, mixing was very rapid, but uniformity of sand distribution was never realized. For this reason, the emphasis was laid on the distribution of the suspended solid throughout the liquid rather than on the rate of mixing.

In the case of an insoluble solid in a liquid, maximum suspension of the solid is attained after a very short period of agitation. Uniformity of concentration of the suspended solid is never obtained, but is approached more closely when the paddle is near the surface of the liquid than when it is close to the bottom of the tank.

Maximum suspension of the solid is obtained when the paddle is near the bottom of the tank, although the liquid above the stirrer is low in suspended matter. There is a hydraulic sizing of particles in the tank. The large particles remain on the bottom near the center of the tank, whereas the small ones are carried into suspension by the flow of the liquid. Sand concentration does not indicate the stream flow of the liquid, although it is probably a practical measure of its velocity.

The equipment used in these tests consisted of a 500-gallon cylindrical steel tank 4 feet 4 inches (132 cm.) in diameter. This was equipped with a paddle agitator with a blade 2 feet 1 inch (63.5 cm.) in length, 3.5 inches (8.89 cm.) wide, and 2 inches (5.08 cm.) thick, mounted on a steel shaft running vertically through the center of the tank and terminating in a step bearing at the bottom. The agitator was driven by a ring gear and pinion through a jackshaft. The paddle, whose ends had been beveled off at an angle of 45 degrees away from the direction of rotation, was movable vertically so that it could be fixed at any desired height above the bottom of the tank. A constant agitator speed of 37 r. p. m. was adopted for these experiments.

Table I. Screen Analysis of Sand Used

Mesh/inch	%
28	0
35	0
48	1.2
65	60.1
100	13.2
150	14.6
200	7.4
−200	3.5

The sand was screened to give a product of approximately 65 mesh. The screen analysis of the material used is shown in Table I.

Samples were obtained by means of glass tubes, 5 mm. in diameter, inserted into the tank through holes in the wall. These holes were spaced vertically 4 inches (10.16 cm.) apart, the lowest 2 inches (5.08 cm.) from the bottom of the tank, and the highest 22 inches (55.88 cm.). The tubes were 26 inches (66.04 cm.) long, and were so fitted that they could be inserted into the tank to any desired distance up to this limit. At their outer end, closure was effected by means of rubber tubing and a pinchclamp.

For these tests, it was decided arbitrarily to keep the water level 2 feet (60.96 cm.) above the bottom of the tank. This corresponds to 220.5 gallons of water.

During a run, samples of the sand-water mixture were withdrawn periodically for analysis. To eliminate the effect of the sand which settled out in the sampling tubes, the tubes were allowed to drain for 15 seconds before collecting the samples. This period was found sufficient to flush out all material trapped from the previous test. The samples thus collected were filtered through weighed Gooch crucibles, the volume of water measured, and the results calculated as milligrams of sand per 100 cc. of water.

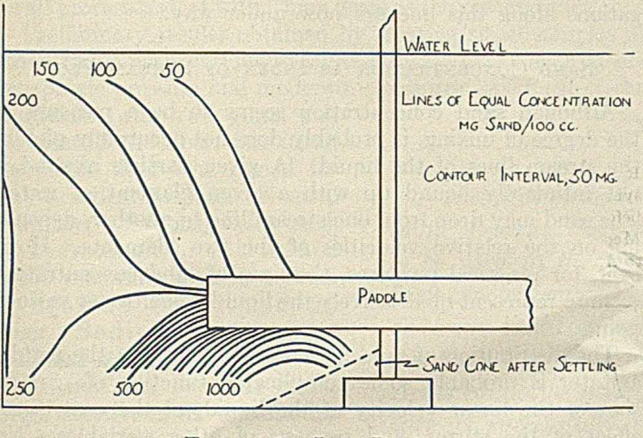

Figure 1. Low Paddle

Two series of runs were made, one using 67 pounds of sand, the other using 20 pounds of sand. In each case the runs could be satisfactorily checked as shown in Table II.

Table II. Sample of Experimental Data

(Sand, 20 lb.; paddle, 17.25 in. from bottom; samples, 0.5 in. from wall of tank)

Distance from Bottom	Time	Amount Sand in Water Run 63	Amount Sand in Water Run 64
Inches	*Minutes*	*Gram/100 cc.*	*Gram/100 cc.*
22	1		0.087
	6	0.126	
	7		0.114
	12	0.121	
	13		0.115
	18	0.118	
	19		0.119
	24	0.119	
18	2		0.128
	5	0.145	
	8		0.130
	11	0.130	
	14		0.129
	17	0.135	
	20		0.127
	23	0.128	
14	3		0.137
	4	0.148	
	9		0.131
	10	0.131	
	15		0.133
	16	0.135	
	21		0.131
	22	0.137	
10	3	0.162	
	4		0.144
	9	0.143	
	10		0.139
	15	0.142	
	16		0.131
	21	0.135	
	22		0.135

For each of the two amounts of sand in the tank, experiments were conducted with the sampling tubes inserted so as to withdraw samples successively at 0.5, 2.0, 6.0, 10.0, 12.0, 14.0, 18.0, and 22.0 inches (1.27, 5.08, 15.24, 25.40, 30.48, 35.56, 45.72, and 55.88 cm.) from the wall of the tank. For each tube, a sample was withdrawn every 5 minutes until five samples were secured; on repeating the run, the times of withdrawal were staggered so as to fill the intermediate times.

Experimental Results

The results of all the runs are summarized in Figures 1, 2, and 3, in which lines of constant sand concentration, expressed in milligrams of sand per 100 cc. of water, are drawn for the tests using 20.0 pounds of sand. In Figure 1, the lower edge of the paddle was 5.25 inches (13.33 cm.) from the bottom of the tank; in Figure 2, 11.25 inches (28.56 cm.); and in Figure 3, 17.25 inches (43.81 cm.). The shape of the curves was the same for 67 pounds of sand, but the sand concentrations were much higher.

In each case, maximum concentration of suspended sand was reached within 2 minutes.

It will be noted that the sand concentration varies widely from point to point throughout the tank, and that there is a marked difference in the action of the paddle for different paddle positions. The lowest concentrations are found above the paddle, with the highest beneath it near the bottom of the tank. This is further verified by the distribution of the sand after settling. There is in all cases a cone of sand enclosing the step bearing of the agitator shaft; for 67 pounds of sand, there is, in addition, an irregular layer of sand across the bottom of the tank. In the case of 20 pounds of sand, there is a layer of sand around the wall of the tank, with a clear space between this ring and the central cone. There is a marked eddy at the end of the paddle, which seems to account for the little sand on the bottom beyond the end of the paddle.

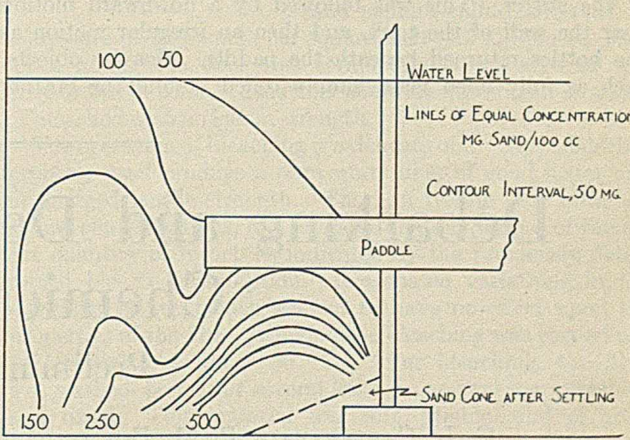

Figure 2. Middle Paddle

It seems, from Figures 1, 2, and 3, that the upper paddle position results in the most uniform distribution of material. The liquid above the paddle is in all cases low in sand, and this space seems to be largely ineffective. In the low paddle position, there is a large amount of suspended solid below the paddle, but this zone does not seem to extend much beyond the agitator. These results are most readily interpreted on the basis of a hydraulic classification of the sand into various size fractions.

In order to confirm the theory that selective separation of sand particles was taking place because of different velocity areas in the tank, the mixture was thoroughly agitated and, while the paddle was kept turning, large samples were run from different portions of the tank. A standard screen analysis on the sand obtained in this manner showed that 50 per cent of the sand was finer than 150 mesh. As only 10 per cent of the sand placed in the tank was finer than 150 mesh, this shows that the velocity of the agitator was such as to place in suspension only the smaller particles, whereas the heavier particles of sand remained on or near the bottom. This accounts for the cone of sand beneath the paddle. The cone is evidently composed of the large sand particles which are never placed in suspension, but are merely moved around a small circle on the bottom.

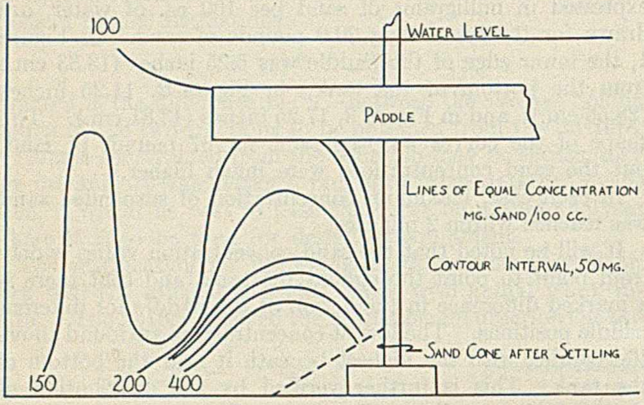

Figure 3. High Paddle

To obtain further evidence on the motion of particles under the influence of the agitator, small glass vials were filled with water until their apparent specific gravity was slightly greater than unity. These were placed in the tank and their motion observed while the agitator was turning. There was found to be little tendency for the vials to rise above the paddle, the motion being outward from the end of the stirrer. This was followed by a downward motion near the wall of the tank, and then an irregular motion as the bottles returned beneath the paddle. Heavier objects, such as fully filled vials, simply rolled around the bottom of the tank at a distance from the shaft of about half the length of the paddle.

Since these experiments show that there is a particle sizing effect due to different velocities in the tank, an ordinary cylindrical tank equipped with a paddle agitator might be used effectively for hydraulic separations. Further investigations along this line are now under way.

Sand Concentration as Index of Stream Flow

Although sand concentration seems to be a measure of the degree of mixing, it probably does not accurately picture the stream lines of the liquid. A given particle of sand is not intimately bound up with a given filament of water. The sand may drop from one stream line to another, depending on the relative velocities of the two filaments. However, for practical purposes, the lines of sand concentration seem to represent qualitatively the liquid velocities at various points.

The distribution of sand under the influence of the paddle agitator is probably some complicated function of particle size, of the linear velocity of the liquid, of the centrifugal effect of the stirrer, and perhaps of other variables. No mathematical treatment of the problem seems possible at this time.

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Debarking and Degumming Ramie by Chemical Means

Preliminary Report

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Although ramie has long been known and sporadically discussed as a possible textile fiber, it has never assumed a position of importance in this field. Relatively small quantities of the fiber are consumed in Europe in the manufacture of specialties, but no expansion of this field can be expected until the price of the fiber is materially reduced. In the Orient large quantities of the fiber are produced in carefully tended small plots, harvested, purified, and consumed locally. Only cheap hand labor allows this fiber to compete on a price basis with other fibers, and almost none is available for export.

From the grower's point of view the crop has been attractive. It propagates from the roots, is free from pests, yields very heavily, and matures evenly as straight unforked stems. It should yield readily to mechanical methods of harvesting. The stems are 0.25 to 0.5 inch in diameter and vary from 4 to 6 feet in height. The fiber is immediately under the bark.

The first step in the manufacture of purified ramie fiber consists of stripping the combined fiber bundles and bark from the stalk, the second of removing the bark from the fiber layer, and the third of removing the gums and other impurities from the fiber.

In the Orient the green wet stalks are stripped and the bark removed by hand. This material dried is the China grass of commerce. Numerous attempts have been made to perfect methods for stripping and debarking by machine. No process which has been made public seems to be commercially successful. The operation of stripping is relatively simple, and, if the removal of the bark can be effected by chemical means, the combined operations will be much simplified. The solution of the bark by chemical means, degumming, and production of a bleached fiber of high tensile strength constitute the objectives to be discussed in this and forthcoming papers.

Preliminary study of stripping indicated that the bark and fiber bundles can be removed from the stalk only when the gums are completely softened by soaking in water, or when they are rendered brittle by drying. Air-dry material is satisfactory even in Louisiana, except during very rainy periods.

The ramie used in this investigation was cut when mature, stripped of leaves, and dried naturally. Care was taken to insure good ventilation, as otherwise mildew would ruin the fiber.

Experimental Procedure

The rather extensive literature covering the various phases of the purification and preparation of ramie fiber for textile manufacture revealed a large array of common acid and alkaline substances recommended for this purpose. Nothing has been published concerning the chemical solution of the bark, as all processes start with China grass as the raw material.

Preliminary results obtained by treating small samples of dried ramie with various reagents indicated that even at atmospheric pressure and moderate concentrations most of the materials removed gums and softened the fiber, but in all cases the fiber was ruined for any practical purpose. Neutral oxidizing solutions, acids such as hydrochloric or nitric, and basic materials such as sodium hydroxide embrittled the fiber. Sodium carbonate and buffered solutions of calcium hydroxide and several others were effective in the degumming operation, but yielded a weak fiber. The chemical debarking and degumming were apparently impossible.

▽

A chemical method for removing the bark from ramie permits the simplification of machinery to be used in the process of purification. The bark can be removed by means of strong alkalies or strong oxidizing agents, but at the same time the fiber is ruined for any practical purpose. Acids cannot be used for the same reason. The bark is successfully removed without injury to the fiber by digestion with dilute solution of ammonium hydroxide and sodium sulfite. This combination is being studied on a larger scale to obtain cost data.

△

A small pressure digester was constructed for cooking with ammonia solutions. It was quickly determined that ammonium hydroxide did not weaken the fiber even at high pressure and temperature. The bark was not satisfactorily removed, however. Later work indicated that a sodium compound was necessary for debarking, and the combination of ammonium hydroxide and sodium sulfite was found to be satisfactory.

Table I. Effects of Various Chemicals on Ramie

(Pressure, 60 lb. per sq. in. (4.2 kg. per sq. cm.); time, 4 hours; weight of sample, 50 grams; weight of cook, 2000 grams)

Sample	Composition of Cook[a]	%	Remarks
1[b]	NH_3 Na_2SO_3	1.0 0.5	Bark not dissolved satisfactorily
2	NH_3 Na_2SO_3	1.0 0.5	Bark not dissolved satisfactorily
3	NH_3 Na_2SO_3	2.0 2.0	Bark dissolved satisfactorily
4	NH_3 Na_2SO_3	1.0 2.0	Bark dissolved satisfactorily
5	NH_3 Na_2SO_3	2.0 1.0	Bark dissolved satisfactorily
6	Liquor from sample 5		Bark dissolved satisfactorily
7	Liquor from sample 6		Bark dissolved satisfactorily
8	NH_3 Na_2SO_3	2.0 0.5	Bark dissolved satisfactorily
9	NH_3 Na_2SO_3	2.0 0.25	Bark not dissolved satisfactorily
10[c]	NH_3 Na_2SO_3	2.0 0.25	Bark not dissolved satisfactorily
11	NH_3 Na_2SO_3	1.0 0.75	Bark dissolved satisfactorily
12	NH_3 $(NH_4)_2SO_3$	1.0 0.75	Bark not dissolved
13	NH_3 Na_2CO_3	1.0 0.75	Bark dissolved satisfactorily; strength of fiber injured
14	NH_3 NaCl	1.0 0.75	Bark not dissolved
15	Na_2SO_3	0.75	Bark not dissolved
16	NH_3 Na_2SO_3	0.13 0.75	Bark not dissolved satisfactorily
17[d]	NH_3 Na_2SO_3	1.0 0.75	Bark not dissolved satisfactorily
18[e]	NH_3 Na_2SO_3	1.0 0.75	Bark dissolved satisfactorily

[a] The per cent composition of each cook is based on the weight of the solution used and not on the weight of the sample.

[b] Time of digestion, 1.5 hours.

[c] Time of digestion, 6 hours.

[d] Weight of sample, 322 grams.

[e] The product of sample 17 was used as sample 18.

At temperatures slightly above 100° C., ramie seems to be sensitive to acids of any kind, and in the presence of hydroxyl ions it quickly loses strength if subjected to mild oxidizing conditions. Sodium sulfite and ammonium hydroxide solutions were therefore investigated as most nearly meeting the conditions for successful cooking.

A rotary digester of about 3.5 liters capacity was used in this stage of the investigation. The conditions of cooking and the results obtained in a few of the many combinations tested are indicated in Table I. After digestion was completed, the debarked fibers were washed thoroughly and then boiled in a neutral soap solution for several hours, washed, and dried. The fiber as it comes from the digester is not completely degummed, and the digestion with soap is necessary to free the fiber. Based on air-dry weights, the yield of purified fiber is about 60 per cent of the weight of crude (stripped but not debarked) fiber. The tensile strength of the wet individual fibers will average 50 grams. The yield of purified fiber (air-dry) is about 1500 pounds per acre, and it is believed that this may be increased to one ton per acre per year.

Using a charge of 50 grams of crude fiber and 2 liters of a one per cent solution of ammonia and sodium sulfite, digested at a pressure of 60 pounds per square inch (4.2 kg. per sq. cm.) for 4 hours, the fiber was completely debarked, and was gray or tan in color. This fiber could be degummed as above or bleached with no loss in strength.

The operation of bleaching is a delicate one. Hypochlorites properly used produce a pure white fiber of good luster and unchanged tensile strength. The best results were obtained at low concentrations, low temperature, and by use of the exact quantity of bleach as indicated by the previously determined bleach consumption. Reasonable variations in the alkalinity of the bleach seemed to have no effect upon the properties of the fiber, provided the bleaching was carried out at temperatures under 50° C. After bleaching, the fiber was washed, boiled for several hours in neutral soap, washed, and dried. This material was soft, pliable, and of good luster.

Experimental work is now being carried on to provide exact cost figures for this material, both as a source of α-cellulose and as staple fiber. Because of the perfect symmetry of its crystal structure ramie should be a most satisfactory raw material for esterification and other chemical manipulation. Its high wet strength should make it a most valuable staple fiber for increasing the strength of fibers lacking this quality.

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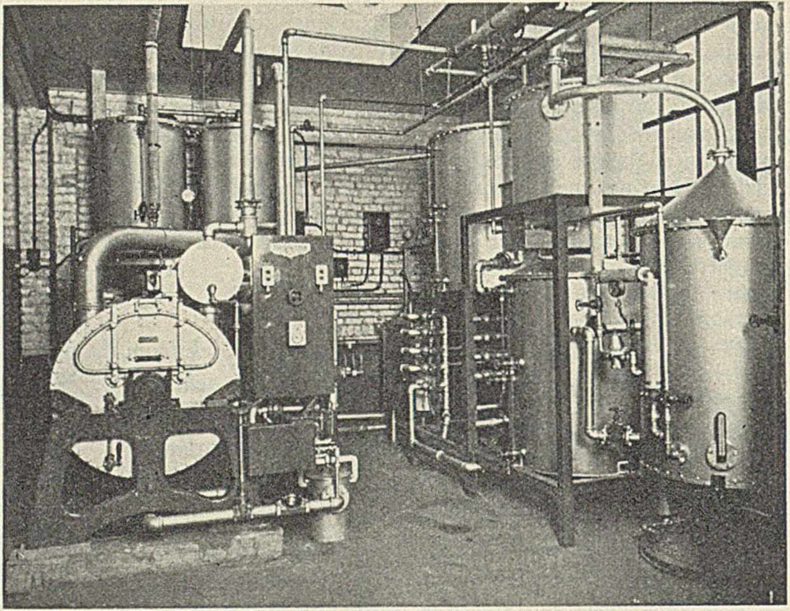

DRY-CLEANING MACHINE FOR USE WITH TRICHLOROETHYLENE

Stability of Chlorohydrocarbons

II. Trichloroethylene

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Trichloroethylene does not decompose in darkness. It is not decomposed in light unless oxygen is present. The presence of traces of certain antioxidants prevents the decomposition in light.

Trichloroethylene does not decompose on heating up to 130° C. It may decompose on heating in the presence of oxygen unless antioxidants are present.

Trichloroethylene does not hydrolyze. It is only slightly affected by ferric chloride. The ordinary metals do not catalyze decomposition of trichloroethylene. Trichloroethylene is not corrosive if antioxidants are present; even in the absence of these substances its corrosive effect is small.

IN A previous article by the authors (*1*) the stability of methylene chloride was discussed. The present article deals with the stability and the behavior of trichloroethylene under various conditions and its corrosive effect toward certain metals.

The increased use of trichloroethylene as a noninflammable low-boiling solvent for extracting oils, fats, waxes, and food products, for degreasing metals, and for dry cleaning purposes, has given rise to inquiries concerning the behavior of this solvent under various conditions. Conflicting opinions as to its stability and corrosive effect are found in scientific literature. Sastry (*7*) and Crudes (*2*) maintain that the decomposition and corrosive effect of trichloroethylene are slight. Griesheim Electron A. G. (*5*) states that trichloroethylene is corrosive, basing this conclusion on its use in the extraction of vegetable oils. Elsner (*3*), studying the splitting off of hydrochloric acids from trichloroethylene, finds that it is slight and that consequently this solvent is not corrosive. Formanek (*4*) finds that the effect of trichloroethylene on copper, brass, tin, and iron after exposure for 8 weeks is negligible.

In a series of tests trichloroethylene was submitted to more drastic treatment than it encounters in actual use, in order to determine its behavior under most extreme conditions. For instance, trichloroethylene was heated with water from 50° to 150° C. (122° to 302° F.) under pressure, to note the amount of hydrolysis at these temperatures.

PHYSICAL PROPERTIES

Trichloroethylene is a heavy low-boiling, noninflammable liquid with a pleasant ethereal odor. The physical properties of highly purified trichloroethylene have been determined in this laboratory and these values are given in Table I. Vapor pressures were determined by the method of Ramsay and Young (*6*) and are given in Figure 1.

PURIFICATION OF TRICHLOROETHYLENE

The trichloroethylene used in determining the physical properties and for stability tests was purified by steam-distilling factory-grade trichloroethylene (boiling range of 0.3–0.6° C.) from 10 per cent of its own weight of milk of lime. The steam-distilled material was chilled to −30° to −50° C. (−22° to −58° F.), and the ice removed by filtration through a chamois skin filter. The dried product was fractionated at an absolute pressure of 252 mm. in a vacuum batch still of 45 kg. capacity, equipped with a 7.6 × 259 cm. column packed with chains, with a 3:1 reflux:product ratio. All parts of the still, except the receivers, were constructed of iron. The receivers were of Pyrex glass covered with black paper to exclude light.

TABLE I. PHYSICAL PROPERTIES OF TRICHLOROETHYLENE

Formula	C_2HCl_3
Molecular weight	131.4
Color	Water-white
Odor	Sweet, ethereal
Specific gravity (0°/4° C.)	1.4996
(15°/4° C.)	1.4762
(30°/4° C.)	1.4514
Refractive index, $n_D^{19.8}$	1.4777
Viscosity (25° C.), centipoises	0.550
(50° C.), centipoises	0.446
(75° C.), centipoises	0.371
Boiling point (760 mm.), ° C.	86.7
Freezing point, ° C.	−88
Coefficient of expansion	0.001193
Heat of vaporization, cal./gram (B.t.u./lb.)	58 (104.4)
Specific heat (liquid)	0.233
Dielectric constant	3.42

Only the middle fraction of trichloroethylene, amounting to about 40 per cent of the total, was saved for use in the experimental work. The boiling range of the middle fraction was within 0.2° C. and the acidity was less than one part in ten thousand; the moisture content was less than 0.005 per cent by weight. In some of the experiments factory-grade trichloroethylene was used without any further purification. The boiling range of this material was within 0.6° C., and the acidity about fourteen parts in ten thousand. No difference was detected in the stability of these two grades of material.

In certain cases noted below, traces of antioxidants were added. Small amounts of certain antioxidants are very effective in stabilizing trichloroethylene toward the accelerating effect of light.

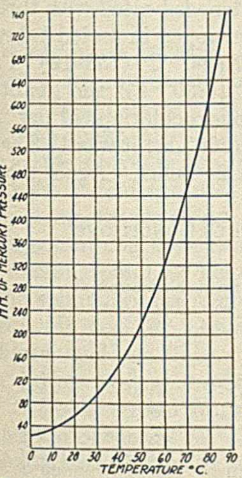


FIGURE 1. VAPOR PRESSURE OF TRICHLOROETHYLENE

METHODS OF ANALYSIS

The method used in determining acidity in all the experimental work consisted in adding 25 cc. of neutral distilled water to 25 cc. of trichloroethylene and titrating with 0.01 *N* sodium hydroxide, using phenolphthalein as indicator, until one drop of caustic gave a faint pink color, permanent for 30 seconds. One cubic centimeter of 0.01 *N* sodium hydroxide thus corresponds to an acidity of 0.001 per cent by weight, calculated as hydrochloric acid. The moisture content was found by determining the temperature where trichloroethylene was saturated with water (cloud point) and reading the per cent from a graph giving the relationship between cloud point and percentage moisture (Figure 2).

STABILITY TESTS

The measurement of stability of trichloroethylene in light was carried out by placing 400 cc. of the material in clean glass-stoppered bottles together with iron strips and exposing the bottles to diffused sunlight. The initial acidity and the acidity at given intervals were determined by titration.

In the stability test in darkness trichloroethylene was stored in 2 × 13 inch (5 × 33 cm.) capped iron pipes. These pipes had been cleaned previously by pickling in 20 per cent sulfuric acid, rinsed free from acid with distilled water, and dried.

The stability tests where trichloroethylene was heated or exposed to light, when it was desired to exclude air, were carried out in 2 × 25 cm. glass tubes provided with a 1 × 10 cm. constricted tube to facilitate sealing after trichloroethylene had been added. These tubes were carefully cleaned, and air was displaced with nitrogen. Trichloroethylene was admitted through a long-stemmed dropping funnel in order not to introduce air, light being excluded in handling the trichloroethylene. These tubes were sealed, placed inside capped iron pipes, and heated in electrically controlled oil baths maintained to within 1° C. of the desired temperature.

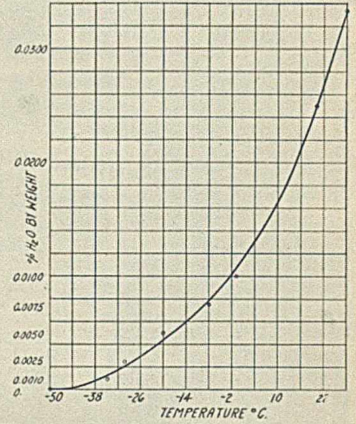


FIGURE 2. SOLUBILITY OF WATER IN TRICHLOROETHYLENE

RESULTS OF TESTS

STABILITY IN DARKNESS AT ORDINARY TEMPERATURES. Pure trichloroethylene or factory-grade trichloroethylene coming directly from the stills does not decompose when stored in darkness in glass tubes, in glass-stoppered bottles, or in steel drums. In tests extending over one year, trichloroethylene has not developed any acidity. Since no decomposition has been noted in factory-grade or purified material, the presence of antioxidants has no apparent effect in darkness.

STABILITY IN LIGHT. Trichloroethylene behaves like chloroform toward light and air. Schoorl (*8*) has found that chloroform decomposes in the presence of oxygen in light and that no decomposition occurs if either factor is excluded. In the absence of oxygen trichloroethylene is not decomposed by direct or diffused sunlight. In a series of experiments trichloroethylene in an atmosphere of nitrogen was exposed to direct light for 30 days, and the acidity was determined at regular intervals and found to be from 6 to 10 cc. of 0.01 *N* hydrochloric acid per 25 cc. of trichloroethylene (Table II). The acidity noted is due to traces of oxygen. The fact that the acidity did not change or increase after the third day indicates that the last traces of oxygen had not been completely removed from the nitrogen.

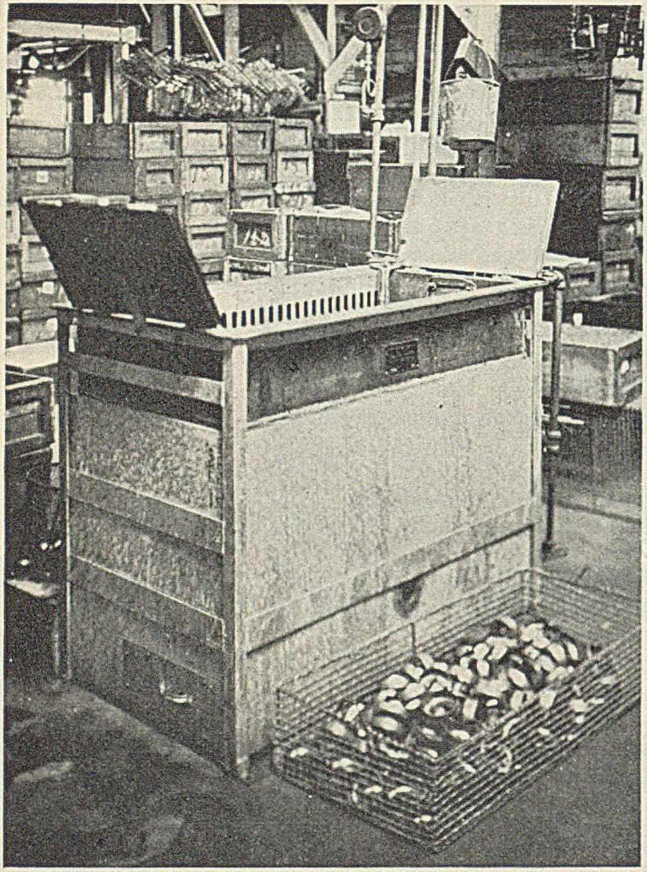
TABLE II. DECOMPOSITION OF UNSTABILIZED TRICHLOROETHYLENE EXPOSED TO DIRECT SUNLIGHT

(In cc. 0.01 *N* HCl per 25 cc. C_2HCl_3[a])

CONDITIONS OF EXPOSURE	—DECOMPOSITION ON BEING EXPOSED:—			
	1 day	3 days	11 days	17 days
In air[b]	140	178	155	118
In nitrogen[b]	6	10	10	9

[a] Throughout this paper 1 cc. of 0.01 *N* HCl per 25 cc. of sample corresponds approximately to 0.001% by weight of acidity calculated as HCl.
[b] In sealed tube.

In direct or diffused sunlight trichloroethylene develops acidity in the presence of oxygen. In diffused sunlight the average amount of acidity after exposure for 3 days at room temperature is about 20 cc. of 0.01 *N* hydrochloric acid per 25 cc. of trichloroethylene. After 7 days it amounts to about 50 cc. of 0.01 *N* hydrochloric acid. The acidity gradually increases so that after a month it may amount to over



Metal Degreaser Using Trichloroethylene

250 cc. of 0.01 *N* hydrochloric acid. Trichloroethylene containing traces of antioxidants (previously mentioned) develops no acidity in diffused sunlight after exposure of over a year.

Effect of Heat. Trichloroethylene, heated in sealed tubes in an atmosphere of nitrogen or in an atmosphere of its own vapors for 24 hours at temperatures below 130° C. (266° F.), develops no acidity that can be ascribed to heat alone. The observed acidities as recorded in Table III, amounting to 10 cc. of 0.01 *N* hydrochloric acid below 130° C., are due to traces of oxygen. At 150° C. (302° F.) thermal decomposition occurs on exposure for 24 hours.

Trichloroethylene vapor is stable at temperatures below 200° C. (392° F.). In Table IV the result of exposing trichloroethylene vapor to the designated temperatures for 4 seconds in contact with iron surfaces is summarized. At 200° C. the free acid amounted to only 0.0012 per cent hydrochloric acid, and at 400° C. (752° F.) it was 0.2 per cent. Though no free acid developed immediately, it is conceivable that heating trichloroethylene to temperatures above its boiling point might start decomposition and consequently render trichloroethylene less stable. Hence, in a series of tests trichloroethylene vapor was exposed for 4 seconds to iron surfaces at certain temperatures and condensed. The condensed trichloroethylene was then exposed to diffused light, the acidity determined after 3 and 7 days, and its stability compared with the original material exposed under the same conditions. The results of these tests are given in Table IV, where the upper figures represent the trichloroethylene that was not heated. The results indicate that trichloroethylene is stable after heating the vapor for 4 seconds to temperatures below 125° C. (257° F.). Trichloroethylene vapor heated to 125° C. or above is less stable, indicating that some change has occurred at these higher temperatures without giving rise to free acids.

Effect of Water. Trichloroethylene does not hydrolyze readily. If one mole of trichloroethylene is heated with three moles of water in an atmosphere of nitrogen in sealed tubes, negligible acidities are developed at 70–90° C. (158–194° F.) as shown in Table III. At 110° C. (230° F.) the acidity amounted to only 2.4 cc. of 0.01 *N* hydrochloric acid per 25 cc. of trichloroethylene. At 130° C. (266° F.) it was 12.3 cc., and at 150° C. (302° F.), 56 cc. after 24 hours. Again these

Table III. Acidity Developed in Trichloroethylene in an Inert Atmosphere under Various Conditions

(In cc. 0.01 *N* HCl per 25 cc. C_2HCl_3)

Experimental Conditions	Time Heated	Acidity Developed on Heating in Nitrogen at: 50° C.	70° C.	90° C.	110° C.	130° C.	150° C.
	Hours						
Pure C_2HCl_3 (unstabilized), dry:							
Alone	2	0.2	0.2	3.0	4.3	4.2	7.7
Alone	4	0.0	0.3	5.5	7.7	9.5	15.0
Alone	8	0.4	4.4	7.9	9.1	11.0	24.0
Alone	24	0.0	0.2	10.2	10.0	16.0	97.0
Under reduced pressure	24	...	..	1.0	0.0	..	...
With soft steel	24	6.4	10.0	11.0	29.0	43.0	85.0
With tin	24	0.0	..	11.0	24.0	43.0	143.0
With copper	24	0.0	0.2	1.2	12.0	21.0	20.0
With brass	24	0.2	2.7	21.0	22.0	47.0	29.0
With lead	24	0.0	0.5	14.0	25.0	15.0	87.0
With aluminum	24	0.2	0.8	9.4	34.0	27.0	69.0
Pure C_2HCl_3 (stabilized), dry:							
Alone	2	0.4	0.0	0.2	0.6	4.3	16.0
Alone	4	0.0	0.1	0.3	0.9	9.3	29.0
Alone	8	0.0	0.0	0.2	7.6	22.0	30.0
Alone	16	...	..	0.0	..	..	...
Alone	32	...	..	0.0	..	..	...
Pure C_2HCl_3 (unstabilized), satd. with water:							
Alone	24	0.5	0.0	7.7	11.0	7.0	62.0
With soft steel	24	0.0	5.5	11.0	27.0	38.0	207.0
With tin	24	0.0	0.0	11.3	13.0	16.0	104.0
With copper	24	0.0	0.0	1.1	11.0	14.0	16.0
With brass	24	0.0	0.0	11.0	11.0	18.0	37.0
With lead	24	1.5	9.4	8.5	11.0	8.8	65.0
With aluminum	24	0.5	3.1	9.3	15.0	28.0	55.0
Pure C_2HCl_3 (stabilized), satd. with water:							
Alone	24	1.1	0.0	0.3	8.1	16.0	96.0
With soft steel	24	0.2	0.0	0.0	6.0	19.0	243.0
With tin	24	0.0	0.0	0.0	0.7	13.0	50.0
With copper	24	0.0	0.0	0.0	2.2	14.0	12.0
With brass		0.0	0.0	0.0	12.0	19.0	50.0
With lead	24	0.0	0.0	0.0	6.8	7.6	6.4
With aluminum	24	0.0	0.0	0.0	11.0	20.0	21.0
Pure C_2HCl_3 (unstabilized), with 44% by weight water	24	0.5	10.0	18.0	14.0	36.0	96.0
Pure C_2HCl_3 (unstabilized), with 44% by weight water and soft steel	24	0.8	1.8	5.6	22.0	24.0	201.0
Pure C_2HCl_3 (stabilized), with 44% by weight water and soft steel	24	0.6	1.6	1.1	2.4	12.3	56.0
Pure C_2HCl_3 (stabilized), with $FeCl_3$	24	2.8	4.7	6.7	13.0	14.0	0.0

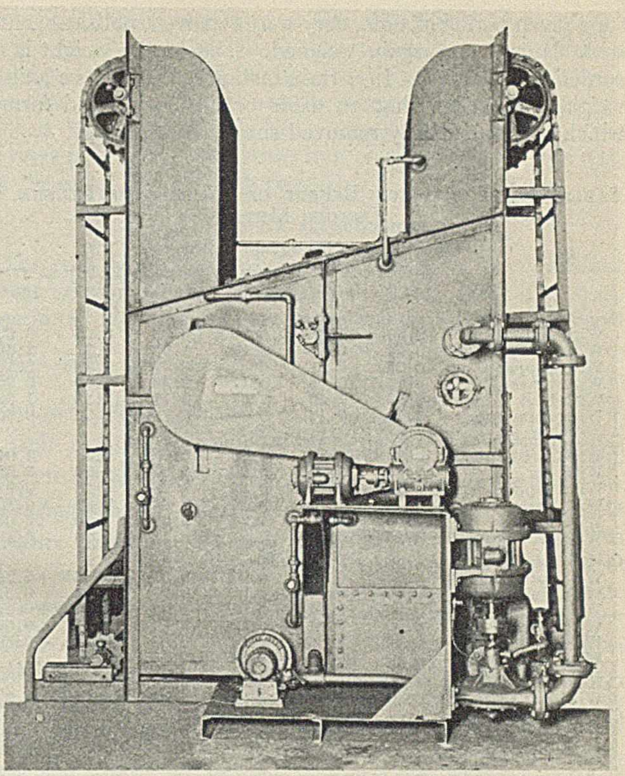
slight acidities may be ascribed to traces of oxygen, except that at the higher temperatures thermal decomposition had probably occurred.

Effect of Ferric Chloride. Ferric chloride is an active chlorinating catalyst and may be just as active in splitting off chlorine or hydrochloric acid; it is conceivable that both ferrous and ferric chloride might be formed on storing trichloroethylene in iron containers. Results indicate that anhydrous ferric chloride increases, to a slight extent, the acidity over and above that which was observed when no ferric chloride was present. Fortunately, the catalytic effect of ferric chloride is not excessive at the boiling point of trichloroethylene. Approximately 1 per cent of hydrochloric acid would be formed on heating trichloroethylene with 0.1 per cent ferric chloride at 90° C. (194° F.) for 100 days in an atmosphere of nitrogen.

Table IV. Vapor-Phase Decomposition of Trichloroethylene

(In cc. 0.01 N HCl per 25 cc. C_2HCl_3)

Temp. of Exposure	C_2HCl_3	Decomposition after Exposure for: 3 days	7 days	Deposit in Reactor Tube	HCl by Weight
° C.					%
90	Original	0.5	2.5	None	None
	Exposed	0.3	0.3		
95	Original	0.27	0.26	None	None
	Exposed	0.46	6.1		
100	Original	0.6	0.3	None	None
	Exposed	0.4	0.6		
110	Original	0.3	0.9	None	None
	Exposed	0.3	0.4		
125	Original	0.8	3.4	None	None
	Exposed	13.0	86.0		
150	Original	0.5	....	None	None
	Exposed	10.3	152.0		
200	.....	...	....	None	0.0012
300	.....	...	....	None	0.0037
400	.....	...	....	Trace of carbon	0.19



Metal Degreaser Using Trichloroethylene

Effect of Oxygen and Heat. Trichloroethylene is attacked by oxygen on heating, giving rise to free acids. Decomposition starts at about 40° C. (104° F.) in pure oxygen and at about 70° C. (158° F.) in air. The presence of antioxidants prevents the decomposition of trichloroethylene in oxygen at temperatures below 90° C. (194° F.); at or above this temperature acids are formed. With air, trichloroethylene containing a stabilizer does not develop any acidity at its boiling point, or below, on heating for 24 hours or longer. The refluxing of trichloroethylene in the presence of water and soft steel for 8 days gave only 3.5 cc. of 0.01 N hydrochloric acid per 25 cc. The experimental data on the effect of oxygen are summarized in Table V.

It would appear from the data that the maximum decomposition occurs at 50° C. (122° F.) in pure oxygen, and, as temperature increases, the decomposition decreases. Actually the variation is due to the limitation of methods used in determining the decomposition—namely, titration of acidities. It should be pointed out that decomposition might occur without giving rise to free acids; even if free acids are formed, these might react with the unsaturated carbon compounds present to give neutral substances. In the presence of oxygen this seems to be the case. It has been found impossible to extract the acid compounds in trichloroethylene by shaking for 10 minutes with double its volume of water. In Table V two sets of figures are given, the upper representing the tri-soluble acid compounds not extractable with water, but obtained by direct titration of the tri-layer with caustic using phenolphthalein as indicator.

Effect of Metals. Soft steel, tin, copper, brass, lead, and aluminum have no apparent effect on trichloroethylene. On heating strips of these metals with trichloroethylene saturated with water or with dry trichloroethylene, there is no increase in acidity over and above that which was observed when trichloroethylene was heated in the absence of these metals. A careful study of Table II seems to indicate that copper, for instance, acts as a stabilizer for trichloroethylene. The metals do not seem to act catalytically on trichloroethylene as is the case with certain other chlorinated hydrocarbons. If these metals were powdered they might react with trichloroethylene on prolonged heating.

Corrosive Effect of Trichloroethylene. The corrosive effect of trichloroethylene under various conditions has been determined. The method used consisted in introducing weighed metallic strips, previously cleaned and polished, into glass tubes prior to adding trichloroethylene. The size of these strips was approximately 1 × 10 cm., and they were exposed partly to liquid and partly to vapor. After the strips had been exposed to the action of trichloroethylene

Table V. Acidity Developed in Trichloroethylene in Air and Oxygen

(In cc. 0.01 N HCl per 25 cc. C_2HCl_3)

	Decomposition on Heating 24 Hours at: −23° C.	0° C.	24° C.	40° C.	50° C.	70° C.	90° C.	110° C.	130° C.	150° C.
Dry pure C_2HCl_3 (unstabilized) in oxygen:										
Acid in C_2HCl_3[a]	...	..	...	440	675	538	300	113	15	...
Total[b]	0	0	0.4	856	1115	1038	820	703	715	...
Dry pure C_2HCl_3 (unstabilized) in air	0.2	0	2.2	...	2.5	192	191	119	150	...
Dry pure C_2HCl_3 (stabilized) in oxygen:										
Acid in C_2HCl_3[a]	...	..	...	...	..	..	105	264	28	20
Total[b]	...	..	...	0	0	0.4	725	1101	921	861
C_2HCl_3 with 0.7% water and soft steel refluxed 8 days	Acidity = 3.5 cc.									

[a] Acid not extractable from C_2HCl_3 with water.
[b] Total of acid compounds extractable and nonextractable with water.

for a given period of time, they were removed, polished gently with flannel, and again weighed. The loss in weight is recorded in Table VI. In certain instances there was a gain in weight, indicating that an oxide or a chloride had formed which was not readily removed simply by rubbing.

TABLE VI. CORROSIVE EFFECT OF TRICHLOROETHYLENE ON VARIOUS METALS

(In milligrams per square centimeter)

	CHANGE IN WEIGHT ON HEATING 24 HOURS AT: 50° C.	70° C.	90° C.	110° C.	130° C.	150° C.
Dry C_2HCl_3 (unstabilized) in nitrogen:						
With soft steel	0.09	0.15	0.09	0.03	0.05	0.02
With tin	0.01	0.20	0.29	1.07	0.37	2.60
With copper	0.37	0.37	0.45	0.47	1.11	2.10
With brass	0.15	0.15	0.17	0.28	0.20	0.25
With lead	0.98	1.29	2.26	2.11	3.30	7.32
With aluminum	0.12	0.14	0.14	0.12	0.05	0.09
C_2HCl_3 (unstabilized) satd. with water in nitrogen:						
With soft steel	0.06	0.08	0.09	0.15	0.27	0.04
With tin	0.37	0.31	0.80	1.02	1.92	3.98
With copper	0.13	0.19	0.23	0.26	0.28	0.93
With brass	0.08	0.13	0.20	0.36	0.39	0.70
With lead	1.50	2.02	1.74	3.00	4.40	22.00
With aluminum	0.15	0.23	0.23	0.10	0.29	0.19
C_2HCl_3 (stabilized) satd. with water in nitrogen:						
With soft steel	+0.02	0.01	0.02	+0.01	0.65	+0.74
With tin	....	+0.01	+0.00	0.02	0.04	0.34
With copper	+0.00	+0.01	+0.01	+0.02	+0.02	+0.19
With brass	0.00	0.01	+0.00	+0.04	0.09	+0.09
With lead	0.02	0.03	0.01	0.03	+0.45	+0.54
With aluminum	+0.02	+0.03	+0.32	+0.33	+0.00	....
C_2HCl_3 (unstabilized) with 44% water in nitrogen:						
With soft steel	....	2.14	3.23	6.02	6.72	42.7
C_2HCl_3 (stabilized):						
With soft steel	0.2	0.169	0.090	0.036	0.019	1.0

The loss in weight for soft steel, tin, copper, brass, lead, and aluminum was negligible, when exposed to trichloroethylene containing antioxidants, saturated with water, and heated in an atmosphere of nitrogen. The surface of the metals, especially soft steel, was slightly dulled by a film which was barely noticeable.

With unstabilized dried trichloroethylene all metals were slightly corroded after heating for 24 hours in a sealed tube in an atmosphere of nitrogen. The amount of corrosion varied with temperature, though this variation is not so great except in one or two cases. Of the various metals, lead was attacked most of all. The amount of corrosion decreased for different metals in the following order: lead, copper, tin, brass, aluminum, soft steel. Unstabilized trichloroethylene saturated with water in an atmosphere of nitrogen attacked the same metals to a slightly greater extent; under these conditions, also, lead was attacked most and soft steel least.

The corrosive effect of trichloroethylene is due to its decomposition products in the presence of oxygen, and, if oxidation is prevented by the use of antioxidants, the common metals are not attacked at temperatures up to 130° C. (266° F.). Soft steel, when refluxed with stabilized trichloroethylene and water for 8 days, showed signs of corrosion. The loss in weight amounted to 0.43 mg. per sq. cm. per 24 hours. On the basis of this loss in weight, the depth of erosion in 365 days of 24 hours each would be about 0.5 mm. or 0.02 inch.

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Influence of Drying Temperature upon Digestibility and Biological Value of Fish Proteins

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MANY thousands of tons of fish products are produced and consumed annually in the United States as protein concentrates for animal feeding. These materials comprise by-products of various industries and represent many different species of fish. The various products are commonly known under the general term "fish meal." Three years ago studies were inaugurated in this laboratory to ascertain whether products which differed as regards origin and method of manufacture also differed significantly with respect to nutritive value. These studies have dealt, for the most part, with the protein component, since fish meals are fed primarily for the purpose of supplying this nutrient.

In the first report from this laboratory, Maynard, Bender, and McCay (*4*) showed that the protein of a vacuum-dried white fish meal was superior to a flame-dried menhaden meal in growth-promoting qualities. In a later study, it was found by Schneider (*7*) that this superiority was due both to a higher digestibility and to a higher degree of utilization of the absorbed nutrient. These two products differed from each other in two respects—species of fish and method of preparation. The question arose, therefore, as to whether one or both of these factors were responsible for the nutritive differences found. The study here reported was carried out to answer this question. The raw material from each species of fish was prepared in the two ways and the four resulting products were compared by the nitrogen-balance method of Mitchell (*5*).

MATERIALS USED

The fish meals used in the studies previously cited were commercial products purchased on the open market. The products used in the present investigation were prepared experimentally to assure the controlled and comparable conditions desired.[1] Since the white fish meal used in the previous studies consisted principally of the waste from the cutting of haddock fillets, haddock waste was used as a source of one product in the present experiment. It consisted of flesh, backbones, tails, and fins. In one case, it was dried

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[1] The products were prepared by The Birdseye Laboratories. The data listed as to methods of preparation were supplied by Donald K. Tressler of these laboratories.

in a direct-flame drier at a maximum temperature of 380° F. (193.3° C.). In the other case it was dried in a Stokes rotary vacuum drier, using a steam pressure between 20 and 25 pounds (1.40 and 1.75 kg.) in the outer jacket and a vacuum of 25 inches (63.5 cm.) in the inner jacket. [This corresponds to a minimum temperature of 133° F. (56.1° C.) within the drum with a probable maximum of 240° F. (115.5° C.) next to the walls.] The menhaden meals were prepared from a batch consisting in part of freshly caught and in part of frozen fish. The frozen product made up 50 per cent of the raw material and was used because a sufficient amount of freshly caught fish could not be obtained at the time. The frozen product was in excellent condition and adjudged superior in quality to the average run of raw material used in preparing commercial menhaden meal. The fish were first cooked and pressed to remove a portion of the oil as is done in the commercial process, and the resulting product was dried by the same two methods described for the haddock. All the products were held under carbon dioxide at a temperature below 40° F. (4.4° C.) until their feeding was actually begun. A storage period of approximately five months was here involved. The essential data regarding these products as used in the experiment are set forth in Table I. The haddock meals correspond very closely in analysis to the commercial product previously used. Due to a less complete removal of the oil, the menhaden products are higher in fat and correspondingly lower in protein and ash than the usual commercial meals.

Haddock waste and menhaden fish which had been previously cooked and pressed for oil were prepared by both flame-drying and vacuum-drying. The four resulting products were studied with rats by the nitrogen-balance method. The protein of the vacuum-dried haddock proved superior to that of the flame-dried product in both digestibility and biological value. In the case of the menhaden products, a large superiority in digestibility was shown for vacuum-drying, but the difference in biological value in favor of vacuum-drying was too small to be statistically significant. For a given drying treatment, the haddock meal proved superior to the menhaden meal in both digestibility and biological value.

TABLE I. PRODUCTS USED IN INVESTIGATION

FISH MEAL	METHOD OF PREPARATION	ANALYSIS Protein	ANALYSIS Fat	ANALYSIS Ash
Flame menhaden	Flame-dried at max. temp. of 380° F. (193.3° C.)	51.08	15.89	16.04
Vacuum menhaden	Steam-dried at 20–25 lb. (1.40–1.75 kg.) pressure; vacuum of 25 in. (63.5 cm.) in inner jacket	53.15	13.75	15.21
Flame haddock	Flame-dried at max. temp. of 380° F. (193.3° C.)	61.80	1.27	24.80
Vacuum haddock	Steam-dried at 20–25 lb. (1.40–1.75 kg.) pressure; vacuum of 25 in. (63.5 cm.) in inner jacket	64.04	2.05	25.30

TABLE II. DIETS USED

INGREDIENTS	N-FREE	1	2	3	4
	%	%	%	%	%
Butter	15	15.0	15.0	15.0	15.0
Lard	12	8.9	9.4	11.8	11.7
Cod-liver oil	2	2.0	2.0	2.0	2.0
Salt mixture	4	0.9	1.1	..	..
Cooked starch	67	52.5	52.5	53.8	54.5
Yeast concentrate	..	1.2	1.2	1.2	1.2
Flame menhaden	..	19.5	..	..	..
Vacuum menhaden	..	..	18.8	..	..
Flame haddock	..	..	..	16.2	..
Vacuum haddock	..	..	..	..	15.6

The diets used are set forth in Table II. The various fish meals were introduced into the nitrogen-free diet in such amounts as to furnish a protein level of 10 per cent. In incorporating the meals, the various ingredients of the nitrogen-free diet were shifted as necessary to hold the calorie and ash content constant throughout. It is noted that the necessary vitamins were adequately supplied in each diet.

Eight growing rats were used. They were first placed upon the nitrogen-free diet, then rotated on the different experimental diets, and finally placed again on the nitrogen-free diet, in accordance with the standard procedure as described by Mitchell (*5*). The experimental periods were 10 days in length. The collection of excreta was made during the last 7 days of each period.

RESULTS OF EXPERIMENTS

The results of the metabolism periods with the significant intermediate data are presented in Table III. The coefficients of digestibility represent apparent digestibility—that is, all of the fecal nitrogen is reckoned as a loss incident to digestion. The data for all the rats with each fish product are presented in full in the table in order that the reader may have a complete picture, but in three instances the figures obtained for digestibility and biological value were not included in the averages. These omitted values are indicated in the table. The values for rat 1 in the vacuum-dried menhaden period are omitted because, during this period, this animal, as shown by the data in the second, third, and fourth columns, ate only a limited amount of food and lost markedly in weight. A calculation showed that the calories ingested were markedly below the requirement for maintenance and that the animal was in marked negative nitrogen balance throughout. It is obvious that a biological value calculated from data obtained under these conditions is meaningless. The reliability of the digestion coefficient is also affected, but probably to a lesser degree.

No digestion coefficients are shown for rats 3 and 8 in the flame-dried haddock period because the fecal samples were lost before they were analyzed, through an accident. For the purpose of working out the biological values in these two cases, the average of the digestion coefficients of the other six rats was used to compute the "average daily fecal nitrogen" values shown for rats 3 and 8. It seemed desirable to show how these values would work out assuming average digestibility, but because of the assumption involved they were not included in the average of the group.

It is clearly shown by the data presented in Table III that digestibility was markedly affected by the variation in the method of drying. In the case of the menhaden meals the difference in favor of the vacuum-dried product is 17 ± 2.3, a very large and significant difference. Including the omitted value in computing the average for the vacuum-dried menhaden would have lowered this difference by one point only. Thus the question involved in the omission here made is of no importance. The difference in favor of vacuum-drying for the haddock meals, 5 ± 0.7, though not so large as in the case of the menhaden, is statistically significant. The question arises as to why the digestibility was affected to such a greater degree in the case of the menhaden products. These products contained much more oil, as shown in Table I. It is clear that the temperature of flame-drying brings about marked alterations in these oils, tending to render them less digestible. It is possible

Table III. Digestibility and Biological Value of Fish Protein

Rat	Initial Wt. *Grams*	Final Wt. *Grams*	Av. Daily Food Intake *Grams*	Av. Daily N Intake *Mg.*	Av. Daily Fecal N *Mg.*	Av. Daily Absorbed N *Mg.*	Av. Daily Urinary N *Mg.*	Av. Daily Food N Utilized *Mg.*	Digestion Coefficient	Biological Value
					NITROGEN-FREE DIET					
1	100	94	6.760	....	12.49	....	26.44	....	..	..
2	110	107	6.344	....	12.62	....	16.34	....	..	..
3	110	100	5.602	....	11.37	....	22.01	....	..	..
4	104	94	4.442	....	10.39	....	19.71	....	..	..
5	109	101	4.931	....	12.16	....	16.49	....	..	..
6	86	83	5.390	....	10.09	....	18.91	....	..	..
7	96	92	4.845	....	8.04	....	23.99	....	..	..
8	101	92	4.530	....	8.90	....	24.21	....	..	..
					FLAME-DRIED MENHADEN FISH MEAL DIET					
1	96	101	5.620	92.62	31.10	71.97	47.56	52.14	66	73
2	106	116	6.493	107.00	35.81	83.20	39.99	61.00	67	73
3	121	127	6.204	102.24	38.00	74.79	46.51	52.27	63	70
4	107	111	4.534	74.72	31.82	51.74	37.47	36.99	57	72
5	131	126	5.564	91.70	45.21	62.07	42.34	44.72	51	72
6	111	108	5.266	86.78	44.93	56.28	44.60	36.93	48	66
7	109	116	6.009	99.03	32.67	79.94	53.44	46.53	67	58
8	123	126	5.264	86.75	27.71	71.92	41.34	57.85	68	80
								Av.	61 ± 2.1	70 ± 1.4
					VACUUM-DRIED MENHADEN FISH MEAL DIET					
1	130	108	2.928	50.30	14.03	41.78	59.93	18.56	72[a]	44[a]
2	155	160	7.483	128.56	16.17	123.09	60.26	92.63	87	75
3	105	118	6.214	106.76	23.13	95.25	44.16	73.56	78	77
4	95	108	6.118	105.11	25.02	93.24	40.53	73.40	76	79
5	124	134	6.321	108.60	32.36	93.24	43.47	73.25	70	79
6	100	108	4.946	84.97	18.14	78.95	38.04	64.66	79	82
7	112	104	3.684	63.29	13.56	57.50	46.53	32.30	79	56
8	112	120	5.810	99.82	22.18	91.12	43.70	73.75	78	81
								Av.	78 ± 1.0	76 ± 1.9
					FLAME-DRIED HADDOCK FISH MEAL DIET					
1	125	128	6.763	123.76	25.67	110.80	59.56	89.13	79	80
2	151	158	8.333	152.49	33.29	132.28	65.84	94.17	78	71
3	147	161	7.754	141.90	28.38[b]	124.14	63.43	89.47	..	71[a]
4	145	161	8.226	150.54	22.92	140.45	59.67	114.04	85	81
5	106	121	6.255	114.47	21.40	109.21	39.70	88.77	81	81
6	94	103	6.170	112.91	23.39	102.85	44.90	80.21	79	78
7	104	117	5.523	101.07	19.29	92.61	43.43	73.10	81	79
8	110	120	5.202	95.20	19.04[b]	87.60	43.90	70.73	..	81[a]
								Av.	80 ± 0.6	78 ± 1.1
					VACUUM-DRIED HADDOCK FISH MEAL DIET					
1	114	119	6.313	109.85	17.66	104.00	48.11	89.73	84	86
2	128	147	8.470	147.38	23.25	138.61	42.94	119.03	84	86
3	141	146	7.170	124.76	17.37	118.36	49.63	95.35	86	81
4	121	140	8.342	145.15	22.38	137.37	43.96	121.18	85	88
5	136	150	7.426	129.21	20.76	129.21	50.63	108.18	84	84
6	116	125	6.391	111.20	18.33	111.20	45.40	93.88	84	84
7	103	108	5.203	90.53	14.05	85.90	38.22	72.58	85	85
8	96	106	5.444	94.73	12.58	93.47	37.90	80.08	87	86
								Av.	85 ± 0.3	85 ± 0.5
					NITROGEN-FREE DIET					
1	107	99	4.094	....	7.72	....	32.67	....	..	..
2	155	143	5.953	....	7.65	....	29.60	....	..	..
3	147	144	7.739	....	9.31	....	24.63	....	..	..
4	151	138	4.929	....	6.72	....	32.06	....	..	..
5	140	129	4.566	....	13.80	....	29.50	....	..	..
6	116	105	3.851	....	12.72	....	25.99	....	..	..
7	111	105	3.949	....	9.51	....	17.13	....	..	..
8	120	111	3.433	....	8.78	....	24.40	....	..	..

[a] Omitted from average. [b] Calculated values.

that these changes in the fat present in turn influence the digestibility of the protein associated with it, particularly where a large amount of fat is present, as was true in the case of the menhaden meals here used.

Taking up the biological values, a difference of 6 ± 2.4 in favor of vacuum-drying is shown in the case of the menhaden products. Considering the probable error here involved, the odds in favor of the vacuum-dried product are only approximately 7 to 1, and thus the difference is not statistically significant. If the omitted value for rat 1 on the vacuum-dried product is included in the average, a calculation shows that even the numerical difference favoring this product practically disappears. However, the justification for omitting this value from the average is believed clear for the reasons previously stated. In the case of the haddock meals, there is clear evidence that the vacuum-drying resulted in a product of higher biological value, as shown by the significant difference of 7 ± 1.2.

Thus, the comparisons for the two heat treatments show a distinct superiority as regards digestibility in the case of both kinds of meal, and a clear superiority in biological value in the case of the haddock products. Although the effect on digestibility was much more marked with the menhaden meals, the difference in biological value in favor of the vacuum-drying in the case of these meals was too small relative to its probable error to be statistically significant. Thus a further study of this question is required before a conclusion can be reached.

Superiority of Haddock Meal

It is shown in Table III that when the meals from the two different species of fish are compared for the same heat treatment, the results without exception are significantly in favor of the haddock products. As regards digestibility, the flame-dried haddock is superior to the flame-dried menhaden by a difference of 19 ± 2.2, and the vacuum-dried haddock is superior to the vacuum-dried menhaden by 7 ± 1. In biological value, the superiority in favor of the haddock is 8 ± 1.8 in the case of flame-drying, and 9 ± 2 in the case of vacuum-drying. It seems rather surprising that a product containing a relatively larger proportion of its protein in fins, tails, and bones, and without internal organs, should prove superior to one including the proteins of the entire fish. In this connection it should be remembered that the haddock waste was dried directly, whereas the menhaden material was first cooked and pressed, as is done in the commercial process of obtaining the oil. A certain amount of soluble protein is lost in this process. It may be presumed that this lost protein is of high digestibility and perhaps also of high biological value. Further, the cooking and pressing may possibly tend to lower the value of the remainder of the protein. To what extent these factors may be responsible for the differences noted between the two kinds of meal dried in the same way cannot be stated.

In view of the differences in raw material and treatment prior to drying, as set forth above, these data cannot be considered to furnish evidence that haddock proteins are superior to menhaden proteins *per se.* However, since the cooking and pressing process, with the resultant loss of soluble protein, is generally employed in the menhaden industry at present, the data have a practical significance with respect to the products used in livestock feeding. From the standpoint of the menhaden industry they serve to strengthen the contention of Harrison (*2*) that procedures should be adopted to lessen or eliminate the losses of water-soluble material.

Daniel and McCollum (*1*) have reported from growth studies that vacuum-dried white fish meal appears to contain a protein of similar quality to vacuum-dried menhaden meal. The white meal was a commercial product consisting of cod and haddock, whereas the menhaden was an experimental product prepared by the Bureau of Fisheries. Since these products differed both in raw material and in the methods of preparation from those used in this laboratory, the results from the two experiments cannot be considered as contradictory. However, they serve to emphasize the conclusion that general statements cannot be made regarding the relative value of white and menhaden meals, since this value is dependent both upon the nature of the raw material and the methods of processing.

The results here presented suggest that the superior nutritive value of the protein of vacuum-dried haddock meal in comparison with flame-dried menhaden meal, as previously found in this laboratory (*4*, *7*), is due both to the method of drying and to the nature of the material dried. They confirm the findings of the nitrogen-partition studies of Invaldsen (*3*) that high temperatures have a detrimental effect upon the quality of fish proteins. A deleterious effect of heat upon cereal proteins has been shown by Morgan (*6*). All of these results point to the practical importance of further study of the influence of the temperatures used in various manufacturing and home processes involved in the preparation of protein foods, both human and animal.

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Viscosity of Corn Sirup

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Using a falling-sphere viscometer for which details of calibration are given, the viscosity of corn sirup as sold (commercial glucose) has been determined for various densities and temperatures. It has been shown that within the range investigated corn sirup acts as a truly viscous solution. The effect of per cent reducing sugars on viscosity has also been studied.

IN THE design of pumps and pipe lines, study of evaporation data, and adaptation of a product to particular uses, a knowledge of viscosity is a factor of prime importance. There have been few data published on the viscosity of commercial corn sirup. Washburn and Shelton (*8*) give data on a glucose sirup and mixtures of this with pure dextrose, but these are incomplete, for one temperature only, and of limited value.

Commercial corn sirup as sold in bulk is manufactured to strict standards of moisture content and degree of conversion, and the products of various companies are surprisingly uniform and comparable. The moisture content of the sirup is specified by giving the Baumé at 100° F. This is measured at 140° F. by means of a hydrometer (145 modulus), and corrected to 100° F. by adding the arbitrary, although approximately correct, figure of 1° Baumé. Thus a sirup which has a density of 42° measured at 140° F. is said to be 43° corn sirup. Corn sirup, or "glucose," is marketed, unmixed, in concentrations of 42°, 43°, 44°, and 45° Baumé, the 43° Baumé predominating. The degree of conversion is specified as per cent purity, or per cent of the dry substance present which reacts as a reducing sugar to Fehling's solution, calculated as dextrose. Except for special products, commercial corn sirup will run from 41 to 43 per cent purity.

DESCRIPTION OF APPARATUS

The falling-sphere viscometer has been applied successfully by Ladenburg (*4*), Sheppard (*6*), Gibson and Jacobs (*3*), and Bennett and Nees (*1*) for determination of the viscosity of turpentine, nitrocellulose, sugar solutions, and molasses. Because of the transparency of corn sirup, this method seemed well adapted. It requires simple equipment, and because of this will give reasonably accurate results without a great deal of special equipment or technic.

The spheres used in this investigation were ordinary steel ball bearings varying in diameter from $^1/_8$ to $^3/_8$ inch according to the viscosity of the sirup. The tubes were ordinary graduates, and 250-cc., 500-cc., and one-liter graduates were calibrated. The larger sizes were used to reduce the end and side corrections necessary when the equations are used instead of a standard liquid for calibration. The tubes were fitted at the top with metal caps or rubber stoppers holding a starting tube of about 1.2 cm. inside diameter, which dipped below the surface of the sirup for several centimeters. A sufficient distance below the starting tube to allow attainment of equilibrium velocity, the starting mark was located, and

6 to 8 cm. from the bottom, the final mark. These were extended around the tube to eliminate parallax. The tubes were placed in a glass-walled constant-temperature bath which could be adjusted to bring them exactly vertical. For removing the balls after completion of the run without disturbing the liquid or introducing air bubbles, a small electromagnet was used.

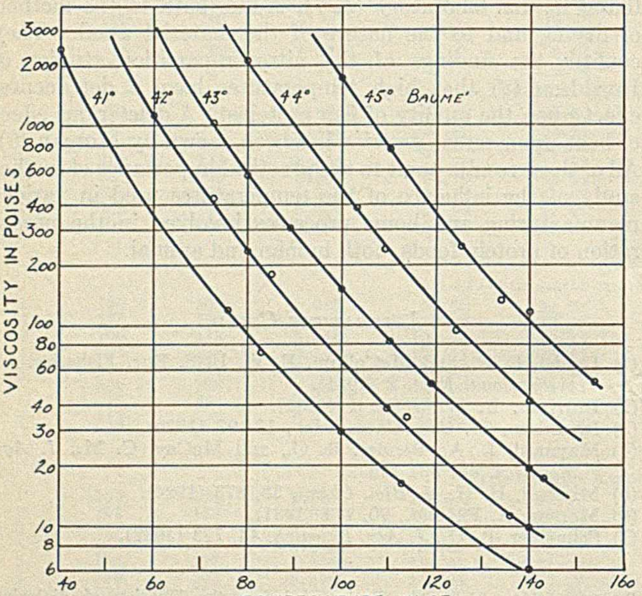

FIGURE 1. VISCOSITY-TEMPERATURE CURVES FOR CORN SIRUP

CALIBRATION OF VISCOMETER

Ladenburg (*4*) gives a modification of the well-known Stokes equation with corrections applying where the liquid is not infinite in extent, as in the relatively small tubes used here. The equation is:

$$\eta = \frac{2gr^2(S - \sigma)t}{9L\left(1 + 2.4\,\dfrac{r}{R}\right)\left(1 + 3.3\,\dfrac{r}{h}\right)} \qquad (1)$$

where η = viscosity in poises
g = acceleration of gravity (980 cm. per sec.^{2})
r = radius of sphere in cm.
S = density of sphere in grams per cc.
σ = density of liquid in grams per cc.
t = time of fall in seconds
L = distance of fall in cm.
R = radius of tube in cm.
h = total height of liquid in cm.

As pointed out by Bennett and Nees (*1*), this equation can be modified for a given viscometer and sphere to the form

$$\eta = K(S - \sigma)t \qquad (2)$$

where K is the tube constant. K can be calculated from Equation 1 or can be determined experimentally for a given tube according to Equation 2 if a liquid of known viscosity is available.

There is a scarcity of calibrating liquids for viscosities of 50 poises and over. The only oil sufficiently viscous and still transparent enough which could be secured was Stanolind No. 200. Viscosity of this oil, as determined by the Bureau of Standards, together with its density is as follows:

TEMPERATURE	VISCOSITY	DENSITY
° C.	*Poises*	*Gram/cc.*
5	85.9	0.881
15	32.1	0.872
25	14.1	0.866

For convenience in measuring viscosities over a wide range, and also to study the applicability of the equations, seven different sizes of balls were calibrated in the three different sized tubes. Ten balls of each size were weighed and found to be quite uniform, the largest deviation from the mean weight varying from 0.06 per cent in the case of the 1/4-inch balls to 0.5 per cent in the case of the 3/16- and 1/8-inch balls. An average density of 7.77 was found for the steel balls. The constants of the tubes were as follows:

	VISCOMETER A	VISCOMETER B	VISCOMETER C
Capacity:	1000 cc.	500 cc.	250 cc.
R, cm.	3.05	2.40	1.78
L, cm.	20.2	18.9	20.5
h, cm.	38	33	35

Data on calculated values for K and those determined experimentally are given in Table I. The experimental data represent the average of several of each size sphere at temperatures of 5°, 15°, and 25° C. for the Stanolind oil.

TABLE I. CALIBRATION OF VISCOMETERS

NOMINAL BALL SIZE	AV. WT.	RADIUS	VISCOMETER A K calcd.	VISCOMETER A K exptl.	VISCOMETER B K calcd.	VISCOMETER B K exptl.	VISCOMETER C K calcd.	VISCOMETER C K exptl.
Inch	*Grams*	*Cm.*						
1/8	0.1273	0.1576	0.234	0.237	0.243	0.245	0.214	0.218
5/32	0.2533	0.1982	0.358	0.368	0.370	0.372	0.324	0.330
3/16	0.4402	0.2383	0.503	0.511	0.515	0.511	0.447	0.467
7/32	0.6999	0.2781	0.665	0.675	0.678	0.678	0.572	0.622
1/4	1.0429	0.3177	0.843	0.855	0.855	0.816	0.730	0.764
5/16	2.0396	0.3972	1.246	1.266	1.250	1.220	1.052	1.042
3/8	3.5242	0.4767	1.702	1.708	1.692	1.485	1.402	1.240

According to Ladenburg, Equation 1 holds when r/R is less than 0.08, whereas Sheppard showed the variation was not great for $r/R = 0.1$. An examination of Table I shows that the calculated values for K are from 1 to 2 per cent in error for values of r/R below 0.12, somewhat erratic and from 4 to 8 per cent off for r/R between 0.12 and 0.16, and as high as 13 per cent for r/R between 0.2 and 0.25. Below 0.12 the variation is less than the experimental error. Previous experimenters (*1, 7*) have also confirmed the equation. Equation 2 with K experimentally determined should hold for any practical dimensions of spheres and tubes. Where calibrating liquids are available it is more convenient to use the smaller tubes, since less time is required for attainment of temperature equilibrium.

DETERMINATION OF VISCOSITY OF CORN SIRUP

The sirup, of known Baumé and purity, was placed in the viscometer tube, covered, and allowed to stand in the bath at 140° F. until free from air bubbles. The temperature of the bath was controlled to within 0.2° F. Following air-bubble removal, the sirup was brought to the desired temperature (this requires several hours in the larger tubes), the starting tube put in place, and the various size balls dropped and timed with a stop watch. Spheres were selected giving times of fall of from 10 to 100 seconds.

Figure 1 shows the data on commercial grades of corn sirup with the logarithm of viscosity plotted against temperature for the different Baumé sirups. Those tested ran from 41.2 to 42.8 per cent purity. Each point represents the average of from 10 to 15 spheres dropped.

From its composition it might be suspected that corn sirup is a plastic material. Disagreement between the viscosities as measured by small and large spheres should indicate this (*5*). However, it was thought advisable to make a few check runs on a transpiration type viscometer to determine whether or not corn sirup was truly viscous and, at the same time, to serve as a check on the falling-sphere viscometer. For these runs a consistometer similar to that described by Bulkley and

Bitner (2) was used. The consistometer was calibrated both by actual measurement and by use of the Stanolind No. 200 oil. The curves secured are not reproduced here since they were all straight lines passing through zero, thus indicating that at least within the range of accuracy and concentrations studied corn sirup was truly viscous. Table II shows comparative results from the two methods. The close checks secured on the two widely varying types of instrument also indicate viscous rather than plastic flow.

TABLE II. COMPARATIVE RESULTS WITH TWO TYPES OF INSTRUMENT

Baumé at 100° F.	Temperature	Sp. Gr.	Viscosity: Falling-sphere viscometer	Viscosity: Transpiration viscometer
	° F.	*100/60° F.*	*Poises*	*Poises*
43.0	100	1.4216	152	148
	140	1.4078	19.3	21.6
43.3	100	1.4258	206	211
	140	1.4119	22.6	23.4

Table III shows the viscosities of corn sirups obtained from different manufacturers. The agreement is within about 5 per cent, and part of this variation is due to difference in the purity of the sirups.

TABLE III. VISCOSITIES OF CORN SIRUPS FROM DIFFERENT MANUFACTURERS

Manufacturer	Baumé at 100° F.	Sp. Gr.	Purity	Viscosity 100° F.	Viscosity 140° F.
		100/60° F.	*% dry substance*	*Poises*	*Poises*
A	43.3	1.4258	42.6	199	22.6
B	43.2	1.4244	42.9	176	21.5
C	43.3	1.4258	42.0	206	25.3
D	43.3	1.4258	42.8	183	22.6
E	43.3	1.4258	42.3	205	25.0

To determine the effect of purity on viscosity, tests were made on several samples of different purity which were available. These included a special low-purity sirup of 29.8 per cent purity, special high-purity sirups of about 55 per cent, unrefined corn sugar liquor of 88 per cent, and a sirup made from crystallized dextrose of 100 per cent purity. Where Baumé of these sirups differed slightly from 43°, the viscosities as determined were corrected to 43° by using percentages obtained from Figure 1. The resulting curve is shown in Figure 2.

ACCURACY OF DETERMINATIONS

The accuracy of the calibration of the viscometer is probably well within 3 per cent. Viscosity of Stanolind varies about 9 per cent per ° C., and temperature control was about 0.1° C. The variation of 0.5 per cent in the weight of balls would cause only about 0.3 per cent error in the time of fall, and hence no correction was attempted. Some of the times recorded were as low as 10 seconds, hence were measured only to 2 per cent.

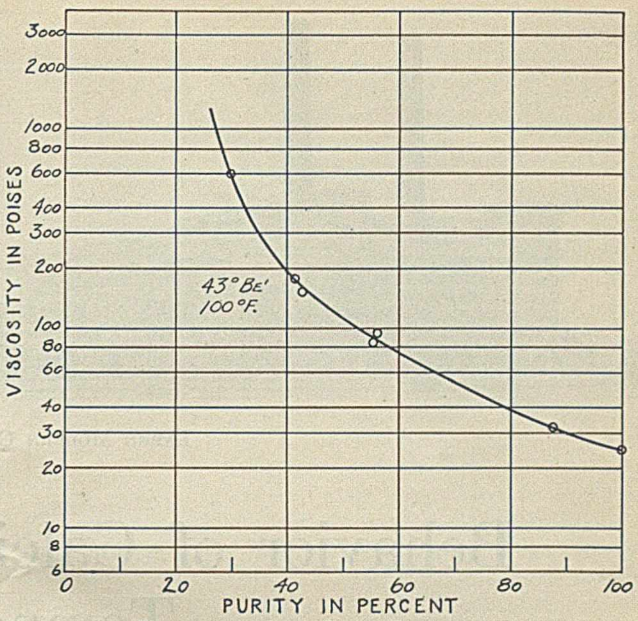

FIGURE 2. EFFECT OF PER CENT REDUCING SUGARS ON VISCOSITY OF CORN SIRUP

A survey of the data on corn sirup shows the following percentage variation in viscosity for unit variation in other variables:

	%
1° F.	5 to 7
0.1° Bé.	8 to 10
1% purity	6 to 7

Since temperature was controlled only to 0.2° F. and gravity measured to only 0.05° Bé., whereas the samples varied about 1 per cent in purity, it would seem that the method of determining viscosity was closer than the control of other variables. The latter might have caused a variation of from 5 to 10 per cent for any individual reading. Results were checked within 4 per cent between the transpiration and falling-sphere viscometers with one exception.

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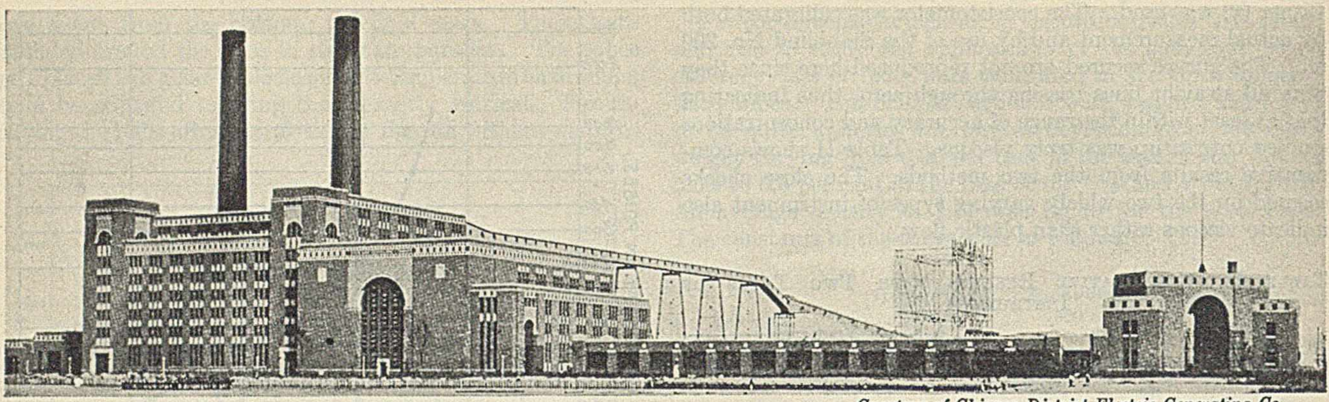
No. 21 of the series appears in this issue, page 1201.

[1] See IND. ENG. CHEM., 23, 966 (1931); News Edition, May 10, 1931, p. 155.



Courtesy of Chicago District Electric Generating Co.

LARGE MODERN CENTRAL POWER PLANT

Behavior of Calcium Salts at Boiler Temperatures

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THE trend of the design of modern steam plants is toward higher pressures and higher rating. Since capital investments are also increasing, the question of "boiler outage" or the amount of time a boiler is out of service becomes very important. In attempting to explain the cause of scale formation and methods of preventing it, much stress has been laid by Hall (*1*), Partridge (*2*), and others, upon the ratio of carbonate to sulfate for the prevention of scale. Calcium sulfate forms a dense adherent scale on the heating surfaces, while calcium carbonate does not usually form an adherent scale in boiler waters having an appreciable hydroxide alkalinity. The earlier explanation offered by Hall was that calcium sulfate, having a retrograde solubility (decreasing with increase in temperature), became less soluble at the heating surface and came out of solution as scale. Calcium carbonate, according to the small amount of data available, was assumed to be more soluble with increase in temperature. Thus, it would remain in solution at the heating surface and be thrown out of solution in the main body of the boiler and form sludge. Working on this assumption, Hall determined the solubility of calcium sulfate in water at temperatures up to 200° C. and calculated the solubility product at these temperatures. He made a rough calculation of the solubility product of calcium carbonate from data available at lower temperatures. The relation between the two solubility products was taken as the amount of carbonate ion necessary to cause preferential precipitation of calcium carbonate. Hall gave this figure as 0.0883 for the ratio of carbonate to sulfate at 185° C., and stated that at higher temperatures this figure would increase.

Partridge (*2*) pointed out that calcium carbonate undoubtedly became less soluble with increase in temperature. The author (*4*, *5*) reported the results of tests run on the solubility of calcium carbonate at temperatures between 182° and 316° C. and showed that the solubility decreases with increase in temperature. Partridge, Schroeder, and Adams (*3*) calculated the ratio of carbonate to sulfate, employing a relation between the stoichiometric solubility product determined directly and correlated by means of the ionic strength as a measure of the total ionic strength. They also determined the ratio roughly by preferential precipitation of calcium carbonate in a laboratory boiler. From these results they arrived at the conclusion that at 185° C. the ratio of carbonate to sulfate was not greater than 0.01.

Thus, it appears evident that, in order to draw definite conclusions as to the cause of scale formation and its prevention, more data are desirable as to what are the stable solid and liquid phases of the various salts encountered in boiler waters at boiler temperatures. The author has run a series of tests involving the calcium salts such as carbonate, sulfate, phosphate, silicate, and hydroxide (separately and combined), in order to determine the several equilibria involved.

TESTS ON CALCIUM SALTS

APPARATUS. The equipment used in making these tests has been reported in detail (*4*, *5*). A photograph and diagram of the steel bomb used for the tests have already been reproduced (*5*). The solid and solution were put into the lower bomb. The completely assembled unit was heated in a constant-temperature air bath. When the lower bomb had been held at this temperature for the desired period of time, the valve between the bombs was opened and part of the liquid in the lower bomb was forced through the filter and the connecting capillary steel tube into the top bomb. The valve was then closed, the unit removed from the heating chamber, cooled, and the volume of the sample collected in the top bomb measured.

MEASUREMENT OF VOLUME OF SAMPLE. The volume of each top bomb was determined by using a standard top having a glass tube in it. The amount of water necessary to fill the bomb to the mark on the tube was determined for each bomb. When the bomb was removed after sampling, the standard top was put on and redistilled water, free from carbon dioxide, was added through the glass tube from a buret. The amount of water added, deducted from the total volume of the bomb, gave the volume of the sample. This volume could be determined within 0.2 cc. with a total volume of about 250 cc., thus giving a possible error of about 0.1 per cent in measuring the volume of the liquid.

The bomb was then rinsed out three times with redistilled water, free from carbon dioxide, into a 500-cc. Erlenmeyer flask. If the hydroxide content was to be determined, the solution was transferred to a 500-cc. volumetric flask and diluted to volume with the purified water. One portion was then pipetted out to be run for hydroxide and sulfate, and the remaining portion run for carbonate and calcium. The size of the samples to be used depended on the approximate amount of the material present. Thus, with a low sulfate content, 250-cc. samples were used for hydroxide and sulfate and with a high sulfate content only 100 cc. were used. If the hydroxide content was not to be determined, all of the sample was run for carbonate and sulfate.

The reaction $CaSO_4 + Na_2CO_3 \rightleftarrows CaCO_3 + Na_2SO_4$ *has been investigated at temperatures between 182° and 282° C. The effect of the presence of sodium hydroxide and sodium chloride combined in the liquid phase has also been studied. Owing to the change in equilibrium between the ions in the liquid phase at the elevated temperatures and room temperature where the solutions are analyzed, it has not been possible to determine the exact equilibrium. However, data are presented which indicate the liquid-phase concentrations measured at room temperature which will cause the precipitation of either calcium sulfate or calcium carbonate at the elevated temperatures.*

PROCEDURE. Since six bombs were run at one time in the constant-temperature boxes, it was found advantageous to run the six samples through the analytical procedure together. When the solutions were prepared before adding to the bombs, a blank using the same amount of the carbon dioxide–free redistilled water as was used for the bombs was put in a 500-cc. Erlenmeyer flask, and the same solution added as was added to one of the bombs. The flask was stoppered and set aside to be run through the analytical procedure with the samples obtained from the bombs after they had been held at the desired temperature for the proper period of time. This blank served to check the concentration of the solution in the bomb at the start, as well as the analytical procedure.

The solids added to the bombs were either calcium sulfate or calcium carbonate. The calcium sulfate was added in previous tests both as $CaSO_4$ and $CaSO_4 \cdot 2H_2O$, and the resulting solubilities were found to be identical, apparently irrespective of which form was used. For the tests being reported, $CaSO_4$ was added as the solid. When calcium carbonate was added, ground crystals of Iceland spar were used; the latter was of standardization quality.

The chemicals to be added in solution were made up in about 0.1 molal solutions by adding the chemicals to carbon dioxide–free redistilled water. The sodium hydroxide solution was stored in a paraffin-lined bottle.

The water was obtained by distillation after adding a small amount of sulfuric acid and potassium permanganate to distilled water and collecting the middle 60 per cent of the distillate. The redistilled water was washed free from carbon dioxide by bubbling carbon dioxide–free air through it for 24 hours. Tests run on liter samples of this water showed the carbon dioxide to be not more than 2 parts per million.

The desired amounts of the concentrated chemicals were calculated, and the total volume deducted from the volume to be added to the bombs (usually 400 cc.). This amount of redistilled carbon dioxide–free water was added to a 500-cc. Erlenmeyer flask and heated until boiling just started. The necessary volumes of solutions of the chemicals were added, and the hot solution was poured into the clean dry bomb containing about 50 millimoles of the desired solid. The bomb was immediately closed.

The bombs were then put in the constant-temperature air baths, brought up to temperature within 5 hours, and held at constant temperature for 84 hours. Tests run at 182° C. gave the same results after 36 hours at this temperature as when held there 84 hours. However, the 84-hour period was used since it fitted in with the operation of four constant-temperature baths. Thus, a set of bombs could be sampled; removed from the bath at 8 A. M.; cleaned, charged, and returned by 3 P. M.; and be up to the desired temperature by 8 P. M. In this way every fourth day was found to be a convenient sampling time.

HYDROXIDE DETERMINATION. The hydroxide was determined by pipetting the solution into a 500-cc. Erlenmeyer flask, adding 25 cc. of a standard solution of 0.02 *N* sodium hydroxide containing about 10 per cent barium chloride; after allowing the mixture to stand stoppered for about 2 hours, the solution was titrated with 0.02 *N* hydrochloric acid to the phenolphthalein end point (colorless). A blank was run using the same volume of carbon dioxide–free water as that contained in the sample being tested. The difference between the quantity of acid used for the blank and that used for the sample gave a direct measure of the hydroxide content. Tests conducted by the author to check the accuracy of this method (*6*) for the determination of hydroxide showed that the possible error was about 3 p. p. m. as sodium hydroxide.

CARBONATE DETERMINATION. The sample to be tested was transferred to a 1000-cc. Erlenmeyer flask, previously swept clean with carbon dioxide–free air. The flask was connected with a reflux condenser. A stream of carbon dioxide–free air was passed through the flask, through the condenser, through granulated zinc, through calcium chloride, and finally through anhydrone. The dry air was then passed through a weighed Wesson bulb containing ascarite and anhydrone. The entire train was swept free from carbon dioxide before adding the flask containing the sample. After the flask was added, dilute hydrochloric acid (1:1) was added by means of an adding funnel put through the rubber stopper; the solution was heated to boiling and boiled slowly, with the air being passed through slowly. After about 30 minutes the Wesson bulb was removed and weighed, the difference in weight being a measure of the carbon dioxide present in the solution. Weighed amounts of pure sodium carbonate were put in solution in carbon dioxide–free water, and the carbon dioxide content tested by this method. It was found that the method was accurate to within one p. p. m. of carbonate (0.02 millimole per liter) when a 250-cc. sample was used.

SULFATE DETERMINATION. The solution left after the hydroxide determination was made distinctly acid to methyl orange by adding a few drops of concentrated hydrochloric acid. It was then boiled down to about 75 cc. volume, allowed to stand for 12 hours, filtered, washed, ignited, and weighed in tared crucibles as barium sulfate. It was thought that, since the barium sulfate was precipitated by the addition of an alkaline barium chloride solution in the cold, the precipitate might occlude other materials. However, tests run by this method, using standard solutions of sodium sulfate, gave results for the sulfate content within 2 p. p. m. of sulfate (0.02 millimole per liter) of those obtained in a volume of 250 cc. in which the barium sulfate was precipitated from a hot, slightly acid solution.

CALCIUM DETERMINATION. The calcium was determined after the carbonate content determination. The acid solution left after the carbon dioxide had been removed was boiled down to about 75 cc. volume, made slightly alkaline with ammonium hydroxide, and then just acid to methyl orange indicator with hydrochloric acid. About 20 cc. of a 4 per cent solution of ammonium oxalate were added to the boiling solution; after a few minutes of boiling, the solution was made slightly alkaline with ammonium hydroxide and boiled for 15 minutes. After cooling, the solution was made distinctly alkaline with ammonium hydroxide, allowed to stand 12 hours, filtered, and washed with distilled water, slightly alkaline with ammonium hydroxide, until free from ammonium oxalate. The precipitate was dissolved in hot sulfuric acid solution (about 25 cc. concentrated sulfuric acid to 1 liter of water), heated to 80° C., and titrated with 0.05 N potassium permanganate solution. The potassium permanganate solution was standardized at regular intervals against sodium oxalate obtained from the Bureau of Standards. If much iron was present, it was removed as ferric hydroxide prior to running the calcium. If the volume of the ferric hydroxide was appreciable, it was dissolved in hydrochloric acid and reprecipitated, and the filtrate added to the first filtrate and run for calcium. The calcium was determined with an error of ±0.2 milligram. Thus, on a 250-cc. sample the error would be ±0.02 millimole per liter.

TABLE I. SULFATE AND CARBONATE CONTENT OF SOLUTIONS OF SODIUM CARBONATE HEATED IN CONTACT WITH SOLID CALCIUM SULFATE

TEMP.	Na_2CO_3 ADDED	SO_4 AT END OF TEST	CO_3 AT END OF TEST	RATIO CO_3:SO_4	
° *C.*	*Millimoles per liter*			*Millimoles*	*P. p. m.*
182	0.48	1.07	0.39	0.36	0.22
	1.20	1.63	0.51	0.31	0.19
	1.20	1.56	0.55	0.35	0.22
	3.60	3.28	0.73	0.22	0.14
	12.00	11.50	1.12	0.09	0.06
	18.00	16.80	1.21	0.07	0.05
207	0.24	0.43	0.52	1.21	0.79
	0.48	0.50	0.67	1.34	0.84
	1.20	1.20	0.75	0.62	0.39
	3.60	3.25	0.90	0.27	0.17
	12.00	11.90	1.05	0.09	0.06
	18.00	17.05	1.40	0.08	0.05
244	0.48	0.23	0.34	1.47	0.92
	1.20	0.71	0.90	1.27	0.79
	3.60	2.78	1.63	0.59	0.37
	12.00	10.40	2.33	0.22	0.14
	18.00	15.40	3.73	0.24	0.15
282	3.60	2.62	1.61	0.62	0.39
	12.00	10.75	3.83	0.35	0.22
	18.00	16.00	3.60	0.22	0.14

SUMMARY OF TESTS. Of the various equilibria studied, the following appears to be of particular interest when considering the cause of sulfate scale formation:

$$CaSO_4 + Na_2CO_3 \leftrightarrows CaCO_3 + Na_2SO_4$$

If the solubility of calcium sulfate and calcium carbonate is known, one should be able to calculate the ratio of carbonate to sulfate which is necessary to cause precipitation of calcium carbonate in preference to calcium sulfate. However, such data depend not only upon the solubility of calcium sulfate and calcium carbonate alone, but in solutions of ionic strength comparable to that in boiler waters, and also with a mixed solid.

Tests have been run under the following conditions at the beginning:

Solid, $CaSO_4$; in solution Na_2CO_3
Solid, $CaCO_3$; in solution Na_2SO_4
Solid, $CaSO_4$; in solution, NaCl, NaOH, Na_2CO_3
Solid, $CaCO_3$; in solution NaCl, NaOH, Na_2SO_4

Complete analyses were made of the solutions removed when equilibrium had apparently been established.

The results obtained from a study of these two systems, approached from both sides of the equilibrium, are given in Tables I to V.

DISCUSSION OF RESULTS

The first system studied, the results of which are given in Table I, involves a study of the reaction:

$$CaCO_3 + Na_2SO_4 \leftrightarrows CaSO_4 + Na_2CO_3$$

starting from the left and proceeding to the right. The results show sulfate and carbonate in millimoles per liter, both at the start and when apparent equilibrium had been reached. The ratio of carbonate to sulfate is also calculated both on the basis of millimoles per liter and parts per million. This ratio does not reach a constant but is continually decreasing as the concentration of sulfate increases.

TABLE II. SULFATE AND CARBONATE CONTENT OF SOLUTIONS OF SODIUM SULFATE HEATED IN CONTACT WITH SOLID CALCIUM CARBONATE

TEMP.	Na_2SO_4 ADDED	SO_4 AT END OF TEST	CO_3 AT END OF TEST	RATIO CO_3:SO_4	
° *C.*	*Millimoles per liter*			*Millimoles*	*P. p. m.*
182	0.25	0.19	0.55	2.90	1.81
	0.50	0.48	0.56	1.17	0.73
	1.25	1.40	0.73	0.52	0.32
	3.75	3.67	1.04	0.28	0.17
	12.50	12.2	1.30	0.10	0.06
	18.75	17.4	1.22	0.07	0.04
207	0.25	0.16	0.55	3.43	2.14
	0.50	0.39	0.65	1.67	1.05
	1.25	1.06	0.74	0.70	0.44
	3.75	3.74	0.82	0.22	0.14
	12.50	11.10	1.31	0.12	0.08
	18.75	18.36	1.44	0.08	0.05
244	0.50	0.46	0.66	1.43	0.89
	1.25	0.98	0.78	0.80	0.50
	3.75	2.85	1.74	0.61	0.38
	12.50	11.38	1.52	0.13	0.08
	18.75	17.23	1.60	0.09	0.06
282	3.75	2.96	1.47	0.49	0.30
	12.80	10.46	1.56	0.15	0.09
	18.75	17.02	3.94	0.23	0.14

Table II gives the result of equilibrium tests of the reaction:

$$CaCO_3 + Na_2SO_4 \leftrightarrows CaSO_4 + Na_2CO_3$$

Starting with calcium carbonate and adding sodium sulfate, the sulfate is all retained in the solution at the lower temperatures, and over 90 per cent remains even at the higher temperatures. This would indicate that the solids contained both calcium carbonate and calcium sulfate. In these tests the ratio of carbonate to sulfate was not constant but decreased with increase in the sulfate content. At the higher sulfate concentrations, however, the ratios agree fairly well with those reported in Table I.

The results of the tests run using solid calcium sulfate and a solution containing sodium chloride, sodium hydroxide, and sodium carbonate at the start are given in Table III. The sodium chloride was 2.5 millimoles per liter, and the sodium hydroxide 11.5 millimoles per liter at the start of all tests. These results are very interesting in that they show the carbonate to remain almost constant at all concentrations and at all temperatures, with the exception of 282° C. where the carbonate increases in the last two tests reported. This may be due to the coating of the calcium sulfate with calcium carbonate, where an excess of sodium carbonate was obtained. The remaining hydroxide varies to some extent and may be influenced by the variation in the amount of solid at the start since this was not constant. The almost constant value of the reported carbonate is undoubtedly due to the fact that in the presence of sodium hydroxide another equilibrium is established which is apparently independent of the one under consideration. Thus, if sodium carbonate is present in solution at these temperatures and corresponding steam pressures, the following reaction may take place:

$$2Na_2CO_3 + 2H_2O \leftrightarrows NaHCO_3 + 3NaOH + CO_2$$

When a sample of the solution is analyzed at room temperature, the carbonate is reported, whereas it undoubtedly existed as acid carbonate at the elevated temperature. The acid carbonate present at these higher temperatures would depend upon the partial pressure of the carbon dioxide and the hydroxide concentration. Being present as acid carbonate, no reaction would take place between it and the calcium sulfate. Under these conditions the reported carbonate, having been acid carbonate at the higher temperatures, would remain constant and be almost independent of the sulfate concentration.

TABLE III. SULFATE, CARBONATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM CARBONATE, HYDROXIDE, AND CHLORIDE, HEATED IN CONTACT WITH SOLID CALCIUM SULFATE

(NaCl added, 2.5 millimoles per liter in all tests; NaOH added, 11.5 millimoles per liter in all tests)

TEMP.	Na_2CO_3 ADDED	SO_4 AT END OF TEST	CO_3 AT END OF TEST	OH AT END OF TEST	RATIO $CO_3:SO_4$	
° C.	Millimoles per liter				Millimoles	P. p. m.
182	0.44	1.93	0.29	4.7	0.15	0.09
	0.44	1.71	0.43	5.9	0.25	0.16
	0.68	1.77	0.41	5.2	0.23	0.14
	0.68	2.25	0.44	4.5	0.19	0.12
	1.40	2.82	0.37	4.0	0.13	0.08
	3.80	4.88	0.33	3.2	0.068	0.04
	3.80	4.68	0.27	3.1	0.058	0.04
	12.00	11.70	0.40	3.9	0.034	0.02
	12.00	12.78	0.46	3.6	0.036	0.02
	18.00	22.40	0.78	2.6	0.035	0.02
207	0.44	1.45	0.42	5.3	0.29	0.18
	0.68	1.92	0.28	6.0	0.15	0.09
	1.40	2.80	0.59	5.5	0.21	0.13
	3.80	4.60	0.54	4.60	0.12	0.08
	12.00	12.30	0.41	2.88	0.033	0.02
	12.00	12.62	0.73	5.33	0.057	0.04
	18.00	18.05	0.54	2.9	0.030	0.02
244	0.44	1.35	0.31	3.3	0.23	0.15
	0.68	1.71	0.41	3.5	0.24	0.15
	1.40	2.50	0.94	4.0	0.38	0.24
	1.40	2.61	0.40	3.0	0.15	0.09
	3.60	4.44	1.05	2.15	0.24	0.15
	12.00	12.72	0.47	2.8	0.037	0.02
	12.00	12.82	0.66	2.7	0.051	0.03
	18.00	19.85	0.85	3.76	0.043	0.02
282	0.44	0.85	0.22	3.2	0.26	0.16
	0.44	0.88	0.46	4.0	0.52	0.32
	0.68	1.47	0.37	2.8	0.25	0.16
	1.40	2.20	0.27	2.6	0.12	0.08
	1.40	2.51	0.61	3.5	0.24	0.15
	3.80	4.83	0.57	2.88	0.12	0.08
	12.00	12.75	0.66	2.5	0.05	0.03
	18.00	19.30	3.78	4.0	0.19	0.12
	18.00	18.15	2.33	3.5	0.12	0.08

When a solid calcium carbonate is in contact with a solution of sodium hydroxide the solubility of calcium is less than 0.0 p. p. m., or 0.0 millimole per liter as shown in Table IV. The sodium hydroxide might react with the calcium carbonate to form calcium hydroxide and sodium bicarbonate. Again the sodium bicarbonate would be controlled by the partial pressure of the carbon dioxide. The results obtained in Table IV indicate that this is possible. The calcium solubility is 0.0 millimole; the hydroxide concentration has been reduced; and the carbonate varies to a large extent. The addition of sodium sulfate to this system should have no influence on the carbonate content if no calcium sulfate existed or was formed as a solid phase. However, if calcium sulfate was formed, then the carbonate should drop to the lower value reported in Table III. The fact that the sulfate remaining at the end is the same as that added, except in the very low concentrations where occlusion of the sodium sulfate by the calcium carbonate or reaction with the iron container would readily explain the small losses, would indicate that no calcium sulfate existed as a solid. Under these conditions the results reported in Table V should not check those in Table III. The solids in the tests reported in Table V were undoubtedly basic calcium carbonate as well as calcium hydroxide. If calcium hydroxide alone had been formed, there would have been a much larger increase in carbonate content. This indicates that a basic calcium carbonate was undoubtedly formed.

In order to predict the carbonate ion necessary to cause preferential precipitation of calcium carbonate, it would be necessary to determine the relative solubility of the calcium carbonate and calcium sulfate in the presence of the various ions and in solutions of ionic strengths similar to those encountered. Thus, in the presence of sodium hydroxide the solubility of calcium carbonate becomes less than 0.0 millimole, while the solubility of calcium sulfate is 0.90 millimole at 182° C. and 0.23 at 316° C. (*5*). Under these conditions the presence of a ratio of carbonate to sulfate at the temperatures under consideration of greater than approximately 0.01 (*3*) should cause precipitation of the carbonate in preference to the sulfate.

If a solution of sodium hydroxide is added to solid calcium carbonate and heated to the temperatures under consideration, the ratio of carbonate to sulfate will be infinite since the sulfate equals zero. There will be some acid carbonate in solution, and the equilibrium will be:

$$CaCO_3 + 2NaOH \rightleftharpoons Na_2CO_3 + Ca(OH)_2$$

If sodium sulfate is added in sufficient amount to make the ratio of carbonate to sulfate less than 0.01, calcium sulfate should precipitate. The carbonate content is high because of the reaction between the sodium hydroxide and the calcium carbonate. Before the ratio of carbonate to sulfate will be less than 0.01, it is necessary to have the sulfate at least 30 millimoles per liter (or 5200 parts per million sodium sulfate), which is much higher than the sulfate content of the tests reported and explains why no calcium sulfate was formed in the tests reported in Table V.

TABLE IV. CALCIUM, CARBONATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM HYDROXIDE HEATED IN CONTACT WITH SOLID CALCIUM CARBONATE

(CO_3 in solution without any solid phase, 0.20 millimole per liter)

TEMP.	OH ADDED	Ca AT END OF TEST	CO_3 AT END OF TEST	OH AT END OF TEST
° C.	Millimoles per liter			
182	11.5	0.0	0.86	5.1
	11.5	0.0	1.18	6.6
	11.5	0.0	0.94	5.7
	11.5	0.0	1.49	5.9
	11.5	0.0	1.00	6.3
	11.5	0.0	1.15	5.0
	11.5	0.0	0.17	5.4

TABLE V. SULFATE, CARBONATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM SULFATE, HYDROXIDE, AND CHLORIDE HEATED IN CONTACT WITH SOLID CALCIUM CARBONATE

(NaCl, 2.5 millimoles per liter in all tests; NaOH, 11.5 millimoles per liter in all tests)

TEMP.	SO_4 ADDED	SO_4 AT END OF TEST	CO_3 AT END OF TEST	OH AT END OF TEST	RATIO $CO_3:SO_4$	
° C.	Millimoles per liter				Millimoles	P. p. m.
182	0.25	0.32	0.62	6.6	1.94	1.21
	0.50	0.48	0.66	5.1	1.37	0.85
	0.50	0.48	0.96	6.0	2.00	1.25
	1.25	1.32	1.08	5.5	0.82	0.51
	1.25	1.28	1.09	6.5	0.85	0.53
	3.75	3.96	1.19	4.8	0.30	0.19
	3.75	3.86	1.00	6.5	0.26	0.16
	12.50	8.95	1.27	7.0	0.14	0.09
	18.75	18.8	1.28	5.8	0.068	0.04
207	0.25	0.12	0.20	5.9	1.67	1.04
	0.25	0.13	0.26	6.5	2.00	1.25
	0.50	0.16	0.18	4.9	1.12	0.70
	1.25	0.18	0.61	6.2	3.38	2.10
	1.25	1.40	1.09	5.8	0.78	0.49
	3.75	3.70	0.70	6.0	0.19	0.12
	12.50	13.0	0.70	5.0	0.054	0.03
	18.75	18.65	1.21	6.5	0.065	0.04
244	0.25	0.12	0.55	5.7	4.58	2.86
	0.25	0.15	0.41	6.5	2.74	1.71
	0.50	0.18	0.32	7.2	1.78	1.11
	1.25	1.85	1.58	4.8	0.85	0.53
	3.75	4.75	0.94	5.5	0.20	0.12
	12.5	13.5	0.38	6.3	0.028	0.02
	18.75	19.4	2.24	6.0	0.12	0.08
282	0.25	0.09	0.86	4.5	9.55	5.95
	0.25	0.11	0.82	4.0	7.45	4.65
	0.50	0.13	0.70	3.7	5.40	3.36
	1.25	1.96	1.93	1.1	0.98	0.61
	3.75	2.81	1.12	2.5	0.40	0.25
	12.50	13.8	2.30	2.8	0.16	0.10
	18.75	21.4	2.78	3.2	0.13	0.08
	18.75	19.6	1.33	2.5	0.068	0.04

The results in Table III show that the reported carbonate is independent of the sulfate concentration up to at least 22 millimoles per liter of sulfate. Thus, if solid calcium sulfate is in contact with a solution containing sodium hydroxide, the introduction of sodium carbonate into the solution forms carbonate ions which, because of the low sulfate content from the calcium sulfate solubility, give a carbonate concentration sufficient to precipitate calcium carbonate, which reduces the carbonate. As long as solid calcium sulfate exists, all of the sodium carbonate added will react to precipitate calcium carbonate and form soluble sodium sulfate until the sulfate concentration becomes high enough to require an appreciable carbonate increase. However, this concentration is higher than 22 millimoles of sulfate (about 3000 p. p. m. sodium sulfate). Since the carbonate reported is the total of the acid carbonate and carbonate existing at the higher temperature, and since there is no marked increase in the reported carbonate even with the sulfonate equal to 22 millimoles per liter, the carbonate existing at the higher temperatures must be low in respect to the acid carbonate.

The data reported in Tables III to V indicate that, in order to maintain a stable phase of calcium carbonate, only a small amount of sodium carbonate is necessary. Thus, with the sulfate as high as 22.40 millimoles per liter (2150 p. p. m.), a carbonate content as low as 0.78 millimole per liter (33 p. p. m.) should prevent the formation of calcium sulfate.

The solubility of calcium carbonate, being zero for all practical cases, gives further insight into the question of scale formation and prevention in steam boilers. Carbonate scale forms readily in feed water heaters and hot water lines, owing to the breakdown of the calcium bicarbonate to form the more insoluble calcium carbonate. Such precipitation takes place rapidly and the precipitate forms on the portions being heated, as well as on the cooler portions. However, with the normal carbonate entering the boiler, which contains free hydroxide in the majority of instances, the solubility is reduced to zero, and the solid phase forms evenly throughout the boiler irrespective of the temperatures. If at any time the hydroxide and carbonate alkalinity disappear and the sulfate increases, then sulfate scale is formed. The solubility of the calcium sulfate is appreciable. Consequently, it is deposited at the heating surface. Small amounts of sodium carbonate in the presence of hydroxide are sufficient to prevent formation of the solid-phase calcium sulfate, even at a temperature as high as 282° C.

A feed water which contains a small amount of sodium carbonate in addition to the theoretical amount required to react with the calcium sulfate present will form sodium hydroxide in the boiler. However, in the average boiler not over 90 per cent of the sodium carbonate decomposes to form sodium hydroxide, and 10 per cent remains in the boiler. Thus, if the total alkalinity (expressed as sodium carbonate) of a boiler water becomes 500 p. p. m., there will be 50 p. p. m. of sodium carbonate remaining in the boiler (when analyzed at room temperature), or approximately 0.5 millimole of carbonate, and calcium sulfate scale should be prevented even in a boiler operating at 1000 pounds steam pressure.

The direct interpretation of these solubility data in terms of boiler operation should be made conservatively. These are equilibrium data, and, until they are correlated with data from actual boiler operation, no specific conclusions should be drawn. There is a possibility that the rate of steam generation at the heating surface may have more to do with the rate of scale formation than the question of solubility, and, furthermore, it is possible that the equilibrium conditions may not be maintained in the various portions of an operating boiler.

CONCLUSIONS

1. At temperatures between 182° and 282° C. in the reaction,

$$CaSO_4 + Na_2CO_3 \rightleftarrows CaCO_3 + Na_2SO_4$$

the presence of as low a concentration as 1.5 millimoles per liter (90 p. p. m.) of carbonate will force the reaction to the right, even when the sulfate concentration is around 18.0 millimoles per liter (1728 p. p. m.).

2. In the following reaction at temperatures between 182° and 282° C.,

$$CaSO_4 + Na_2CO_3 \rightleftarrows CaCO_3 + Na_2SO_4$$

in the presence of sodium hydroxide (5.0 millimoles per liter) and sodium chloride (2.5 millimoles per liter), the presence of as low a concentration as 0.5 millimole per liter (30 p. p. m.) of carbonate will force the reaction to the right, even when the sulfate concentration is around 18.0 millimoles per liter (1728 p. p. m.).

3. The ratio of carbonate to sulfate is not a constant for the reactions studied owing to the fact that the carbonate measured at room temperatures undoubtedly exists to a large extent as acid carbonate at the higher temperatures.

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CRUDE BARITE INDUSTRY. In 1931 the crude barite industry in the United States was characterized by declines in total mine production, shipments, and prices, and an increase in total stocks at the mines. The total quantity of crude barite mined and sold in the United States, which had been annually more than 200,000 tons for the past six years (1925–30, inclusive), fell to about 174,500 tons in 1931, or 26 per cent below the corresponding figure for 1930. On the other hand, total imports of crude or unmanufactured barite for consumption in the United States in 1931 increased 40.2 per cent in quantity as compared with 1930. With the exception of 1929, imports in 1931 were higher than for any year for which imports of unmanufactured barite have been recorded—namely, 1884–1931, inclusive.

The total value of crude barite mined and sold in the United States in 1931, which had exceeded $1,000,000 annually for the nine-year period 1922–30, inclusive, dropped in 1931 to approximately $994,600, or about 35 per cent below the total value reported for 1930. The total average value per ton was $5.70, or 85 cents a ton below that of 1930.

With one exception (1929), stocks of crude barite at the mines have steadily increased since 1923, and reached a maximum in 1931.

Missouri held first place, as usual, in order of output; Georgia ranked second, California third, and Tennessee fourth. Washington County, Mo., produced about 70 per cent of the total shipments of crude barite from Missouri in 1931, and the combined output of Georgia and Missouri constituted more than 75 per cent of the total output of crude barite in the United States during the year.

The commodity is largely utilized in this country by the manufacturers of barium products and chemicals and is exported by them in manufactured form.

Distribution of Ether Extractive in Turpentined Slash-Pine Trees

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A study of the ether extractive in young turpentined slash pine reveals that outside the wounded area there is no material difference in the amount or in the composition of the extractive from that in unturpentined trees. The uniformity of the variation in the amount and nature of the extractive is not so striking in the turpentined as in the unturpentined trees. The extractive in back of the face may vary considerably both in quantity and in character.

PREVIOUS studies at this laboratory on young unturpentined slash pine have demonstrated a clearly defined variation in the ether extractive content and in the nature of this extractive with position in cross section of the trunk (*3*). The present paper describes the distribution of the ether extractive in a similar number of turpentined slash pines that were logged from the same stands and at the same time as the unturpentined trees. Both the turpentined and the unturpentined trees received the same treatment. A study of the data from the two groups will, therefore, give a comparison of the extractive present in turpentined and unturpentined slash-pine trees varying in age from 11 to 35 years. The term "extractive" as used in this paper refers to the ether-soluble material present in the wood and is distinct from the oleoresin that is formed by a wounded tree.

Our knowledge of the source of the oleoresin in pine trees has been developed largely by microscopical studies (*1*). Oleoresin exudes from the parenchyma cells in the sapwood. It appears that these resin-yielding cells remain alive longer than the other wood cells or fibers and function actively until approximately that time when the inner rings of sapwood change into heartwood, which is the dead part of the tree at the center of the trunk. Wounding stimulates the activities of the living parenchyma and also increases their formation in the new wood formed subsequent to the wounding. The oleoresinous exudation is not the sap of the tree, but is a secretion of materials not used in the production of wood, leaves, or bark.

It has been known that turpentining has but little effect on the extractive present in the heartwood. From an investigation of the extractive present in the heartwood of long-leaf pine, Gomberg (*2*) concluded that there is as much difference between unturpentined as between turpentined trees.

Extractive Present in Turpentined Slash Pine

The results of the investigation of the distribution of the ether extractive in young turpentined slash pine are presented in Table I. The extractive was determined for the individual trees rather than for a composite sample from several trees in order to determine the extent of variation among the trees. As a result of this, a distinction can be made between rapid-growing and slow-growing trees, and usually between trees containing a high proportion of springwood and those containing a high proportion of summerwood. A discussion of the results can be divided into two parts: (1) the area outside the influence of the face, and (2) the area within the influence of the face.

Area outside Influence of Face. The distribution, quantity, and nature of extractive in young turpentined trees in that portion of the trunk not in the vicinity of the face were unaffected by the turpentining operations. In all the trees there was an increase of extractive from the bark to the center of the trunk. The outer rings showed very little variation in the amount of extractive from top to bottom. At the center of the trunk there was an increase of extractive with decrease in height until the 4-foot height was reached. The 4-foot height, generally, included the face. In brief, the amount of extractive increased with the age of the sapwood. The chemical constants for the extractive from turpentined trees outside the influence of the face did not differ materially from those of the extractive from unturpentined trees. The ratio of volatile oil to nonvolatile extractive agreed quite well for the two classes of trees. This ratio is, however, less than for oleoresin.

Area within Influence of Face. The quantity and character of the extractive present in the vicinity of the face were influenced by the conditions to which the tree had been subjected. In the younger trees (15 to 16 years) which had been turpentined but a short period before they were felled, the nature and amount of the extractive behind the face were not markedly changed. In the older trees (24 to 35 years) which have long faces the wood behind the face was often heavily impregnated with resin. This may have been caused by the prolonged turpentining or by fires (Figure 1). The material in this area usually had a comparatively high acid number and was low in saponifiable matter, and the unsaponifiable content was lower than for the extractive

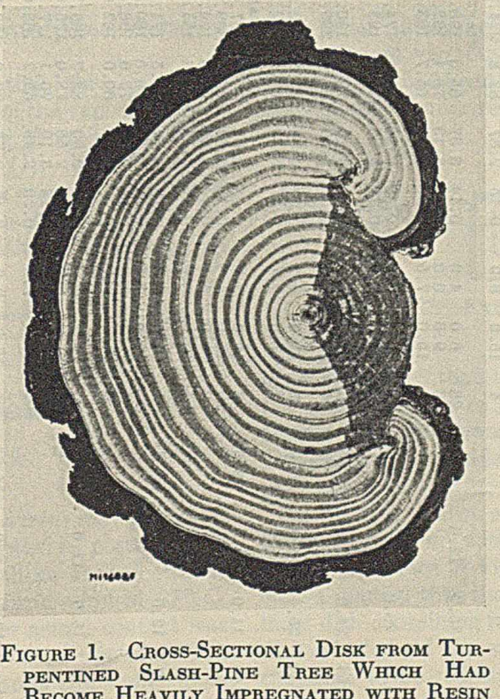

Figure 1. Cross-Sectional Disk from Turpentined Slash-Pine Tree Which Had Become Heavily Impregnated with Resin in Back of Face

TABLE I. ETHER EXTRACTIVE FROM TURPENTINED SLASH PINE

(Calculations on weight of oven-dry extracted wood)

				CROSS-SECTIONAL DISK			OUTER RINGS					INTERMEDIATE RINGS					CENTER					BEHIND FACE				
TREE	CROWN Length	CROWN Width	TOTAL HEIGHT	Height above ground	Total ring count	Diam. inside bark	Volatile oil	Ether extract	Acid no.	Saponification no.	Unsaponifiable residue	Volatile oil	Ether extract	Acid no.	Saponification no.	Unsaponifiable residue	Volatile oil	Ether extract	Acid no.	Saponification no.	Unsaponifiable residue	Volatile oil	Ether extract	Acid no.	Saponification no.	Unsaponifiable residue
	Feet	*Feet*	*Feet*	*Feet*		*Inches*	%	%			%	%	%			%	%	%			%	%	%			%
STAND 1, WIDE SPACING, RAPID GROWTH, 16 YEARS OLD																										
131	29.0	16.0	43.0	24	9.0	4.5	0.26	3.30	55.8	197.5	8.4	..	..	..	...	..	0.33	7.66	45.7	194.5	5.9	...	...	...	...	...
				12	13.0	6.8	0.20	3.29	48.2	186.2	8.4	0.24	5.48	43.1	200.1	5.8	0.43	10.05	56.6	196.0	14.8	...	...	...	...	...
				4	15.0	9.0	0.21	2.23	86.2	299.5	16.3	0.24	5.88	35.6	260.0	6.1	0.28	6.92	47.5	198.5	5.8	0.22	4.54	47.8	205.0	5.5
132	29.0	14.0	47.0	24	10.0	4.0	0.20	2.71	62.1	192.0	16.1	..	..	..	...	..	0.29	7.50	51.2	176.0	16.2	...	...	...	...	...
				12	13.0	6.5	0.10	2.29	80.2	191.9	14.9	0.16	4.20	68.9	187.0	11.7	0.30	11.90	112.5	149.0	23.8	...	...	...	...	...
				4	16.0	8.5	0.10	3.00	83.0	189.0	11.5	0.15	4.80	83.4	193.0	10.6	0.14	4.25	62.8	210.0	12.5	0.15	3.37	93.5	202.0	11.9
133	40.0	14.0	58.0	24	12.0	6.0	Trace	2.09	46.9	163.5	12.6	Trace	3.27	37.5	183.4	9.9	0.17	5.37	61.7	188.0	11.9	...	...	...	...	...
				12	13.0	7.2	0.20	2.87	60.3	189.3	8.9	0.10	3.92	55.6	195.2	8.9	0.31	6.96	71.0	201.0	12.1	...	...	...	...	...
				4	16.0	9.2	0.14	3.36	79.2	186.0	7.2	0.20	3.24	50.5	192.3	6.9	0.40	5.27	57.1	197.3	10.6	0.32	3.62	60.9	198.3	11.5
Av.	32.7	14.7	49.3	24	10.3	4.8	0.15	2.70	54.9	184.3	12.4	..	..	..	...	..	0.26	6.84	52.9	186.1	11.3	...	...	...	...	...
				12	13.0	6.8	0.17	2.82	62.9	182.5	10.7	0.17	4.57	49.8	197.4	8.8	0.35	9.64	80.0	182.0	16.9	...	...	...	...	...
				4	15.6	8.9	0.15	2.87	82.8	224.8	11.7	0.20	4.64	58.5	215.1	7.8	0.27	5.45	55.8	201.9	10.1	0.23	3.84	67.4	201.7	9.6
STAND 2, WIDE SPACING, RAPID GROWTH, 15 TO 24 YEARS OLD																										
152	25.0	12.0	42.0	28	6.0	4.2	0.14	3.37	65.3	198.1	11.3	..	..	..	...	..	0.17	6.92	54.2	194.0	8.7	...	...	...	...	...
				16	9.0	6.0	0.13	2.13	78.1	192.0	13.7	0.17	3.72	60.0	171.1	10.2	0.21	7.28	53.1	189.0	8.7	...	...	...	...	...
				4	15.0	7.5	0.13	2.53	65.7	183.7	12.2	0.15	3.41	52.3	182.8	10.2	0.20	4.90	53.8	181.7	9.7	Face was below 4-foot height				
153	28.0	16.0	38.0	20	8.0	5.5	0.16	2.86	65.1	174.5	11.6	0.22	4.05	53.6	174.5	9.1	0.33	8.02	52.5	191.5	6.2	...	...	...	...	...
				5	13.0	8.0	0.19	3.23	113.3	198.0	9.8	0.25	4.15	53.0	188.5	7.8	0.59	11.10	85.0	240.0	16.7	0.35	5.25	192.5	280.0	10.7
154	24.0	18.0	41.0	16	17.0	7.0	0.20	3.19	79.0	180.0	11.9	0.21	3.64	69.1	182.0	13.5	0.29	8.36	91.5	290.0	18.1	...	...	...	...	...
				4	23.0	10.5	0.18	3.59	101.2	225.0	16.0	0.22	5.14	61.4	164.5	11.3	..	Lightwood		...	..	9.1	76.0	157.0	160.5	8.0
Av.	25.6	15.3	40.3	17	11.3	6.2	0.17	2.72	74.1	182.2	12.4	0.20	3.88	60.9	175.9	10.9	0.28	7.89	65.7	223.5	11.0	...	...	...	...	...
				4	17.0	8.7	0.17	3.12	93.4	202.2	12.7	0.21	4.23	55.6	178.6	9.8	0.40	8.00	69.4	210.8	13.2	4.73	40.62	174.6	220.3	9.4
STAND 3, CLOSE SPACING, SLOW GROWTH, 25 TO 30 YEARS OLD																										
146	11.0	8.0	52.0	32	18.0	3.7	0.23	2.96	75.4	187.6	12.2	..	..	..	...	..	0.27	3.68	85.8	183.5	12.2	...	...	...	...	...
				20	23.0	4.6	0.15	2.64	82.4	209.0	11.8	0.28	3.06	75.5	197.0	13.7	0.38	4.17	102.0	176.0	22.1	...	...	...	...	...
				8	25.0	6.0	0.14	3.38	82.5	174.2	13.9	0.16	3.50	99.4	205.0	13.3	..	...	...	...	..	12.6	67.8	156.9	164.7	6.7
				4	26.0	6.5	0.16	3.15	76.4	181.0	9.0	0.31	4.51	48.0	182.0	9.3	..	Lightwood		...	..	6.1	52.2	78.0	85.0	5.9
147	12.0	8.0	58.0	32	19.0	4.0	0.13	2.63	58.5	171.5	11.9	..	..	..	...	..	0.24	5.61	81.1	185.8	22.8	...	...	...	...	...
				20	22.0	4.7	0.08	2.39	56.6	180.5	15.6	0.08	3.36	53.1	191.0	13.1	0.48	9.27	111.0	170.0	28.9	...	...	...	...	...
				8	27.0	5.9	0.15	2.38	72.6	196.5	10.1	0.10	4.45	65.5	184.0	8.0	..	...	...	...	..	5.04	38.9	143.0	182.5	7.3
				4	19.0	7.0	..	2.16	60.0	182.0	11.7	0.17	3.99	55.0	175.6	7.8	0.70	19.0	136.0	226.0	19.0	6.27	50.3	157.4	162.4	7.8
148	15.0	11.0	54.0	32	19.0	4.0	0.16	2.60	82.2	186.7	13.8	..	..	..	...	..	0.32	4.93	125.8	150.5	24.7	...	...	...	...	...
				20	21.0	5.0	0.11	2.50	78.0	175.0	16.6	0.14	2.69	80.6	179.0	16.2	0.26	6.96	131.5	173.6	27.9	...	...	...	...	...
				8	23.0	6.0	0.18	3.10	79.1	177.3	10.6	0.11	3.01	81.3	182.0	8.7	..	...	...	...	..	5.20	46.3	147.2	173.0	6.5
				4	27.0	7.3	0.20	2.45	65.2	183.0	10.6	0.26	3.76	78.6	176.4	8.0	..	Lightwood		...	..	7.57	71.0	149.0	154.0	6.3
Av.	12.7	9.0	54.7	32	18.7	3.9	0.17	2.73	72.0	188.6	12.6	..	..	..	...	..	0.28	4.74	97.6	173.2	19.9	...	...	...	...	...
				20	22.0	4.7	0.11	2.51	72.3	188.0	14.7	0.17	3.04	69.7	189.0	14.3	0.37	6.80	114.8	173.2	26.3	...	...	...	...	...
				8	25.0	5.9	0.16	2.95	78.1	182.7	11.5	0.12	3.65	82.1	190.0	10.0	..	...	...	...	..	7.61	51.0	149.0	173.3	6.8
				4	27.3	6.9	0.18	2.59	67.2	182.0	10.4	0.25	4.09	60.5	178.0	8.4	..	...	...	...	..	6.65	57.8	127.1	133.8	6.6
STAND 4, CLOSE SPACING, SLOW GROWTH, 34 TO 35 YEARS OLD																										
32	15.0	13.0	57.0	36	17.0	4.3	0.08	2.60	45.7	215.0	8.4	..	..	..	...	..	0.21	4.61	88.8	166.2	11.8	...	...	...	...	...
				24	21.0	5.5	0.20	2.52	76.8	192.5	12.9	0.27	3.08	55.0	180.0	12.6	0.66	6.38	103.0	201.0	14.0	...	...	...	...	...
				12	26.0	6.2	0.13	2.66	73.8	204.0	12.5	0.15	3.52	53.6	173.1	9.7	1.21	11.45	136.5	167.5	15.2	...	...	...	...	...
				4	34.0	7.3	0.12	3.38	84.2	175.1	9.6	0.16	3.75	58.2	182.3	8.1	1.03	13.30	139.5	178.5	13.9	0.24	4.09	64.0	188.0	10.8
46	13.0	7.0	57.0	36	19.0	4.1	0.09	2.24	68.3	187.1	13.7	..	..	..	...	..	0.23	4.19	86.9	182.5	15.7	...	...	...	...	...
				24	22.0	5.0	0.10	1.85	73.2	196.5	11.1	0.18	2.69	63.6	195.0	14.8	0.24	5.71	87.6	183.3	15.9	...	...	...	...	...
				16	25.0	6.1	0.08	1.97	42.0	181.5	14.6	0.08	2.48	51.5	191.5	6.7	0.54	7.69	92.6	136.0	20.3	...	...	...	...	...
				8	29.0	6.6	0.08	2.10	55.4	199.0	12.1	0.08	3.74	58.3	182.6	9.7	1.00	15.20	116.0	169.5	9.5	Trace	1.83	64.4	195.0	12.2[a]
				4	34.0	7.0	0.12	2.47	43.7	173.3	7.6	0.18	3.55	64.2	182.0	7.1	0.26	4.59	76.0	178.0	14.0	8.60	57.80	158.0	173.0	9.4
47	13.0	10.0	60.0	36	17.0	3.4	0.08	1.88	58.9	188.2	12.4	..	..	..	...	..	0.16	3.56	87.1	196.0	14.9	...	...	...	...	...
				24	21.0	5.3	0.10	1.83	61.5	197.8	10.5	0.13	2.67	49.5	180.5	9.1	0.27	4.73	95.6	202.0	15.0	...	...	...	...	...
				16	24.0	6.1	0.16	2.13	47.3	193.4	12.7	0.21	2.31	50.9	187.2	7.1	0.31	5.90	98.2	135.5	18.6	...	...	...	...	...
				4	33.0	7.2	0.10	2.97	91.3	177.0	13.4	0.13	2.35	71.5	177.3	10.4	..	Decayed		...	...	0.08	7.31	132.5	133.0	9.4
Av.	13.7	10.0	58.0	36	17.6	3.9	0.08	2.27	57.7	176.9	11.5	..	..	..	...	..	0.20	4.09	87.6	181.6	14.1	...	...	...	...	...
				24	21.7	5.3	0.13	2.08	70.5	195.6	11.5	0.19	2.81	56.0	185.1	12.1	0.39	5.61	95.4	195.4	14.6	...	...	...	...	...
				15	25.0	6.1	0.12	2.25	54.3	192.9	13.2	0.15	2.77	52.0	183.9	7.8	0.69	8.34	109.1	146.3	18.0	...	...	...	...	...
				4	33.7	7.2	0.11	2.94	73.7	175.1	10.2	0.16	3.21	62.6	180.5	8.5	0.64	8.94	107.7	178.3	14.0	2.97	23.06	118.1	164.9	9.9

[a] One foot above a 7-foot face.

outside the area. The extractive near the center of the trunk behind the face of the younger trees, and also of tree 46, had apparently flowed out to the wound, as was evidenced by a lower extractive content at the center of the trunk at this lower height than at the center of the trunk at a higher level (a condition which was not found in the unturpentined trees).

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Chemical Nature of Germicidal Vapors Emanating from Irradiated Oils

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In industry, especially in the fields of food and textile technology, there are many situations where it is needful to maintain surfaces free from the changes wrought by growing microorganisms and at the same time to avoid poisonous or corrosive gases or contact with any germicidal liquid or solid. For such problems involving antisepsis in inclosed spaces, the use of irradiated oils, the vapors from which are composed in part at least of volatile peroxides of definite germicidal potency, may offer a rational solution.

In this paper the theory of Wrenn that secondary radiations are involved is disproved, and the authors show that the phenomenon which they have described and substantiated is a continuing one.

These laboratories have noted that organic peroxides formed by the irradiation of certain substances with ultra-violet light in the presence of oxygen exert a germicidal effect upon bacteria with which they are brought in contact (*3*). It has also been reported in the literature that invisible emanations from irradiated oils exert a similar germicidal effect on bacteria (*7*). This effect has been variously attributed to a secondary radiation emitted from these oils in the dark (*4*). In the present paper, evidence is presented to show the fallacy of such an explanation and to support the view that this germicidal effect is due to a gaseous emanation composed partly of volatile peroxides rather than to a secondary radiation.

Preliminary experiments substantiating the results of Wrenn relating to the germicidal effects of the vapors emanating from irradiated oils, and extending them with a large number of oils are reported elsewhere (*1*). In the present study, 5-cc. portions of various oils were placed in open Petri dishes 18 inches (45.7 cm.) below a 6-inch (15.2 cm.) horizontal Uviarc lamp for one hour without agitation. In similar dishes, agar smear cultures of *S. aureus* were prepared, inverted over the irradiated oils, and sealed in position with adhesive tape, the distance between culture and oil surface being about 2 cm. (Figure 1). After incubation at 37° C. for 24 hours, in such a position that no actual contact was possible between oil and culture, there was no sign of growth on the inverted agar plates. The controls employing unirradiated oils usually showed the expected abundant growth on the agar surface, whereas controls with no oil always showed abundant growth. Upon removal of the oil and substitution of an empty dish, further incubation developed no growth on the smears, showing that the bacteria were killed and not merely inhibited from developing.

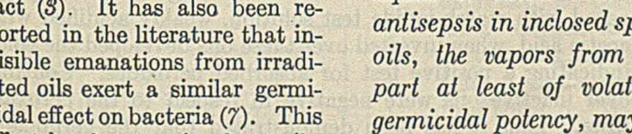

Figure 1. Standard Culture Chamber

To prove that this germicidal effect is not due to a secondary radiation, as proposed by Wrenn and by Ried, the experiments were repeated with the insertion of a quartz plate, 4 mm. thick, between the irradiated oil and the agar smear in each of several pairs of Petri dishes. This quartz plate had a high percentage transmission of ultra-violet down to and including the region near 2000 Å. After incubation, as before, vigorous growth on the agar showed that no germicidal effect had been transferred from oil to culture. Wrenn has reported similar results with interposed quartz plate, but his assumption, that the germicidal effect in the absence of the quartz is due to ultra-violet radiation of wave length shorter than that transmitted by quartz, is regarded by the writers as unjustifiable in view of the experimental evidence presented below.

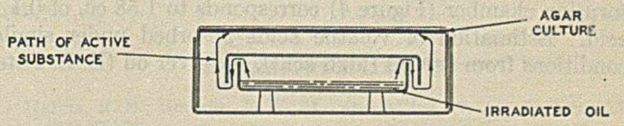

Figure 2. Experimental Culture Chamber

In another set of experiments, a series of shallow glass dishes was set up with one inside the other alternately inverted, as shown in Figure 2, and separated by glass rods in such a manner that there was free air passage from the innermost dish containing irradiated oil to the outermost inverted dish which held the smeared agar, but with no chance for radiation to be reflected from oil to agar. After the usual incubation, no growth of bacteria was visible, demonstrating that the germicidal effect had been transmitted from oil to culture over a tortuous path. From this series of tests it may be concluded that the germicidal effect is due not to a secondary radiation, as formerly thought, but to a substance or substances of gaseous nature.

TESTS FOR SOURCE OF GERMICIDAL EFFECT

That this germicidal gaseous substance is not a volatile aldehyde has been shown in the following manner: By employing the apparatus shown in Figure 3, the gaseous substances evolved from irradiated oils were absorbed into a fuchsin test solution which failed to develop the characteristic color even after 24 hours of standing at room temperature, whereas controls containing small quantities of volatile aldehydes produced the color in a relatively short period of time. It may be concluded, therefore, that the germicidal substance is not a volatile aldehyde.

Vogel's recent claim (*6*) that the cause of photoactivity observed with irradiated oils is due to butyric acid produced by the autoxidation of these oils, suggested that the possibility of a relation between butyric acid content of irradiated oils and the germicidal effect of their vapors should be investigated. Various concentrations of this acid, in mineral oil, were tested under agar cultures to determine whether vapors of this acid might be responsible for the germicidal effect. Concentrations as high as 1 per cent of butyric acid, in mineral oil, failed to produce the germicidal effect.

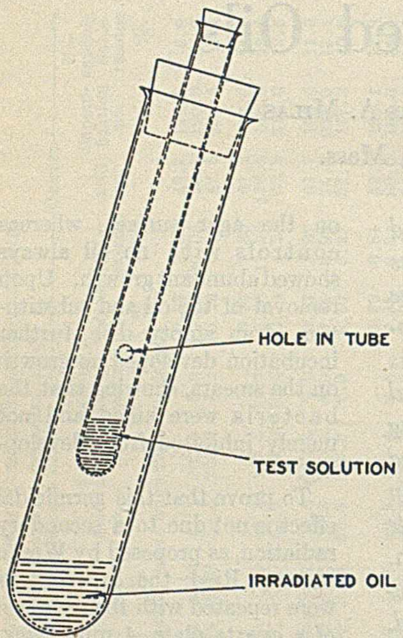

FIGURE 3. ABSORPTION TUBES FOR TESTING THE GASEOUS EMANATIONS FROM IRRADIATED OILS

From 5 cc. of the above solution, the volatile acids absorbed into 0.1 *N* barium hydroxide at 37° C. in 24 hours in an absorption chamber (Figure 4) corresponds to 1.58 cc. of 0.1 *N* acid. Estimation of volatile acids absorbed under similar conditions from fish oil (high acid), cod-liver oil (E. L. Patch Company), perilla oil, and fish oil (L. C. P.), all previously shown to be germicidally potent, gave values of 0.08 cc., 0.16 cc., 0.16 cc., and 0.12 cc. of 0.1 *N* acid, respectively. These results demonstrate conclusively that the germicidal effect of the vapors from these oils cannot be due to butyric acid, since the total amount of acid absorbed from the vapors of these germicidal oils is in each case less than the amount of butyric acid absorbed from a system which was not germicidal.

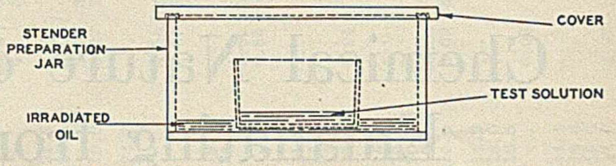

FIGURE 4. ABSORPTION CHAMBER FOR ESTIMATION OF VOLATILE CONSTITUENTS OF EMANATIONS FROM IRRADIATED OILS

Qualitative tests were undertaken to determine the presence of volatile peroxides emanating from the irradiated oils because of the fact that one of the authors had already isolated peroxides from irradiated ethers (*2*) and because of the report of evolution of hydrogen peroxide from oils exposed to light (*5*). In the present tests the vapors emanating from irradiated oils were absorbed into an acidified starch-iodide solution or into an aqueous solution of *p*-amidodimethylaniline hydrochloride (Figure 3) and both reactions were positive, showing the presence of peroxides. In addition, agar plates impregnated with starch-iodide test solution, weakly acidified with acetic acid, when inverted over these oils developed the color indicating a positive test for absorbed peroxides. Controls over inactive oils were negative in respect to the peroxide tests. Thus it has been demonstrated that the germicidal vapors are composed in part of volatile peroxides.

In order to eliminate ozone as a possible contributing factor in this germicidal effect, an inquiry into the nature of the induced changes in irradiated oils was initiated. Samples of irradiated cod-liver oil and cottonseed oil were degassed with shaking under a vacuum of about 2 mm. Agar plates seeded with *S. aureus* were exposed to the degassed oils which showed that considerable germicidal vapor effect was still present. The tests indicate that free ozone, either in vapor or in dissolved form, is not a factor in this germicidal effect. Other irradiated oils have been tested after storage for 9 months at room temperature, and there has been but slight diminution of their germicidal vapor potency. These tests indicate that the effect is not transitory, and suggest that peroxide formation and subsequent evolution continues in the irradiated oils for a length of time as yet undetermined.

TABLE I. COMPARISON OF QUANTITATIVE ESTIMATION OF PEROXIDES IN OILS BEFORE AND AFTER IRRADIATION AND GERMICIDAL EFFECTS OF THEIR VAPORS

	UNIRRADIATED		BEFORE IRRADIATION		AFTER 1 HOUR OF IRRADIATION		INCREASE OF PEROXIDIC OXYGEN
OIL	Acid value	Iodine number (Hanus)	Peroxidic oxygen	Bacterial smear over oil	Peroxidic oxygen	Bacterial smear over oil	
	Mg. KOH/gram oil	*Grams I_2/100 grams oil*	*Grams/100 grams oil × 10^3*		*Grams/100 grams oil × 10^3*		*Grams/100 grams oil × 10^3*
Cod	16.15	161.0	4.95	Growth	23.90	No growth	18.95
Cod-liver (Patch)	1.17	152.4	2.38	Growth	40.30	No growth	37.92
Cod-liver (technical)	1.64	156.0	7.35	Growth	24.40	No growth	17.05
Elastoil D	0.80	114.2	2.49	Growth	7.31	No growth	4.82
Elastoil R	1.02	176.2	4.02	Growth	22.30	No growth	17.05
Fish (high acid)	65.50	170.5	2.43	Doubtful	3.75	No growth	1.32
Fish (L. C. P.)	1.12	181.4	0.37	Growth	11.00	No growth	10.63
Linseed	2.36	165.1	8.69	Growth	12.41	No growth	3.72
Mustard-seed	1.08	103.4	4.79	Growth	4.95	Growth	0.16
Perilla	0.80	201.8	3.71	Growth	8.35	No growth	4.64
Poppy-seed	4.26	137.0	4.92	Growth	5.89	Growth	0.97
Salmon	5.83	159.0	2.47	Growth	19.80	No growth	17.33
Seal (sweet pale ref.)	0.68	145.0	3.72	No growth	30.90	No growth	27.18
Sunflower seed	0.80	127.5	3.75	Growth	4.21	Growth	0.46
Tuna-fish	63.40	167.8	1.23	Growth	21.10	No growth	19.87
Tung	2.47	165.0	0.97	Growth	1.31	Growth	0.34
Walnut	8.68	133.4	3.74	Growth	14.62	No growth	10.88

Relation between Peroxidic Content and Germicidal Effect

In order to determine the relation between peroxide content of irradiated oils and the germicidal effect of their vapors, quantitative estimation of peroxidic oxygen in the oils was made by the method of Milas (*2*) with the exception that the samples and controls were kept for 30 hours in the dark at room temperature before titrating with standard thiosulfate solution. These results are presented in Table I, in which there is included for comparison the effect of each oil on the growth of bacteria suspended above it for 24 hours. In order that each oil may be definitely identified, its acid value and iodine number were determined before irradiation, and these are given in columns 1 and 2 of the table.

An examination of the data in the table shows that neither the initial nor the final peroxidic oxygen content of the oils seems to correlate with the germicidal effect of the vapors emanating from them. However, a definite correlation is indicated between the increase in peroxidic oxygen content during irradiation and the germicidal vapor activity.

Because of the above apparent correlation, a quantitative estimation was made of the peroxides in the vapors emanating from certain of these oils by placing 5-cc. portions of each of several oils, previously irradiated for a definite length of time, in Stender jars inclosing smaller uncovered glass dishes containing acidified potassium iodide solution for the absorption of vapors (Figure 4). After holding the sealed chambers for 24 hours at 25° C., the test solution was titrated with standard thiosulfate solution. The amounts of absorbed peroxides, expressed as peroxidic oxygen, are plotted against time of irradiation in Figure 5. Inspection of the curves in Figure 5 indicates that the amount of peroxide absorbed from the vapors emanating from irradiated oils seems to depend upon the nature of each oil and the length of time of irradiation.

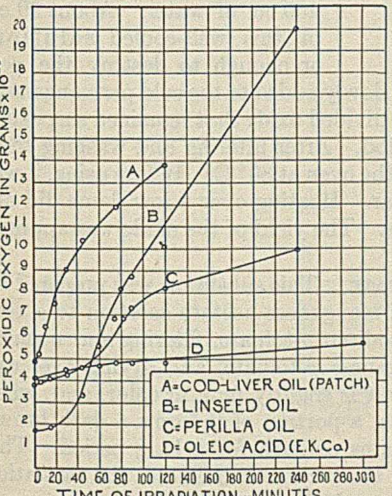

Figure 5. Total Peroxidic Oxygen Absorbed in 24 Hours from Oils Irradiated for Different Periods

The total amount of peroxides given off at different periods of time from oils irradiated for a definite length of time is shown by the successive estimation of these peroxides absorbed by the test solution contained in the inner dishes (Figure 4). Because of the development of a blue color in the test solution between the conclusion of one estimation and the beginning of the subsequent one, it was found necessary to apply a correction factor which was determined in control chambers containing no oil. The corrected values thus obtained are plotted against time of standing and are shown in Figure 6.

The times of irradiation of the selected oils reported in Figure 6 are based upon experiments reported elsewhere (*1*) and represent the minimum periods of irradiation under standard conditions, as already described, for the production of maximum germicidal vapor effect.

The portion of the mercury arc spectrum which is most active in inducing in oils the changes necessary for the evolution of germicidal vapors is indicated by a series of preliminary tests employing a diversity of filters each adjusted so that the total energy at wave length 3130 Å. over a selected period is equal to the total energy of this line in the bare arc spectrum for 15 minutes under the above mentioned experimental conditions. The degree of activation of the oils under such controlled conditions is essentially the same, indicating that the region in the neighborhood of 3130 Å. seems especially important in this regard.

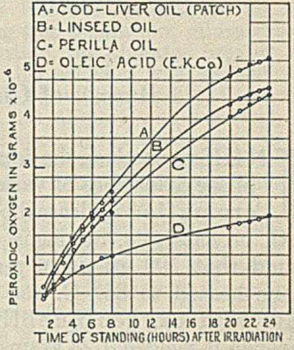

Figure 6. Total Peroxidic Oxygen Absorbed over Different Periods from Oils Irradiated for a Definite Period

A. Irradiated 15 minutes
B. Irradiated 75 minutes
C. Irradiated 90 minutes
D. Irradiated 240 minutes

Summary

1. The fact that irradiation of certain oils with ultra-violet light induces germicidal properties in the vapors given off from these oils has been verified and extended.

2. The region of the mercury arc spectrum which is photochemically most active in the production of germicidal vapors seems to be in the neighborhood of 3130 Å.

3. It has been shown definitely that the germicidal effect produced by emanations from irradiated oils is not due to secondary radiations but to substances of gaseous nature composed in part of volatile peroxides.

4. The germicidal effect of these emanations cannot be attributed to volatile aldehydes, butyric acid, or ozone.

5. A semiquantitative correlation has been found between the germicidal effect of the vapors given off from irradiated oils and the increase in peroxidic content of these oils effected by irradiation.

6. The development and subsequent evolution of peroxides in irradiated oils stored in the dark continues over a period of time, the limit of which has not yet been determined.

Acknowledgment

Several of the oils used in this investigation were kindly donated by H. P. Trevithick of the New York Produce Exchange.

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Catalytic Oxidation of *p*-Cymene in the Liquid Phase

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A study has been made of the catalytic effect of manganese dioxide in the liquid-phase oxidation of p-cymene, with oxygen as the oxidizing agent. Particular efforts were made along two lines: the preparation of the oxide in a finely divided form that could be well suspended in the liquid, thus lending itself to the best possible surface action; and the efficient breaking up of the oxygen stream to give a similar effect. A description of the apparatus is given, as well as the detailed method of preparing the catalyst. Runs were made also to determine the accelerating value of a number of other metallic oxides. Tables show relative temperature, time, and catalytic values.

Oxidation products identified were: p-toluic acid, p-tolylmethyl ketone, formaldehyde, formic acid, terephthalic acid, water, and carbon dioxide.

IN HIS research on the liquid-phase oxidations of various aromatic hydrocarbons, with no catalysts, Stephens (*3*) found that 100 grams of *p*-cymene heated to 85° C. for 14 days with oxygen bubbling through it yielded 1.23 grams of cumic aldehyde and 0.81 gram of cumic acid. Also, he found that, when 50 grams were heated to 102–104° C., other conditions remaining the same, 0.96 gram of *p*-tolylmethyl ketone as well as some cumic acid and aldehyde were formed; and finally that 50 grams of *p*-cymene and 25 grams of water, when oxidized at the boiling point for 18 days, yielded 1.8 grams of *p*-tolylmethyl ketone, but no acid or aldehyde. From 50 grams of ethylbenzene oxidizing at a temperature of 110–115° C. for 24 days, he obtained 9.5 grams of acetophenone. None of this ketone was found after passing oxygen for 31 days through 50 grams of ethylbenzene and an equal weight of water at the boiling point.

In studying the catalytic oxidation of ethylbenzene, King, Swann, and Keyes (*1*), operating at a temperature of 102–104° C. for 24 hours and using a high-speed stirrer for bringing about better contact of liquid and gas, found that the yield of acetophenone increased from 1.67 per cent, when no catalyst was used, to 20.6 per cent when 2 per cent of manganese acetate was used as a catalyst. Various oxides and other acetates showed little accelerating value.

In an investigation of the vapor-phase partial oxidation of *p*-cymene, the authors (*2*) observed that, when a finely divided manganese dioxide was used as a catalyst at the relatively low temperature of 300° C., slight explosions occurred. This result, together with the data obtained by the previously mentioned investigators, led to the conclusion that the oxidation of *p*-cymene in the liquid phase probably could be greatly accelerated under the catalytic influence of a manganese compound. Some preliminary runs were made in an apparatus essentially the same as that described later to ascertain the relative catalytic values, if any, of manganese acetate and manganese dioxide. It was found that the passage of oxygen through the heated mixture of *p*-cymene and manganese acetate always resulted in the formation of a sludge by the latter substance on the porous disk, which prevented the steady flow of oxygen. It was observed, also, that the salt turned brown, owing undoubtedly to the formation of an oxide of manganese; to this could probably be attributed any catalytic effect. Since the finely divided manganese dioxide showed definite accelerating value and did not present the difficulty encountered with the acetate, its catalytic value and that of manganese toluate were investigated further; later a less detailed study was made of the effect of the oxides of chromium, iron, nickel, cobalt, and cerium.

EXPERIMENTAL PROCEDURE

PREPARATION OF MANGANESE DIOXIDE. A modification of Witzemann's method (*4*) for preparing this oxide from permanganate and formaldehyde solution was found to give a very active form. Thirty-seven and a half grams of potassium permanganate were dissolved in one liter of hot water and cooled to 15° C. or under. The formaldehyde solution was made up by adding 20 cc. of 40 per cent formaldehyde and 1 gram of sodium carbonate to 100 cc. of water. About 90 cc. of this well-cooled solution, or enough to destroy the permanganate color, were slowly added to the cold permanganate. This gave a very finely divided oxide that remained suspended for a considerable period. After filtering and washing thoroughly, it was dried in the oven at 80° C. Before using, it was ground well in a mortar. Heating over a low flame did not change its effectiveness. The yield of the oxide was approximately quantitative.

MANGANESE *p*-TOLUATE. This substance was prepared by adding a concentrated manganese acetate solution to a concentrated solution of sodium *p*-toluate, filtering and washing the precipitated manganese *p*-toluate, and drying over calcium chloride. The salt is slightly pink in color, and, when added to hot *p*-cymene, a portion of it forms a dark brown suspension which remains as such for a long period. This behavior of the salt in the *p*-cymene indicates the formation of an oxide to which its catalytic value is attributed.

Other metallic oxides shown in Table III had some catalytic value, but of such order that space need not be given to the methods of preparation.

APPARATUS. In order to obtain a finely divided stream of oxygen through the liquid, an alundum disk of approximately 3 cm. diameter was fitted tightly into the base of the Pyrex reaction chamber, as shown in Figure 1. To insure against leakage of gas around the edges of the disk, water glass was used. The cylinder was heated in the oven and later over a free flame.[1] Oxygen measured by a meter was led in from a cylinder as shown. A mercury safety tube was placed in line to denote any back pressure which developed when some catalysts were used that did not disperse well in the *p*-cymene. With any indication of clogging, manual stirring was employed to clean the disk and reëstablish the normal pressure. With

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[1] At the time this investigation was nearing completion, Keyes and Snow published in the University of Illinois Engineering Experiment Station Bulletin 238 a similar method of bringing about intimate contact of liquid and gas in the partial oxidation of ethyl alcohol.

the manganese dioxide which gave best results, excellent dispersion and stirring were obtained by the well-broken stream of oxygen.

A side-arm delivery tube was sealed into the reaction chamber to carry off water or other volatile products formed in the reaction. Some *p*-cymene escaped with these products but was readily condensed and recovered.

In operating the apparatus, the glycerol bath was brought to the desired temperature, and 42 grams of purified *p*-cymene, together with the catalyst, were poured into the reaction chamber. Oxygen was then passed through the apparatus at a definite rate for the desired period of time. At the end of the run the product in the reaction chamber was weighed and examined as outlined below.

ANALYSIS OF PRODUCTS. When oxidizing at temperatures of 140–160° C. with 100 cc. of oxygen per minute and manganese dioxide as a catalyst, the following products were found in the reaction mixtures taken from the oxidizing chamber:

	IDENTIFICATION METHOD
p-Cymene	B. p., 178° C.
p-Toluic acid	M. p., 180.2° C.; b. p., 274–275° C.; neutralization equivalent, 136
p-Tolylmethyl ketone	B. p., 225–226° C.; m. p. of its oxime, 87.4° C.; m. p. of its semicarbazone, 202–203° C.
Terephthalic acid (small quantities present only after long period of oxidation)	M. p. of methyl ester, 138–139° C.
Dark brown resin	....

Test for aldehydes with the fuchsin reagent was negative.

Tests for alcohols with (1) sodium and (2) 3, 5-dinitrobenzoyl chloride were negative.

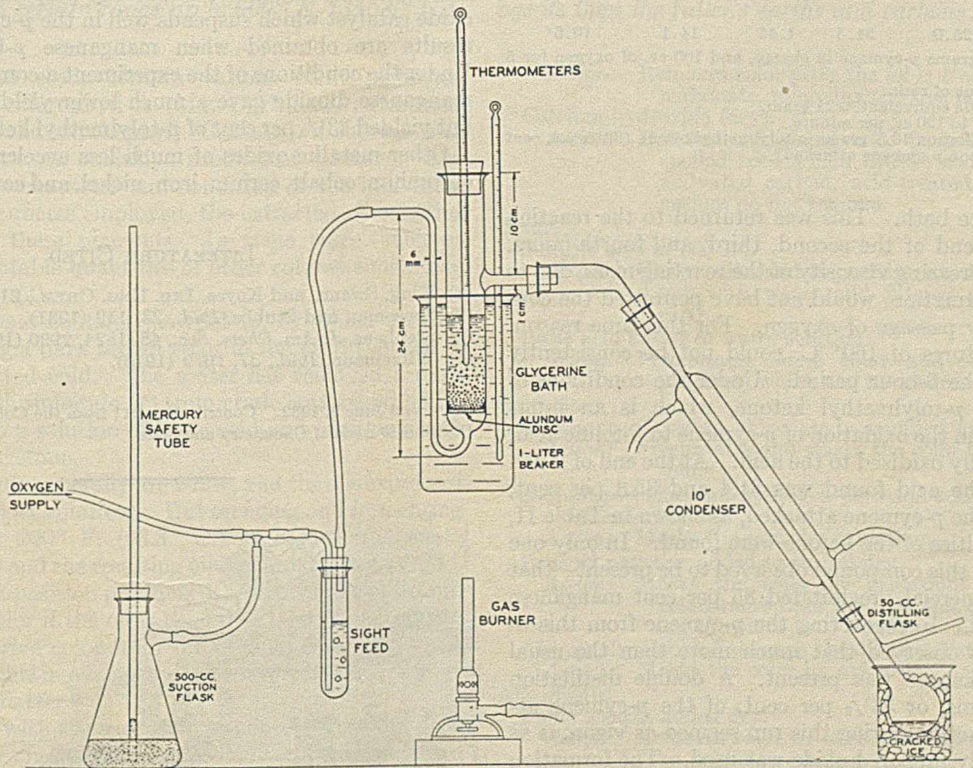

FIGURE 1. APPARATUS FOR LIQUID-PHASE OXIDATION

In the condensates collected in the ice bath, the following were found:

	IDENTIFICATION METHOD
p-Cymene	B. p., 178° C.
Water	B. p., 100° C.; cupric sulfate test
Formaldehyde	Resorcinol test
Formic acid	Mercuric oxide test

Carbon dioxide and formaldehyde were identified in the uncondensed gas.

In the various comparative runs, quantitative data were collected on the amount of *p*-toluic acid formed and the *p*-cymene unattacked. For obtaining these, the following method was used:

> The material from the oxidizing chamber was shaken in a separatory funnel with sodium bicarbonate solution to take up the acid products. Following this separation, dilute sulfuric acid was added to the water solution, the liberated organic acid was extracted with ether, and this solution was washed with small amounts of water until free of sulfuric acid. It was then made up to a definite volume, an aliquot was removed, the ether was evaporated, and a small quantity of alcohol and several volumes of water were added. It was titrated with 0.1 *N* sodium hydroxide solution, phenolphthalein being used as an indicator. From this titration the quantity of acid was calculated. For determining the *p*-cymene unattacked, the residue remaining after the acid was extracted with sodium bicarbonate was distilled in several fractions. That boiling above *p*-cymene was treated in the cold with concentrated sulfuric acid, a separation was made, and the portion insoluble in the sulfuric acid was again distilled. Some *p*-cymene was recovered in this manner. To these quantities was added that obtained from the condensate in the ice bath.

DISCUSSION OF RESULTS

In the four tables showing the effects of different variables, the percentage of *p*-cymene recovered from each run has been calculated from distillation results. These data in turn have been used in calculating the percentage of acid obtained from the *p*-cymene attacked. Inasmuch as more or less loss is always inherent in a distillation method, the same degree of accuracy cannot be claimed for them as for the other data given. However, they give an approximation of the efficiency and extent of the oxidation, and it is believed that a more accurate analytical procedure would have indicated greater efficiency of the process.

In Table I are given the results obtained through variation in temperature with 100 cc. of oxygen per minute over a period of 5 hours. In the experiment made at a temperature of 170° C., much *p*-cymene was carried over and collected in the

TABLE I. TEMPERATURE EFFECT[a]

Temp.	p-Cymene		p-Toluic Acid Yield		
	Recovered	Attacked		Based upon p-cymene attacked	Based upon p-cymene in charge
° *C.*	%	*Grams*	*Grams*	%	%
140	36.9	26.5	10.1	38.1	24.0
150	38.1	26.0	12.0	46.1	28.6
160	21.4	33.0	13.7	41.5	32.6
170	25.0	31.5	13.9	44.1	33.1[b]

[a] All runs made with 42 grams p-cymene, 1 gram manganese dioxide, 100 cc. oxygen per minute, and an oxidizing period of 5 hours.

[b] p-Cymene distilling over was returned to reaction chamber at end of second, third, and fourth hours.

TABLE II. TIME EFFECT[a]

Time	p-Cymene		p-Toluic Acid Yield		
	Recovered	Attacked		Based upon p-cymene attacked	Based upon p-cymene in charge
Hours	%	*Grams*	*Grams*	%	%
2	50.0	21.0	6.6	31.4	15.7
4	28.6	30.0	10.6	35.3	25.2
5	21.4	33.0	13.7	41.5	32.6

[a] Conditions of runs: 42 grams p-cymene and 1 gram manganese dioxide n charge, and 100 cc. of oxygen per minute, at 160° C.

TABLE III. VARIATION IN FORM AND QUANTITY OF MANGANESE CATALYST[a]

Catalyst	p-Cymene		p-Toluic Acid Yield		
	Recovered	Attacked		Based upon p-cymene attacked	Based upon p-cymene in charge
	%	*Grams*	*Grams*	%	%
1 gram MnO_2	21.4	33.0	13.7	41.5	32.6
0.21 gram MnO_2	20.2	33.5	13.4	40.0	31.9[b]
0.8 gram manganese p-toluate[c]	29.8	29.5	12.5	42.4	29.8
0.8 gram manganese p-toluate[c]	25.2	31.4	15.7	50.0	37.4[d]
0.247 gram commercial 85% MnO_2[c]	25.0	31.5	4.45	14.1	10.6[e]

[a] Conditions: 42 grams p-cymene in charge, and 100 cc. of oxygen for 5 hours at 160° C.

[b] Obtained 10 grams of resin.

[c] Manganese dioxide equivalent, 0.21 gram.

[d] Oxygen used, 100 to 120 cc. per minute.

[e] Obtained by distillation 10.5 grams p-tolylmethylketone (33$^1/_3$ per cent weight yield based upon p-cymene attacked).

receiver in the ice bath. This was returned to the reaction chamber at the end of the second, third, and fourth hours. Otherwise the increasing viscosity of the reacting mass, due to acid and resin formation, would not have permitted the continued and ready passage of oxygen. For the same reason, runs at temperatures of 160° C. could not be consistently carried beyond the 5-hour period. Under the conditions of the experiment, p-tolylmethyl ketone, which is an intermediate product in the oxidation of p-cymene to p-toluic acid, is apparently easily oxidized to the acid. At the end of 2 and 4 hours, when the acid found was 31.4 and 35.3 per cent, respectively, of the p-cymene attacked, as shown in Table II, only small quantities of the ketone were found. In only one case was much of this compound observed to be present—that in which a commercial precipitated 85 per cent manganese dioxide was used. In recovering the p-cymene from this 5-hour run, it was observed that much more than the usual amount of the ketone was present. A double distillation yielded 10.5 grams, or 33$^1/_3$ per cent, of the p-cymene attacked. The reaction during this run seemed as vigorous as when the specially prepared oxide was used. The formation of water, carbon dioxide, and formaldehyde was observed almost immediately after starting the oxygen. The p-toluic acid yield, however, was only 4.45 grams, or 14.1 per cent, of the p-cymene attacked. These results are given in the last line of Table III. Other data in this table reveal that 0.21 gram of the specially prepared oxide, or 0.5 per cent of the p-cymene used, checks closely the results obtained when 1 gram, or 2.3 per cent, of catalyst was used; also, that manganese p-toluate, whose behavior in p-cymene is described under the preparation of the salt, accelerated the reaction in a similar manner, and, that by increasing the flow of oxygen from 100 cc. per minute to 100–120 cc., the yield of acid was greater than that for any other run. (Partial clogging of the alundum disk caused the slowing of the flow of oxygen during the run.)

In Table IV are given comparative data on the accelerating values of different oxides for acid production. Attention is called to the fact that, although the yields obtained when using other oxides did not approach those obtained when using manganese dioxide, methods were not available for producing them under the more favorable conditions of low temperature and semi-colloidal state.

TABLE IV. EFFECT OF VARIOUS CATALYSTS[a]

Catalyst	p-Cymene		p-Toluic Acid Yield		
	Recovered	Attacked		Based upon p-cymene attacked	Based upon p-cymene in charge
	%	*Grams*	*Grams*	%	%
None	73.8	11.0	0.38	3.5	0.9
MnO_2	21.4	33.0	13.70	41.5	32.6
Cr_2O_3	36.9	26.5	4.50	17.0	10.7
Co_2O_3	28.6	30.0	3.06	10.2	7.3
CeO_2	42.4	24.2	2.76	11.4	6.6
Fe_2O_3	35.7	27.0	2.70	10.0	6.4
Ni_2O_3	41.9	24.4	2.62	10.7	6.2
CuO	32.1	28.5	2.45	8.6	5.8

[a] Conditions: 42 grams p-cymene and 1 gram oxide in charge, and 100 cc. of oxygen per minute for 5 hours at 160° C.

CONCLUSIONS

The oxidation of p-cymene, at elevated temperatures, to p-toluic acid by means of well-dispersed oxygen is greatly accelerated by the use of a specially prepared manganese dioxide catalyst which suspends well in the p-cymene. Similar results are obtained when manganese p-toluate is used. Under the conditions of the experiment a commercial grade of manganese dioxide gave a much lower yield of p-toluic acid but yielded 33$^1/_3$ per cent of p-tolylmethyl ketone.

Other metallic oxides of much less accelerating value are: chromium, cobalt, cerium, iron, nickel, and copper.

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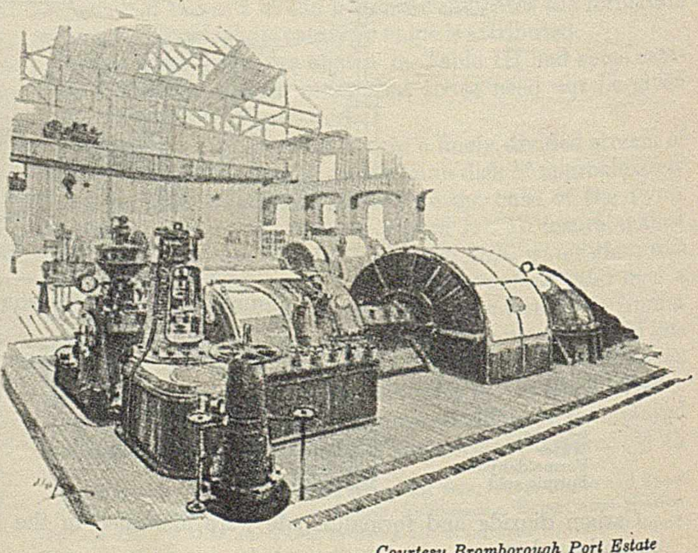

Courtesy Bromborough Port Estate

Characteristics of Colors in Vegetable Oils and Methods of Removal

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High color content is characteristic of seed and pulpy fruit oils (with iodine number above 20). Freedom from color is typical of nut oils (with iodine number below 20). When the higher melting-point fractions of an oil crystallize, the color is expelled from this portion similar to a salt crystallizing free from impurities in the mother solution. Refining agents have specific action like acids and have more power to remove red and yellow than caustic, and acid-treated silica clays have more effect on red than carbon and fuller's earth.

Aging oils refined with caustic and fuller's earth in the dark will reduce the color further, an action not like sunlight exposure, but similar in the resulting effect. Acid-treated oils change little by aging in the dark, but sunlight has a marked reducing effect. High temperature has a bleaching and precipitating effect over a certain range up to 600° F. (315.6° C.), and a darkening results if the oil is held at this temperature for an extended time. Heat-bleaching is most effective on oils containing a high proportion of yellow, whereas oils containing high proportions of red and black are not bleached, but the color becomes fast and is then not removed by any reagent.

Fuller's earth, activated carbons, and acid-treated clays bleach mainly by absorption (6). The effectiveness of the absorption can be measured by the surface exposure or the specific gravity of the individual bleaching agent. The more efficient a fuller's earth is in removing color, the lower the pH; again, this type of fuller's earth has a greater oxidizing effect. It would seem that acid-treated clays having a greater pH and containing some actual free acid are for that reason better decolorizing agents than the fuller's earths and carbons.

FRUITS and seeds contain various plant pigments, including chlorophyll A (Mg, $C_{55}H_{72}N_4O_5$); carotene ($C_{40}H_{56}$); and xanthophyll ($C_{40}H_{56}O_2$), a substance of dark brownish tint, an oxidation product of carotene. Depending upon the character and condition of the individual product and the process employed, the extracted oil contains more or less of these pigments. In some cases, such as cottonseed (*8*), notable quantities of other colored substances are also extracted (*4*).

Cottonseed meats contain gossypol (*2*, *9*) which are oil-soluble, producing a dark brown color in the oil if the seed is pressed or extracted cold. The writer has removed a dark red lecithin-like phosphatide (*7*) from crude cottonseed oil by precipitating with a solution of boric acid and purifying with hot alcohol and acetone.

The meats of nuts generally are white, and the oils expressed therefrom are almost colorless. But on aging and fermenting or desiccating at 200° F. (93.3° C.) or higher, the white meats turn brown and the resulting oil is colored (*5*).

Likewise, decomposition products of seeds, soluble in the oil, will increase in color if the oil is heated to high temperatures. Vegetable oils derive color from the original seeds and nuts, and anything soluble in oil which prevents it from being water-white is coloring matter.

Vegetable oils, with the exception of olive, are seldom used for edible purposes in this country in their crude or unrefined state, but are refined to remove free fatty acids and color (impurities). A description of the reagents and methods used for removing or reducing color are as follows:

- Alkali and alkali metal reagents.
  - Caustic soda in dilute solution (sodium hydroxide plus water).
    - *Action:* Removes free fatty acids and color, and impurities such as phosphatides and gossypol; has little effect on yellow colors.
  - Sodium carbonate, moist or in solution.
    - *Action:* Removes free fatty acids and a little color and impurities.
  - Magnesium oxide (dry).
    - *Action:* Removes color after the oil is treated with sodium carbonate, removing the free fatty acids.
  - Calcium hydroxide (dry).
    - *Action:* Removes additional color from oils derived from spoiled seed which caustic soda, fuller's earth, activated carbon, acid-treated clay, and magnesium do not remove.
- Acids.
  - Sulfuric acid as 60° Bé.
    - *Action:* Chars color and impurities which can be washed out with water and filtered out with fuller's earth.
  - Boric acid added in water solution.
    - *Action:* Precipitates some color and impurities (phosphatides) which can be settled out.
- Oxidation.
  - Sodium or potassium chromate in acidified solution.
    - *Action:* Precipitates and masks the color by nascent oxidation.
  - Sodium peroxide and hydrogen peroxide added in presence of water in the oil.
    - *Action:* Masks the color by oxidation.
  - Benzoyl peroxide added to the oil dry.
    - *Action:* Masks the color by oxidation; reduces yellow colors more than the reds, but discolors on heating the oil to 220° F. (104.4° C.).
  - Air, usually bubbled through the oil at elevated temperatures.
    - *Action:* Masks the color by oxidation.
- Absorbents.
  - Fuller's earth added dry.
    - *Action:* Removes color by absorption and possibly acts as an oxidizing catalyst (*1*, *3*).
  - Activated carbons and bone black added dry.
    - *Action:* Removes color by absorption.
  - Acid-treated clays or silicas added dry.
    - *Action:* Removes color by absorption and acid attraction.
- Reduction and increase of colors (by artificial and natural means).
  - Heating to high temperatures.
    - *Action:* Precipitates or bleaches colored substances of some oils; darkens others.
  - Hydrogen in the presence of an active metal catalyst.
    - *Action:* Reduces color.
- Actinic rays.
  - Sunlight.
    - *Action:* Reduces or masks colors.

Ultra-violet light.
Action: Reduces or masks colors.
Aging.
Action: Even in tightly closed containers and/or under vacuum, colored oils fade in the dark.

It is advisable to use well-known typical oils in describing specific color characteristics and the methods of removal. The general method for measuring color of vegetable oils is the Lovibond tintometer and all color readings reported are the Lovibond red and yellow scale.

Crude cottonseed oil varies from pale cherry red to black. Hydroxy alkalies in dilute solution have a marked decolorizing effect, combining with and precipitating colored and other impurities, and free fatty acids. The alkali must be added to the oil at 100° F. (37.8° C.), or lower, to be efficient in removing color; at 120° F. (48.9° C.), or higher, considerable power to remove color is lost. Concentrated alkali solutions remove very little color. Alkali carbonates have little noticeable effect on cotton and other seed oils other than neutralizing the free fatty acids which are colorless. However, a subsequent treatment of a cottonseed oil (neutralized with an alkali carbonate) with dry magnesium oxide added cold (under 100° F., or 37.8° C.) and mixed with fuller's earth and heated to 180–200° F. (82.2–93.3° C.) will decolorize it as much as if treated with caustic alkali and bleached with the same amount of fuller's earth under the same refining conditions. It is evident that the hydroxyl has a precipitating action on certain colors if the oil is cold. If cottonseed oil is heated to 300° F. (148.9° C.) in the crude state, none of the above reagents will then remove the color. Calcium hydroxide removes additional color from this oil which has resisted refinement with sodium hydroxide and been bleached with fuller's earth and activated carbon. A dark cottonseed oil made from unsound seed, after refinement as mentioned above, had a color of 35 yellow, 17 red. After mixing in cold hydrolyzed lime and allowing the oil mixture to stand a few weeks, the color had been reduced to 35 yellow, 9 red. Lime had no effect apparently on the oil before refining. However, caustic alkali refining reduces the color of all vegetable oils, except palm oil which is affected considerably less than the others with the exception of China wood oil, on the color of which caustic has no action. It can be generally stated that alkalies have a greater power to remove the red, black, and green colors than any of the reagents except concentrated sulfuric acid. These two reagents remove phosphatides and soluble carbohydrates, whereas boric acid has an apparent selective action on lecithin or phosphatide-like colors only.

Table I shows the effect of refining reagents on crude soy-bean oil, and Table II shows that alkali has very little decolorizing effect on crude palm oil.

TABLE I. COMPARISON OF CRUDE AND VARIOUS REFINED SOY-BEAN OILS

SOY-BEAN OIL	SP. GR. AT 15.5° C.	IODINE NO. (WIJS)	ACID NO.	COLOR (LOVIBOND) Yellow	COLOR (LOVIBOND) Red	DEPTH OF COLUMN *Inches* (*cm.*)
Crude	0.926	138	3.4	100	9	2 (5)
Filtered crude through dry soda ash	0.926	138	3.0	100	8	2 (5)
Acid-refined	0.926	138	4.6	35	3.1	5.25 (13.3)
Alkali-refined and bleached with fuller's earth	0.926	139	0.5	35	6.2	5.25 (13.3)
Slightly blown crude[a]	0.952	115	3.9	35	7.7	5.25 (13.3)
Blown crude[a]	0.990	84	8.1	50	7.0	5.25 (13.3)

[a] Treated with air at 180° F. (82.2° C.)

The drying oils, such as linseed and soy-bean, are almost free from solid fats. Those like coconut and palm kernel are solid crystallized fats at room temperature (74° F. or 23.3° C.). When the solid or crystallized portion of an oil or fat is removed, the majority of the color goes into the liquid portion or higher iodine-number portion. For example, a coconut oil before separation had a color of 7 yellow, 1.0 red; the solid crystallized portion a color of 3 yellow, 0.2 red; and the liquid portion a color of 13 yellow, 1.8 red. Neutralized alkali-refined palm oil had a color of 45 yellow, 9.0 red; the crystallized portion a color of 40 yellow, 6.1 red; and the liquid portion a color of 60 yellow, 17.6 red (read on a 1-inch or 2.5-cm. column).

TABLE II. DECOLORIZATION OF PALM OIL

(Bleaching materials were added at 200° F. (93.3° C.) and agitation continued for 30 minutes)

PALM OIL	COLOR Yellow	COLOR Red	DEPTH OF COLUMN *Inches* (*cm.*)
Crude	35	24	1 (2.5)
Crude with 2% acid-treated clay at 320° F. (160° C.)	35	10	5.25 (13.3)
After neutralizing	35	17	1 (2.5)
Treated with 1% acid-treated clay[a] reduced to:	35	14	1 (2.5)
Treated with 2% acid-treated clay[a] reduced to:	35	11.8	1 (2.5)
Treated with 2% acid-treated clay[a] at 320° F. (160° C.)	35	6	5.25 (13.3)
Treated with 5% activated carbon reduced to:	35	11.8	1 (2.5)

NOTE: Neutralized palm oil heated to 255° C. had a color of 35 yellow, 2.8 red which was very green, showing that the original color of the oil changed to a different tint (green and blue) by heat treatment.

[a] Silica clay.

Concentrated acids such as sulfuric of 60° to 66° Bé. concentration have a great effect on the color of seed oils. It is not clearly understood whether the action is a precipitation or a charring of the color and impurities. (Some light on this question may be given by the fact that dilute sulfuric acid has little decoloring effect.) In Table I a comparison shows that concentrated-acid refining produces a soy-bean oil with 50 per cent less red color than the same oil alkali-refined. Dilute acids with bleaching agents such as the chromates and peroxides have a marked decolorizing action due to oxidation. Free chlorine and sulfur are not classed as decolorizers because they combine with the glycerides while decolorizing somewhat at the same time. The action of oxidizing agents is more effective than the oxygen of the air. Nitrogen and carbon dioxide blown through oils at room temperature and up to 450° F. (232.2° C.) do not combine with the oil nor do they have an effect on color, even though a considerable amount is adsorbed by the oil at the time of contact. In Table I the decolorizing effect of blowing soy-bean oil with air at 180° F. (82.2° C.) until the specific gravity is increased from 0.926 to 0.952, and over 75 per cent of the yellow color is reduced; however, if air-blowing is continued, until the specific gravity reaches 0.990, the yellow begins to increase or revert. Air has a decolorizing effect mainly on the yellows; however, if the oil has been refined with concentrated acids, air will cause the red colors to increase:

AIR-BLOWN ACID-TREATED LINSEED OIL	RED
Original	4.5
After 1 hour	6.0
After 2 hours	6.5
After 3.75 hours	8.5

NOTE: Cold-pressed linseed oil (not acid-treated) with a color of 35 yellow, 11 red, after being blown for 4 hours at 180° F. (82.2° C.) had a color of 25 yellow, 5 red.

Palm oil before or after neutralizing is considerably decolorized at or above 212° F. (100° C.) by air-blowing, and, if exposed to the air at room temperature in diffused daylight, it slowly loses color and becomes a solid white fat. Alkali-treated seed oil containing appreciable yellow is lightened by air-blowing, but nut oils darken; they contain comparatively little yellow.

Heat applied rapidly and up to 600° F. (315.6° C.) produces marked decolorizing effects on linseed, soy-bean, palm, or any oil containing appreciable and excess yellow. Crude cottonseed oil, containing excess red and dark impurities, darkens by this treatment, whereas crude linseed shows a heavy flocculent precipitate or "break" at 520° F. (271.1° C.) which practically decolorizes the oil. This break contains calcium and iron phosphatide. If cold-pressed linseed oil is heated to 550° F. (287.8° C.) *in vacuo*, no break occurs, and the oil bleaches almost colorless. Neutralized linseed, soybean, and corn oils behave in the same manner. Heating crude palm oil *in vacuo* to 600° F. (315.6° C.) reduces the intense color to 35 yellow and 10 red (5.25-inch or 13.3-cm. column). All the reagents mentioned have little effect on palm oil without the aid of high temperatures. Bleaching at 350° F. (176.7° C.) with 5 per cent acid-treated clay, a neutralized palm oil was reduced to a color of 20 yellow, 2.5 red (5.25-inch or 13.3-cm. column). The effect of heat-bleaching on cold-pressed linseed oil and the comparative effectiveness of various earth- and clay-bleaching agents is as follows (using 2 per cent of various earths 10 minutes at 82° C., plus 4 minutes at 110° C., taking 4 minutes to heat from 82° to 110° C.):

Earth	Color		Heat Bleached[a]		Weight of 14 cc. of Agent
	Yellow	Red	Yellow	Red	*Cc.*
Imported fuller's	45	3.8	20	0.5	12.8
English fuller's	45	3.4	25	1.3	14.0
Georgia fuller's	45	4.1	12	0.1	7.8
Acid-treated clay	35	2.5	9	0.7	7.5

[a] At 600° F. (315.6° C.).

Table III shows the effect of heat-bleaching and color reversions in bodying oil.

Table III. Effect of Heat-Bleaching and Color Reversions

(Bodying experiments run in a plant varnish kettle on cold-pressed linseed oil, bleached with fuller's earth and acid-treated clay)

Sample	Viscosity[a]	Color		Sp. Gr.	Time on Fire[b]
		Yellow	Red		
1	2.2	10.5	1.5	0.936	1 hr. 57 min.
2	4.0	6.5	1.0	0.941	30 min.
3	5.5	9.0	1.1	0.946	1 hr.
4	12.5	10.0	1.2	0.951	1 hr. 30 min.
5	19.5	17.0	1.4	0.957	2 hr.
6	29.0	25.0	2.1	0.960	2 hr. 30 min.
7	47.0	35.0	3.1	0.962	3 hr.

[a] Ford cup test viscometer.
[b] At 585° F. (307.2° C.).

The fuller's earths, acid-treated clays or silica, and the activated vegetable and bone carbons are the most efficient bleaching agents for refined oils, and their pH has some bearing on their decolorizing efficiency:

	pH	Crude Coconut Oil[a]		Crude Linseed Oil[a]	
		Yellow	Red	Yellow	Red
Color before bleaching	...	45	5.1	35	18
Acid-treated clay	5.7	4.9	0.6	35	13
Georgia fuller's earth	6.1	6.9	1.1	35	13
Activated carbon from lignite	6.4	2.0	0.9	..	..
Activated carbon from wood waste	6.9	1.9	0.7	35	11
Florida fuller's earth	7.0	..	...	..	..
English earth	7.6	..	...	..	..
Activated carbon	8.8	..	...	..	..
Imported activated carbon	9.7	3.9	1.2	..	..

	pH	Neutralized Unbleached Coconut Oil[b]	
		Yellow	Red
80% activated carbon from lignite and 20% imported activated carbon	6.9	3.9	0.5
65% activated carbon from lignite and 35% activated carbon	6.9	4.0	0.5
60% English fuller's earth and 40% Georgia fuller's earth	6.9	7.0	0.9
90% English fuller's earth and 10% acid-treated clay	6.9	6.7	0.9

[a] Two-inch (5-cm.) column.
[b] 13 yellow, 1.7 red.

An acid-treated clay or silica having an acidity (as sulfuric acid) of 0.46 removed twice the amount of red color from refined palm oil that a similar acid clay or silica did with an acidity of 0.25 per cent. These acid-treated clays remove more red and less yellow than the activated carbons do from coconut oil, and both have more decolorizing effect than an acid-reacting natural Georgia fuller's earth.

The relative efficiencies of one neutral and slightly acid fuller's earth and one acid silica clay, indicating that weak-acid decolorizing agents are more effective color removers than neutral or alkaline ones, are as follows:

	pH	Neutralized Hot-Pressed Linseed Oil[a]	
		Yellow	Red
Florida fuller's earth	7.0	35	7.8
Georgia fuller's earth	6.1	35	5.7
Acid-treated silica clay	5.7	25	2.7

[a] 40 yellow, 12.3 red.

When the pH of Georgia earth was decreased by boiling in 10 per cent sulfuric acid, and when the pH was increased by 10 per cent sodium hydroxide solution, the decolorizing power was lowered in both cases, and neither the addition of free acid nor alkali had any beneficial effect on the decolorizing power of fuller's earth.

Sun rays and ultra-violet light are powerful but slow decolorizing agents, and are not used commercially. What happens when oils are acted upon by light rays is hardly understood; a cod liver placed in a closed glass jar and exposed to sunlight, will decompose, and free and bleach the oil from the liver tissues. Linseed and cottonseed oils in glass containers *in vacuo*, exposed to diffused light, will lose color and at the same time increase in specific gravity and decrease in iodine number. Actinic rays affect oil color similarly to heat-bleaching, with this exception: they will bleach all well-known vegetable oils, whereas heat will darken certain oils (i. e., acid-refined).

Aging in the dark, however, presents a contrast. The following shows the colors of the original linseed oils and the changes in color from time to time, in the dark:

	Hot-Pressed, Neutralized, and Bleached with Fuller's Earth		Cold-Pressed		Cold-Pressed and Bleached with Fuller's Earth	
	Yellow	Red	Yellow	Red	Yellow	Red
Initial color	35	5.3	35	11.5	35	8.2
After 7 months	35	3.6	50	11.0	35	7.5
After 15 months	35	3.0	40	9.2	40	6.1
After 22 months	35	2.5	35	5.0	35	5.5
After 37 months	30	3.0	35	5.0	35	5.7

All oils were in tight bottles free from air. The three oils were still sweet as to odor, showed no signs of rancidity, and bleached under heat:

	Treated with Sulfuric Acid, Refined, Hot-Pressed[a]		Neutralized, Bleached with Fuller's Earth, Hot-Pressed[a]	
	Yellow	Red	Yellow	Red
Exposed to diffused daylight (light and dark storage) 5 months	35	3.6	10	1.1
In dark 5 months	35	6.5	35	2.4

[a] 5.25-inch (13.3-cm.) column.

No bleaching results from dark storage on linseed oil, hot-pressed and refined with sulfuric acid:

	Yellow	Red		Yellow	Red
Initial color	35	6.7	After 4 months	35	6.2
After 1 month	35	6.3	After 5 months	35	6.5
After 2 months	35	6.4			

Hydrogen with an active nickel catalyst decolorizes nut oils almost completely but has comparatively much less effect on seed- and fruit-pulp oils.

All highly bleached hot-pressed vegetable oils will revert in color on standing in warm temperatures—that is, 140° F. (60° C.) or higher, unless made from seed and nuts either cold-pressed or thoroughly neutralized by alkali refining prior to bleaching with fuller's earth and carbon. The use of a high excess of alkali to remove all color and impurities possible at the beginning of the refinement prevents color reversion.

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The Differentiation of Hemicelluloses

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Hemicelluloses fall into two groups: (1) those incrusting substances not closely associated with the cellulose, and containing in practically all cases a uronic acid, and (2) those very intimately associated with the cellulose and never containing a uronic acid. These two groups are accurately separated in the Cross and Bevan cellulose determination, provided that there is no pretreatment of the material with either acid or alkali before chlorination. The name "polyuronide," suggested by Candlin and Schryver, should be applied to all those in the first group containing uronic acid, and for the second a new term "cellulosan" is proposed.

THE general conception of the characteristics of the hemicelluloses has not changed greatly since this group of plant constituents was first described by Schulze (*36*). This worker, who gave the generic name, considered the hemicelluloses as closely related to cellulose in chemical constitution, although less resistant to acid hydrolyzing agents. Further, he was of the opinion that the hemicelluloses were intermediate substances in the development of cellulose itself. Schulze prepared such compounds from a large number of plant materials and thought them polysaccharide in nature. Arabinose, xylose, and galactose were the sugars usually concerned; his preparations mostly contained more than one sugar unit. Except for their relative ease of hydrolysis with acid, the most characteristic property of this group is their solubility in dilute alkali, and it is by extraction with alkali that they are usually obtained. Unless the treatment is drastic and prolonged, no change appears to take place in the polysaccharide, which may then be obtained in a crude condition on acidification and addition of alcohol to the extract. Further purification is accomplished by resolution and reprecipitation. Until recently, the view was held that the substances obtained in this way were true hexosans or pentosans or, more frequently, hexopentosans, containing both anhydrohexose and anhydropentose units. During the past few years, however, it has been found that the majority of the hemicelluloses thus prepared are not true polysaccharides in the strictest sense of this term, but often contain also considerable amounts of uronic acids (*4, 28, 30–34, 37*). Glucuronic and galacturonic acids are those commonly found, though mannuronic acid has been obtained from certain marine algae (*2, 26*). The widespread occurrence of the uronic acids in several types of plant constituents is now recognized. Pectin contains nearly 80 per cent of galacturonic acid, and several gums and mucilages have also been shown to contain a high percentage of uronic acids (*3, 27, 29*). Candlin and Schryver (*4*) suggested the use of the term "polyuronide" for compounds that contain uronic acids in combination with sugars. The term has not yet come into general use but would be of considerable value in connection with the composite group of hemicelluloses. Hemicelluloses containing uronic acids linked to anhydrosugar units may rightly be described as polyuronides, although substances other than hemicelluloses (pectin and gums, for example) are also polyuronides.

The purpose of this review is to examine and correlate recent work on hemicelluloses from many sources, and especially the polyuronide group, so that the results of conventional analytical methods may be interpreted more correctly in terms of actual constituents.

METHOD OF DIFFERENTIATION

An alkali extract of wood or of other plant material contains hemicelluloses of two distinct types, or rather, from two different sources. The major part will consist of the incrusting material from the cell wall and is largely polyuronide in nature; this material is identified only as "pentosans not in cellulose" in the Forest Products Laboratory methods of analysis. A second part will come from the polysaccharide that is very intimately associated with the cellulose itself and is normally isolated with it in the Cross and Bevan cellulose fraction. Perhaps the most direct evidence of a dual source occurs in the work of Hawley and Campbell (*11*), who analyzed wood both before and after treatment with dilute alkali, finding that both the Cross and Bevan cellulose and the "pentosans not in cellulose" had been diminished by this treatment. Quite mild treatment was sufficient to remove a certain amount of the associated polysaccharide from the Cross and Bevan cellulose. Further evidence is supplied by the work of Miller and Swanson (*25*) on the graded hydrolysis of wood with boiling hydrochloric acid. Additional support is given by the high β- and γ-cellulose content of Cross and Bevan cellulose from woods, and especially by the presence of mannan and pentosan in the β- and γ-cellulose fractions (*38*).

There is no direct published evidence that the alkali-soluble material from the Cross and Bevan cellulose of wood is precipitated by the methods commonly used for preparing the polyuronides, but there is indirect evidence in the large amounts of β-cellulose usually found. Qualitative tests on this point kindly made by Ritter have shown that a dilute alkali extract of the Cross and Bevan cellulose from white spruce wood will give considerable quantities of a precipitate on acidification followed by the addition of alcohol.

The alkali solubility of the polysaccharide associated with cellulose in the Cross and Bevan cellulose fraction has been unquestionably demonstrated for certain straws, esparto grass, bamboo, and similar plants. Moreover, it has been shown for these materials that this polysaccharide can be obtained from the extracts in the way usually employed for the precipitation of hemicelluloses (*9, 14, 15, 21–23, 28, 41*). An alkali extract, therefore, as ordinarily employed for the preparation of hemicelluloses, is likely to contain compounds from these two sources—the cell-wall incrusting material, and the Cross and Bevan cellulose fraction. The fact that a mixture is obtained is not particularly serious, because a hemicellulose preparation as isolated from wood or straw has never been considered a single chemical compound. O'Dwyer (*32*) effected a separation of a crude hemicellulose preparation into two groups, slightly different in properties and considerably different in the proportions of sugars and uronic acids present, by precipitation first with acid and then with acid alcohol. More recently, Norris and Preece (*30*) have obtained a separation into six fractions by various methods of precipitation. Whether, even then, the resulting preparations are chemical entities is a matter of some doubt, though the fact that certain of their fractions are not represented in some materials examined tends to indicate that their scheme of fractionation has its basis in fairly clearly defined differences. No others have attempted such a thorough separation, most investigators confining themselves to the two groups—material precipitated by acid, and material precipitated by acid-alcohol—first suggested by O'Dwyer (*32*).

Although recognizing that both these fractions are undoubtedly mixtures, it is still important to remember the double source of such a preparation, and the fact that there may be present in it some nonpolyuronide hemicellulose from the Cross and Bevan cellulose fraction. This last fraction has always been considered to be strictly polysaccharide in nature—that is, to contain sugar units only. (Schwalbe and Feldtman (*37*) have reported the presence of glucuronic acid in a wood pulp, but even well-cooked pulps are not entirely Cross and Bevan cellulose, usually containing appreciable quantities of pentosans not in cellulose.) Ritter, in unpublished work on the chlorination of cellulose in sunlight, has had occasion to determine uronic acids in normally chlorinated Cross and Bevan cellulose, and has obtained only such traces of carbon dioxide as are ordinarily given by all carbohydrate material under the conditions of this determination. Norman (*28*) obtained only 0.22 per cent carbon dioxide from the Cross and Bevan cellulose from oat straw; this was probably due in part to slight oxidation during the chlorination process, as demonstrated by Heuser and Stöckigt (*19*) and Hibbert and Parsons (*20*). It seems likely, therefore, that the polysaccharide associated with the cellulose in the Cross and Bevan fraction does not contain uronic acid. Accordingly, the polyuronides that have been isolated and studied are probably mixtures of polyuronides from the incrusting cell-wall material, together with hemicellulose, free from uronic acid, from the Cross and Bevan cellulose fraction. Additional studies of the polyuronide hemicelluloses should therefore be made on products uncontaminated with any material from the Cross and Bevan cellulose. It is possible further to suggest the source of such a product—namely, the liquors obtained from the chlorination and sulfite extraction during the isolation of Cross and Bevan cellulose. Such a liquor, of course, contains also chlorinated lignin, but the development of a method for the isolation of the polyuronide should be possible. There is already some evidence (unpublished) that the polyuronides removed by this process and present in this liquor are not hydrolyzed during the chlorination and extraction.

As mentioned previously, no attempts have been made to investigate by direct preparation the nature of the polysaccharides associated with the Cross and Bevan cellulose of woods, but extraction and hydrolysis have indicated the sugar units concerned. The standard procedure in analytical practice is to determine the yield of furfuraldehyde from the Cross and Bevan cellulose, since pentose material is almost invariably present, often to a considerable extent. The nature of the pentose has been investigated in many instances and always found to be xylose, present, of course, as xylan. Arabinose has never been obtained from a properly chlorinated cellulose. Methylpentosans have been reported by many workers as present in small amounts. The evidence for their presence, however, is still unsatisfactory, since the methylfurfuraldehyde said to be obtained on hydrolysis with 12 per cent hydrochloric acid might actually be ω-hydroxymethylfurfuraldehyde, which is given in small quantities from hexosans (and therefore from cellulose itself) under the conditions of this determination.

Although the cellulose from all hardwoods examined contains varying amounts of pentosan, that from the softwoods is always distinctly lower in furfuraldehyde-yielding material. In this group, however, appreciable quantities of hexosan material are also found associated with the cellulose. Schorger (*35*) examined quantitatively a large number of gymnosperms and showed mannan to be present in amounts varying from 7.68 per cent in Monterey pine, downward. These determinations were made on the total wood, not on the Cross and Bevan cellulose from it, but subsequent work on hydrolysis points to the Cross and Bevan cellulose as the source of this mannan. Schorger examined a number of hardwoods at the same time, in no instance identifying mannan. Other workers, however, have reported small quantities of mannan in certain hardwoods. It would be interesting to reëxamine these hardwoods, since the mannan in them is probably not associated with the cellulose. Of other hexosans, although small amounts of glucose have been obtained in the hydrolysis of wood cellulose (*8*, *38*), galactose has never been obtained from this fraction. To summarize, therefore, it appears that the polysaccharide associated with the cellulose of woods is usually xylan, though in softwoods mannan may also be present to a considerable extent, while some glucosan has been found in both hardwoods and softwoods, though in relatively small amounts.

In plant materials other than woods, there is still less evidence, since no such systematic analyses as those of woods have ever been made. In the specimens examined, the associated polysaccharide was a xylan. It is, however, not meant to imply that the cellulose of all nontimber materials contains only xylan, since the number of sources investigated is small. The xylan associated with esparto cellulose has probably received most attention from investigators, though the first well-authenticated xylan preparation was obtained from chlorinated straw pulp (*14*). It was precipitated as a copper compound from an alkaline extract and subsequently purified, yielding on analysis furfuraldehyde equivalent to more than 95 per cent xylan. Some properties of this compound were investigated by Heuser and Ruppel (*17*), Heuser and Schlosser (*18*), and Heuser and Jayme (*16*). A complete constitutional investigation of that from esparto cellulose was commenced by Irvine and Hirst (*21*) and completed by Hampton, Haworth, and Hirst (*9*). These workers established unquestionably the fact that xylan from this source is composed of 1,5-anhydro-β-xylose units and differs in configuration from cellulose only in that the terminal carbinol group is missing. The xylan has also been prepared from the cellulose of bamboo by Hess and Lüdtke (*13*), from corn seedlings by Link (*22*), and from young barley plants by Norman (unpublished).

The lack of a more general survey of the distribution of this associated polysaccharide in nonwoody plants is regrettable. The scanty evidence available, however, indicates close similarities between the Cross and Bevan cellulose fraction of such materials as cereal straws, esparto, and bamboo, and of the hardwoods. Indeed, as Hawley (*10*) has pointed out, the relationship between the cellulose of such materials and that of the hardwoods is much closer than the relation between the hardwoods and the softwoods. Mannans have not yet been found in the cellulose fraction of any group other than the gymnosperms.

Thus far in this discussion no attention has been paid to the possibility of true hexosans, or pentosans, existing otherwise than in the Cross and Bevan cellulose fraction. Probably such substances, except in a few instances, are distinctly rare. Although the literature does contain many references to such polysaccharides, these must be discounted because the ubiquity of the uronic acids has only very recently been realized and their presence sought. However, there are certain well-authenticated instances in which hexosans, free from uronic acids, have been found. The mannan of the ivory nut (*Phytelephas macrocarpa*) and of salep roots, and the galactan of agar-agar, are cases in point, but these materials are probably very different in physiological significance from the polyuronides.

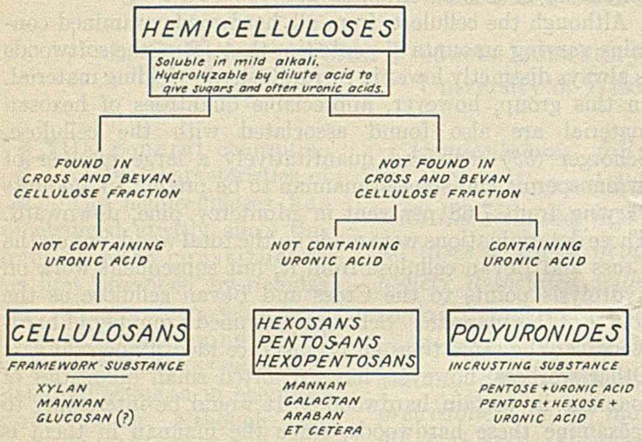

FIGURE 1. THE DIFFERENTIATION OF HEMICELLULOSES

INTERPRETATION OF SOME STANDARD ANALYTICAL METHODS

The effect of this new conception of the nature of the hemicelluloses on the interpretation of the results of some analytical methods, especially those employed for wood by the Forest Products Laboratory, is important. The polyuronide group of hemicelluloses causes some deviations from accuracy unless the presence of uronic acids is specifically taken into account. The standard Forest Products Laboratory methods determine three groups of polysaccharides: (1) Cross and Bevan cellulose, (2) pentosans in Cross and Bevan cellulose, and (3) pentosans not in Cross and Bevan cellulose. By an additional determination, either that for α-cellulose or for hydrolysis number (*12*), a fourth group, either β- and γ-cellulose, or the more readily hydrolyzed portion of the Cross and Bevan cellulose, is sometimes obtained. As has just been shown, group 1 (the Cross and Bevan cellulose) contains the "pure" cellulose together with associated polysaccharide. Since this associated polysaccharide does not contain uronic acid, the validity of this determination is unaffected. Group 3 (pentosans not in Cross and Bevan cellulose) is obtained from the difference between total pentosans and pentosans in Cross and Bevan cellulose, pentosan being calculated from furfuraldehyde by employing the Kröber factor. As pointed out by Norman (*28*), this involves the assumption that the furfuraldehyde is derived only from pentose units, whereas in actuality a portion is derived from the uronic acid units of the polyuronides. In point of fact, the calculation employed at present, in which the polyuronides are expressed as pentosans, invariably gives low results, for while pentosans yield about 64.5 per cent furfuraldehyde, uronic acid anhydrides yield only 16.6 per cent. This inaccuracy, however, is not serious with most woods, since the uronic content of the polyuronides of wood is quite low. To give an example, the highest yield of carbon dioxide from the uronic acids of a hardwood was obtained by Anderson (*1*) from catalpa; his results indicated 5.76 per cent of uronic acid anhydride. The furfuraldehyde yield from this quantity of uronic acid would be 0.96 per cent, which if calculated as pentosan would be 1.5 per cent, thus showing a quantitative error for the wood of 4.26 per cent; these percentages refer to the weight of the original wood. Softwoods seem to yield appreciably less carbon dioxide than hardwoods. In all instances the figures obtained are probably a little high, since a small amount of carbon dioxide is given by carbohydrate units other than uronic acids. Cellulose preparations invariably seem to yield carbon dioxide in amounts up to 0.25 per cent, but it is not as yet possible to correct for this. The error caused in the analysis of woods by calculating uronic acid furfuraldehyde as pentosan may, of course, be readily avoided by determining separately the uronic acid content of the material and then correcting the pentosan figure accordingly. Such a procedure is recommended for a more nearly exact and complete analysis of wood.

There is another possible error to consider: With straws, an appreciable proportion of the polyuronide is accounted for by hexose units, which would not be included by either furfuraldehyde or uronic acid determinations. With woods, however, errors from this source are practically negligible. There is no direct evidence of the presence in wood of hemicellulose hexosans, excepting those in the Cross and Bevan cellulose of softwoods.[1] In fact there is some good evidence to the contrary. Ritter, whose report is as yet unpublished, has shown that in both a hardwood and a softwood the total reducing value of the polysaccharide constituents when quantitatively hydrolyzed can be approximately accounted for by the Cross and Bevan cellulose plus the pentosans not in cellulose. In straws and similar materials, in which the hexosan content of the polyuronides is appreciable, the situation is much more difficult and a wholly satisfactory method of estimation has not yet been given. Norman (*28*) had recourse to an indirect and tedious method for the determination of the polyuronides, but his method is open to some criticism for reasons that will be pointed out later. Norris and Preece (*30*) avoid this difficulty of the indeterminacy of the hexoses by determining the polyuronides as a whole, using direct preparation, and then subsequently analyzing them for their constituent units. Such a procedure is far from simple and its accuracy is uncertain.

Turning to other systems of analysis, that of Dore (*5–7*) deserves attention. Devised especially for softwoods, it was intended to yield figures that could be summed up to 100 per cent. Though he prepared his Cross and Bevan cellulose fraction without previous treatment (*6*), in general he did not determine the pentosan in the cellulose. In his method, mannan was determined separately on a fresh sample of wood. He neglected to determine whether the mannan was associated with cellulose. The figure given for soluble pentosans was found by determining the furfuraldehyde yield of the chlorination liquid. Moreover, as he points out, hemicelluloses are not completely covered in this scheme. Later (*7*) he modified his method with the intention of making it more readily applicable to hardwoods, introducing a pre-chlorination treatment with cold 5 per cent sodium hydroxide. This he found to reduce greatly the time of chlorination. He gave

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[1] The presence of ϵ-galactan in western larch is not an exception, since this is water-soluble and may be classed as an extractive rather than a hemicellulose. The trace of galactose reported in other woods (up to 1.56 per cent in oak, 7) may possibly be due, at least in part, to the presence of galacturonic acid in the polyuronides, or may perhaps be due to galactose groups in them.

figures to show that this pretreatment did not affect the yield of Cross and Bevan cellulose, though the results of other workers and also the relative amounts of α-, β-, and γ-cellulose fractions cited by him would hardly support this view. He considered that the furfuraldehyde-yielding substances in woods may be divided into three classes: pentosans soluble in cold dilute alkali (corresponding to the polyuronide group); the furfural-yielding constituents of cellulose (thought by him to be oxycellulose); and a small amount of resistant pentosan removed during chlorination. In the light of recent work, the objections to Dore's procedure for softwoods are similar to those already raised against the Forest Products Laboratory methods, and may be met by the modifications suggested for those methods. With hardwoods, however, the situation is more serious, and the alkaline pretreatment recommended probably invalidates the method, as mentioned previously.

More recently a method of proximate analysis of plant materials has been put forward by Waksman and Stevens (*40*) and extensively used by Waksman in his work on the decomposition of many types of plant tissue. Though possibly of value for comparative purposes, this scheme is far from satisfactory in several particulars, especially for the hemicelluloses, since it does not indicate correctly either the distribution of this group or the quantity present. Waksman and Reuszer (*39*) have in part admitted these shortcomings. After preliminary extractions with ether, water, and alcohol, the tissue is subjected to hydrolysis for 5 hours with 2 per cent hydrochloric acid, with the intention of converting the hemicelluloses to sugar. The quantity of "hemicellulose" is then obtained by multiplying the reducing sugar in the extract by 0.9. Although it is true that the polyuronides will be hydrolyzed by this treatment, it is also true, as shown by Miller and Swanson (*25*), that a portion of the polysaccharide associated with the cellulose will also be hydrolyzed and removed. Further, the presence of uronic acids in the polyuronides provides another disturbing factor, since, as shown by Link and Niemann (*24*), these acids are in part decarboxylated to give degradation products of unknown composition and indefinite reducing power. A further and perhaps more serious error is introduced by the calculation of the hydrolyzed sugar obtained as hexose, whereas, in point of fact, from most materials, it is mainly pentose. The residual material after hydrolysis is treated with 80 per cent sulfuric acid and, after dilution and boiling, the sugars given are determined and then calculated as glucose. This on multiplication by 0.9 is said to give the cellulose content of the plant material. Although this procedure is accurate for cotton cellulose, in which no associated cellulosic polysaccharides are present, it must give a high result for many woods and cereal straws, the cellulose of which is accompanied by considerable quantities of xylan, only a portion of which would be attacked by the preliminary 2 per cent hydrochloric acid treatment. These objections render this system of analysis unsuitable when accurate information as to the amount of hemicelluloses is required.

Norman (*28*) recently examined the distribution of the furfuraldehyde constituents of straws, and proposed a method for their evaluation. Although this method takes into account both the presence of uronic acids and hexose units in the polyuronides, it is vitiated by the fact that he employed a pretreatment with hot 1 per cent sodium hydroxide for 20 minutes before chlorination, following in that the original Cross and Bevan procedure. Since an alkaline extraction was employed in obtaining the crude hemicellulose preparation that is the basis of the calculation, the preparation was probably contaminated with a portion of the xylan from the cellulose fraction, and the figures for furfuraldehyde not from cellulose were thus correspondingly increased. The former objection may be raised to the procedure suggested by Preece (*34*) in his work on boxwood. This worker also differentiates between free and combined polyuronides; the free are removed through extraction with 4 per cent cold sodium hydroxide, whereas, the combined require a hot alkali treatment for their solution. Whether this differentiation has its basis in actual chemical differences is somewhat doubtful, since the cause, at least in part, may be mechanical and physical difficulties of extraction.

This review makes clear the fact that some objections can be raised to practically all the methods of analysis and evaluation used at present. It is very desirable that each method should be critically reëxamined in the light of the recent work on the nature of hemicelluloses. As far as is possible the theoretical basis of the various shortcomings has been indicated, and means have been suggested by which the most serious ones may be avoided. A detailed survey of the distribution of the hemicelluloses in nontimber sources, which is at present lacking, would undoubtedly assist in the better understanding of this complex group.

NOMENCLATURE

The nomenclature of the hemicelluloses would be much improved by the proper use of Candlin and Schryver's term "polyuronide." More confusion than before will result, however, if this new term is used loosely to cover all the plant constituents previously called "hemicelluloses." It has been pointed out that two distinct major groups of hemicelluloses must be recognized, and that the term "polyuronide" is applicable only to the one containing uronic acid units. The other group, which has previously been referred to as polysaccharide associated with Cross and Bevan cellulose, or the readily hydrolyzable portion of Cross and Bevan cellulose, does not fall within the category of polyuronides, since, as has been shown, uronic acid units are absent. This group of substances should also have a specific name. The name "hemicellulose" itself applies accurately to this fraction, now that the polysaccharides not closely associated with the cellulose have been separated and provided with a satisfactory title. Indeed the authors would have suggested that the term "hemicellulose" be retained and limited to this group except for the fact that it would still carry its old meaning to many persons for a long time. A new name is needed, and an appropriate one appears to be "cellulosans."[2] This term indicates that this polysaccharide is composed of anhydrosugar units—hexosans or pentosans—that are intimately associated with the cellulose itself and isolated with it in the Cross and Bevan cellulose fraction.

This is not the place for a discussion of the relationship of the cellulose to the cellulosans; the relationship, however, is such that any quantitative determination of the cellulosans by methods involving either alkali-extraction or hydrolysis by acid must be on an arbitrary basis. The amount removed will depend on the experimental conditions, and there is no very obvious break in the continuity of the reaction until a portion of the pure cellulose has obviously been attacked.

The authors would retain the term "hemicellulose" as the generic name for this whole group of alkali-soluble and readily hydrolyzable polysaccharides, even though certain workers, such as Hess and Heuser, have maintained, not without reason, that literally it is both incorrect and misleading. It is thought that by this differentiation into two major groups—polyuronides and cellulosans—the members of which differ in

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[2] Preece (*34*) proposes the reintroduction of the old term "p-xylan" for the xylan associated with the cellulose of boxwood. This term, however, is obviously unsuitable for the softwoods in which xylan is not the only associated polysaccharide present, and accordingly the new term "cellulosans," which covers both hexosans and pentosans and mixtures of these, is preferable

structure, distribution, and function, the situation will be distinctly clarified and confusion avoided. Figure 1 summarizes the basis of this differentiation.

Furthermore, this classification of the hemicelluloses into two major groups gives an additional significance to the Cross and Bevan cellulose determination, since it is only by the isolation of this fraction that the two groups can be separated and be determined quantitatively. Though the differentiation effected by the chlorination process was suspected and commented upon some years ago (*12*), the basis of it is now made clear. To be emphasized also is the necessity of determining Cross and Bevan cellulose in material that has previously been treated only by neutral solvents, and of rejecting for critical work the numerous proposed modifications that include any chemical treatment before chlorination, lest, as a result, the cellulosans be diminished from their true value.

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United States Trade-Mark Law and Practice for the Chemist

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THE use of trade-marks is thought to have started many centuries ago when few people were able to read or write. The marks at that time usually comprised some figure, such as a cross within a circle, a cat's head, or some simple device that could be easily remembered. The makers of swords, hatchets, and other devices placed these marks upon their products in order that the users might know how to identify them and thus be sure of getting a hatchet of similar quality when they next needed one.

WHAT IS A TRADE-MARK?

United States law does not define a trade-mark. The United States Courts have been reluctant in defining a trade-mark. One of the most satisfactory definitions which has been given is as follows:

> A trade-mark is a distinctive word, emblem, symbol, or device, or a combination of these, used on goods actually sold in commerce to indicate or identify the manufacturer or seller of the goods.

A trade-mark must not be descriptive, because any person has a right to use descriptive terms in connection with his product, and no one has a right to withdraw such terms from public use and maintain a monopoly upon them. Furthermore, a mere phonetic spelling of a descriptive term may not be employed as a trade-mark.

On the other hand, a trade-mark must not be misdescriptive, because such a term would tend to deceive the public. The use of the mark "Syrup of Figs" for a laxative which contained no appreciable amount of fig juice was held to be deceptive by the Supreme Court in Clinton E. Worden & Company *vs.* The California Fig Syrup Company (187 U. S. 516). However, words that are merely suggestive may be employed as trade-marks, and commercial people are usually strongly in favor of this form of mark.

A color alone cannot be used as a trade-mark. For instance some of the gasoline companies have colored their gas and have attempted to register the color as the trade-mark. The applications were refused on the grounds that mere color, aside from some particular symbol or design, such as, for example, a circle, square, triangle, cross, or star, cannot constitute a valid trade-mark. This was decided in the case of In re General Petroleum Corporation of California (49 Fed. Rep. [2nd] 966).

HOW IS OWNERSHIP SECURED?

In the United States and in many other countries the owner of a trade-mark is the first person who places the trade-mark upon the goods; that is, the first person who actually uses a trade-mark is the owner of that trade-mark. This ownership comes under the old common law.

The common-law right to a trade-mark does not apply everywhere. In many countries, particularly in South America, trade-mark rights are secured by registration of the trade-mark; that is, the first person to register a trade-mark in the trade-mark office is the owner of that mark, regardless of who is the first user.

The registration plan employed in South America has caused much trouble to manufacturers in the United States by reason of the fact that natives of South America have registered trade-marks employed in the United States and then brought suit against the United States manufacturer when that manufacturer placed his goods on sale in South America. In many instances it has been necessary for the United States manufacturer to go to considerable expense to purchase the registered trade-mark. However, ownership by mere registration may change in the future, for such strong pressure was brought to bear at the last meeting of the International Convention for the Protection of Industrial Property that many of the registration countries have changed their laws to permit the filing of opposition to the registration of trade-marks within a short period after they are published, thus giving manufacturers in other countries an opportunity to object to the registration of their trade-marks by others.

In the United States, Congress has provided for the registration of a trade-mark after it has been used upon goods sold in interstate commerce. Registration of a trade-mark in the United States is not compulsory; in fact, it is not absolutely necessary. However, every trade-mark should be registered, because by this means prima facie proof of ownership is provided when suit is brought. The competitor is much more likely to respect a registered trade-mark than an unregistered one.

There are two laws relating to registration, the Act of 1905, as amended, and the Act of 1920.

Registration under the Act of 1905

The Act of 1905, as amended, provides that the owner of a trade-mark used in commerce with foreign nations, or among the several states, or with Indian tribes, may obtain registration of such trade-mark by complying with the following requirements:

> First, by filing in the Patent Office an application therefor in writing, addressed to the Commissioner of Patents and signed by the applicant, specifying his name, domicile, location, and citizenship, the class of merchandise and the particular description of goods comprised in such class to which the trade-mark is appropriated, a statement of the mode in which the same is applied and affixed to goods, and the length of time during which the trade-mark has been used; a description of the trade-mark itself shall be included, if desired by the applicant or required by the Commissioner, provided such description is of a character to meet the approval of the Commissioner. With this statement shall be filed a drawing of the trade-mark, signed by the applicant or his attorney, and such number of specimens of the trade-mark, as actually used, as may be required by the Commissioner of Patents. Secondly, by paying into the Treasury of the United States the sum of 15 dollars, and otherwise complying with the requirements of this act and such regulations as may be prescribed by the Commissioner of Patents.

The law also provides that no mark, by which the goods of the owner of the mark may be distinguished from other goods of the same class, shall be refused registration as a trade-mark on account of the nature of said mark unless such mark:

> (*a*) Consists of or comprises immoral or scandalous matter.
> (*b*) Consists of or comprises the flag or coat of arms or other insignia of the United States or any simulation thereof, or of any State or municipality or of any foreign nation, or of any design or picture that has been or may hereafter be adopted by any fraternal society as its emblem, or of any name, distinguishing mark, character, emblem, colors, flag, or banner adopted by any institution, organization, club, or society which was incorporated in any State in the United States prior to the date of the adoption and use by the applicant: Provided, That said name, distinguishing mark, character, emblem, colors, flag, or banner was adopted and publicly used by said institution, organization, club, or society prior to the date of adoption and use by the applicant: Provided, That trade-marks which are identical with a registered or known trade-mark owned and in use by another and appropriated to merchandise of the same descriptive properties, or which so nearly resemble a registered or known trade-mark owned and in use by another and appropriated to merchandise of the same descriptive properties as to be likely to cause confusion or mistake in the mind of the public or to deceive purchasers shall not be registered: Provided, That no mark which consists merely in the name of an individual, firm, corporation, or association not written, printed, impressed, or woven in some particular or distinctive manner, or in association with a portrait of the individual, or merely in words or devices which are descriptive of the goods with which they are used, or of the character or quality of such goods, or merely a geographical name or term, shall be registered under the terms of this Act: Provided further, That no portrait of a living individual may be registered as a trade-mark except by the consent of such individual, evidenced by an instrument in writing:...... And provided further, That nothing herein shall prevent the registration of any mark used by the applicant or his predecessors, or by those from whom title to the mark is derived, in commerce with foreign nations or among the several States or with Indian tribes which was in actual and exclusive use as a trade-mark of the applicant, or his predecessors from whom he derived title, for ten years next preceding February twentieth, nineteen hundred and five: Provided further, That nothing herein shall prevent the registration of a trade-mark otherwise registerable because of its being the name of the applicant or a portion thereof.

Preparation of Application for Registration

The application comprises a statement and petition accompanied by a declaration and a drawing, the forms for which are given in the pamphlet on Trade-Mark Laws issued by the Patent Office.

In filling in the statement and petition, it is necessary to name the specific goods upon which the trade-mark has been used. One cannot claim or include in the application any goods upon which he expects to use the trade-mark in the future.

Considerable difficulty is often encountered in naming the specific goods. Naturally the attorney or applicant wants to name the specific goods as broadly as possible, while the Patent Office examiner tries to keep the description as narrow as possible.

While the applicant must specify the particular goods upon which his trade-mark has been used, it does not necessarily mean that his trade-mark is limited solely to that particular kind of goods. The Courts have repeatedly held that the owner of a trade-mark has a certain field of protection around the goods upon which his trade-mark is registered, such field being the ground into which his business will normally expand under ordinary conditions of trade.

The number and the class of merchandise in which the goods fall must be given. The merchandise is divided into classes which are listed on the last page of the trade-mark publication. If the wrong class is selected, the examiner will so notify the applicant, and the application can be amended to name the correct class.

Although the Patent Office has divided merchandise into fifty classes, and the same trade-mark may be registered by different persons for different classes, the examiners and the Courts have gone further and practically divided each class into a number of subclasses.

Under the recent decisions goods are of the same class when they are placed in the same class in the official classification by the Patent Office. It is also safe to say that this rule extends even farther in view of the decision in California *vs.* Tilman (1930 C. D. 215), holding coffee, and canned fruits, vegetables, etc., are goods of the same descriptive properties, although coffee would probably be classified in Beverages, Class 45, and canned fruits in Foods, Class 46. In other words, if goods are so closely related in manufacture or distribution as to be apt to cause confusion with respect to their origin, they will be considered to have the same descriptive properties for the purpose of trade-mark registration. Other recent cases holding goods to be of the same descriptive properties are flour, and raisins, baking powder, etc., in Sunmaid *vs.* American (1930 C. D. 238); horse-radish, etc., and coffee and tea, Cheek-Neal *vs.* Hal Dick (1930 C. D. 251); gargles and mouth wash, and cosmetics, Malone *vs.* Horowitz (1930 C. D. 494.)

The next step is to state under which act one desires to file. Generally, the Act of 1905, as amended, should be named. If that is wrong, the examiner will permit amending in order to place the application under the Act of 1920.

The date when the trade-mark was first used in the applicant's business must be next determined and inserted at the proper place in the application form.

How the trade-mark is applied to the goods must be stated. Trade-marks are usually applied by fastening to the goods or apparatus small steel plates bearing the mark, or by stamping or printing the trade-mark directly upon the goods, or by molding or cutting the trade-mark in the goods. Five trade-marks as actually used must accompany the application. Where they are printed or applied by small steel tags, it is easy to send the five samples with the application. When the trade-mark is molded, stenciled, or cut into the goods or apparatus, photographs of the trade-mark may be substituted for the actual copies of the mark.

THE DRAWING

The law is clear in stating that the mark which is shown on the drawing must be the same as the mark which is actually used. There is no provision for the registration of a mark not in actual use, or where it differs from that in actual use. Therefore, care should be exercised, in making the drawing for the application, to have it appear as an exact reproduction of the trade-mark actually used on the goods.

Although the Patent Office will not permit the registration of trade-marks that are purely descriptive, it does allow the registration of marks that are suggestive but not descriptive. The registration of such marks frequently involves considerable argument with the examiner as to whether or not they are descriptive or suggestive.

An interesting recent case held that "Dry-Ice" for solid carbon dioxide is not a valid trade-mark, for it is descriptive of solid carbon dioxide which resembles ice and possesses qualities of ice in having a low temperature and being serviceable as a refrigerant. To quote the Court: "A word or collocation of words is not subject to registration as a trade-mark if it is descriptive of a quality or characteristic of the article with which it is used, though part of it is the name of something else which merely is like or resembles that article, the two things not being identical." Dry Ice Corporation of America *vs.* Louisiana Dry Ice Corporation (54 Fed. Rep. [2nd] 882).

The Supreme Court held that the word "Rubberoid" is not a valid mark for roofing material, as it is a descriptive term, because, even though the roofing contained no rubber, it had the characteristics of soft, flexible rubber. This was decided in Standard Paint Company *vs.* Trinidad Asphalt Company (220 U. S. 446).

During the time an application for the registration of a trade-mark is on file it may become involved in an interference with another party in practically the same manner as applications for patents become involved in interferences. The practice in connection with trade-mark interferences is practically the same as the interference practice relating to patent applications and, therefore, nothing further need be said about such interferences.

After an application for registration of a trade-mark is allowed, it is published in the Patent Office Gazette. The law provides for a period of 30 days after the publication within which an opposition to the registration of the trade-mark may be filed by any person who believes he would be damaged by the registration of the trade-mark. The opposer files a notice of opposition in the Patent Office. The Patent Office sends a copy of the notice of opposition to the applicant with a statement that an answer thereto must be filed within a certain time, usually 20 days. After the answer is filed, the Patent Office sets the times for taking testimony by the opposer and by the applicant, and the opposition proceeds by following the rules in equity.

Some large corporations owning large numbers of valuable trade-marks have stopped the practice of filing oppositions. When they notice the publication of a trade-mark that infringes their mark, they immediately notify the applicant that the use of his published trade-mark will be an infringement on their trade-mark, and that they will bring suit against the applicant as soon as they can locate any actual use of the proposed trade-mark. They believe that, when they file a notice of opposition, they are at a disadvantage in the Patent Office because the burden of proof is upon the opposer and the Patent Office is rather inclined to favor the applicant. However, when they go into a court of equity, they find the judge favorably inclined to uphold well-established trade-marks, and the burden of proof is upon the other party.

After a trade-mark is registered, cancellation proceedings may be brought at any time by any person who deems himself injured, for the purpose of having the registration canceled. This proceeding is brought in the Patent Office.

REGISTRATION UNDER 1920 ACT

Some years ago the United States joined the South and Central American countries in creating a trade-mark union for the purpose of permitting an applicant in one country to register his trade-mark in all associated countries for the sum of fifty dollars. This union has not been very successful so far because some of the countries in Central and South America have declined to join. One of the disadvantages of this plan, however, is that the clerks in the various countries are sometimes careless and fail to register the trade-mark. Some authorities are of the opinion that, if the trade-mark is valuable enough to register, it is worth individual registration in each country.

After this union was formed, it was found that a number of Central and South American countries provided for the registration of words and trade-marks which the United States Congress did not believe should be registered. Therefore, this country could not carry out its part of the agreement with the union. In order to overcome this defect, Congress, in 1920, passed what is known as the 1920 Act, which provides that the Commissioner of Patents shall keep "(*a*) a register of all marks communicated to him by the International bureaus, etc., and (*b*) all other marks which are registerable under the Act of 1905 except those specified in paragraphs (*a*) and (*b*) of Section V of the 1905 Act, but which have been in bona fide use for not less than one year in interstate or foreign commerce, or commerce with the Indian tribes by the proprietor thereof, etc."

The 1920 Act makes no provision for interferences, oppositions, or cancellation proceedings. The extent to which this law may be used is not even yet clearly understood, but presumably it was passed mainly for the purpose of carrying out the agreement with the union, and also for enabling citizens of the United States to register certain trade-marks which could not be registered under the Act of 1905 and thus get them registered throughout the countries belonging to the union. However, this may be, the examiners are much more lenient in registering mere descriptive words, proper names, etc., under the 1920 Act than they are under the 1905 Act. Frequently the examiner informs an applicant, after he has filed under the 1905 Act, that the application will not be allowed, but that if it is amended to come under the 1920 Act, it will then be allowed.

When the application under the 1920 Act is allowed, it is published in the Official Gazette and issued at once.

A registered trade-mark expires 20 years after its date of registration, unless it is renewed before its expiration. If it is not renewed before the expiration date, a new application must be filed and be subject to a new examination, etc.

DAMAGES

The trade-mark laws provide that the several Courts vested with jurisdiction of cases arising under the present act shall have power to grant injunctions, according to the course and principles of equity, to prevent the violation of any right of the owner of a trade-mark registered under this act, on such terms as the Court may deem reasonable; and, upon a decree being rendered in any such case for wrongful use of a trade-mark, the complainant shall be entitled to recover, in addition to the profits to be accounted for by the defendant, the damages the complainant has sustained thereby, etc.

Also the Court may order that all labels, signs, prints, packages, wrappers, or receptacles in the possession of the defendant, bearing the trade-mark of the plaintiff, etc., shall be delivered and destroyed.

ASSIGNMENT OF TRADE-MARKS

The ownership of a trade-mark cannot be assigned unless the goodwill and business in the article covered by the trade-mark is also assigned; neither can a license be granted to anyone else to use a trade-mark. The reason for this is that the owner of the trade-mark and the person who controls the quality of the goods bearing the trade-mark must be one and the same. In a recent case, for example, the following situation arose: The U. S. Ozone Company was organized to take over the business of Electric Water Sterilizer & Ozone Company, but the organization was never completed. The trade-mark was registered in the name of the U. S. Ozone Company, but it had no business and owned no goods. The U. S. Ozone Company and Electric Water Company entered into contracts appointing a selling agent who purchased goods outright and sold for their own account, the mark being applied to the goods. The Court held that the U. S. Ozone Company acquired no right to the trade-mark, that assignment by it of the registration carried no title, and that the mark belonged to the agent. (U. S. Ozone Company *vs.* U. S. Ozone Company of America, 7 U. S. Daily 710).

ABANDONMENT OF TRADE-MARKS

It takes considerable abandonment of a trade-mark to make it an abandoned trade-mark. For instance, if a trade-mark is not used for a year or two, it does not mean that it is abandoned. The abandonment must be clearly proved as an intentional wilful abandonment; otherwise, the courts will refuse to call it an abandonment. For instance, Beechnut chewing gum is a well-known product, and, when Beechnut chewing tobacco first appeared on the market, it was thought that it would be considered an infringement of the trade-mark "Beechnut" on chewing gum. However, the tobacco company had purchased a small company which had at one time used the trade-mark "Beechnut" upon chewing tobacco at a time prior to the use upon chewing gum; and that, while it had stopped the manufacture and distribution of such tobacco for about five years because of commercial conditions, it had never formally abandoned the trade-mark or given any indication of intending to abandon it. Thereupon the Supreme Court in Beechnut Packing Company *vs.* Lorrillard (273 U. S. 629) held that the tobacco company had a right to take up the use of the trade-mark again and use it.

While trade-marks are now very important, as is indicated by the saying that a trade-mark is a firm's commercial signature, they will be exceedingly important in the future if the Capper-Kelly Bill passes. This bill has been brought out by the Committee on Interstate and Foreign Commerce with the recommendation that it be passed. Among other things, the bill provides:

> That no contract relating to the sale of a commodity which bears (or the label or container of which bears) the trade-mark, brand, or trade-name of the producer of such commodity, and which is in fair and open competition with commodities of the same general class produced by others, shall be deemed to be unlawful, as against the public policy of the United States, or in restraint of interstate or foreign commerce, or in violation of any statute of the United States, by reason of any agreement contained in such contract.

In other words, the manufacturer may control the resale price of his product.

The object of the bill is to prevent the selling of well-advertised trade-marked goods at "cut-throat" prices and thereby eliminate a certain amount of unfair competition.

RECEIVED June 2, 1932.

PRACTICALLY DEPENDENT on outside sources before the war for its requirements of chemicals and allied products, Brazil today produces more than half of its consumption of these commodities, according to the Commerce Department.

The development of the domestic industry has been retarded by a number of factors, including insufficient native raw materials, lack of technicians and skilled labor, an inadequate internal transportation system, high manufacturing costs, and sharp foreign competition. On the other hand, however, domestic production has been markedly favored by fluctuating exchange, by the provisions of the Brazilian customs regulations, and by the establishment in the country of branch plants of foreign chemical interests.

The great bulk of Brazil's domestic output of chemicals is in the lower-priced commodities. For quality and the higher-priced chemical products the country looks to the United States and Europe, and imports annually some $15,000,000 to $20,000,000 worth. With the exception of certain waxes, oils, gums, and animal fertilizers Brazil is not a chemical-exporting country, although it supplies practically the entire world consumption of carnauba wax.

In 1928 Germany supplanted the United States as the leading foreign shipper of chemicals to Brazil and has since maintained this position. The United Kingdom ranks third and France fourth as a source of supply. In 1931 there was a marked falling off in the value of United States chemical trade with Brazil, resulting primarily from the sharp drop in rosin and turpentine totals, partly attributable to price declines.

President's Address

Stabilized Research—A National Asset

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THIS, the eighty-fourth meeting and fifty-sixth year of our Society, finds us at the turning point, we hope, of one of the most severe crises of our economic history. Following as it does the most destructive war and the greatest prosperity ever experienced, it is well that we evaluate our science of chemistry in its present and probable future relation to the economic order.

Chemistry's successes have been many. One need mention only a few of them to bring to mind an almost endless list of achievements—achievements that have revolutionized our mode of living and produced our present civilization. The vulcanization of rubber has made possible not only the raincoats and life preservers for which Goodyear struggled, but also the change from the noisy clatter and restricted course of the metal wheel and its fixed track to the quiet comfort and freedom of the pneumatic tire and the open highway of our modern transportation; new metals, alloys, and insulation have made possible our modern radio with its now commonplace miracles, such as the carrying of the voice of our nation's chief executive to the remotest hamlet; synthetic dyes, motor fuels, medicines—but we need not continue.

These successes represent only a beginning, for whether we wish it or not the scientific order with all its implications is upon us. We must press on in our search for new knowledge and a better order of things. This we can do only as we so organize and control our effort that it may become the most stable of all our activities. Certain it is that research, academic and industrial, stabilized through prosperity and depression, represents a potential national asset of tremendous value. Our problem therefore is to find the means whereby we can render this effort stable and continuous. Ultimately our problem may be: How can we best remove from the minds of our executives the now all-too-prevalent feeling that research is only partly necessary, to be suspended in times of depression and neglected as unimportant even in times of great prosperity? But is not our immediate problem: How can we ourselves acquire a personal conviction that matches the fact of the importance to our future welfare of unremitting research effort?

Research as a mode of living, as a means of employing one's intellectual power, as an ideal, is dear to the hearts of all of us; but how many of us think of it in times of depression as a real asset of the nation, an intellectual gold mine, the seed and germ of all new economic life, the stocks and bonds of future effort which will not need to sell at a discount in Wall Street? How many of us are so convinced of the value of new knowledge that we would recommend to our board of directors, to our universities, or to our government, that financial reserves be sacrificed rather than intellectual reserves? If we find our personal reserves, our corporation reserves, our national reserves shrinking three to one and in some cases reaching the vanishing point, which would we consider as the activities last to be abandoned in a program of retrenchment?

Let us for the moment imagine that we are called in to advise our government what to do to meet the present crisis. If we were bankers, probably we would feel we should stress the necessity of a high gold ratio to the issued currency, or, if labor union leaders, the need of providing labor for those out of employment. As research men what would we recommend? Is it our conviction that the most needful thing is that we proceed to get our records as full of new knowledge as our vaults are of gold?

We cannot complain that our leading governments today lack interest in the discovery of new facts and new relationships, but it can be questioned whether they do not divert too much of their research effort toward armament and munitions compared with that expended in the field of pure science and in the utilization of now unused knowledge for the increase of general welfare. Our statesmen are to be congratulated on the extent to which science has been employed in the promotion of agriculture, forestry, fishery, transportation, and other of our physical activities. Yet we would raise the question of whether or not we are diverting enough of our accumulated wealth toward the furtherance of the broader aspects of life's needs, neglect of which is causing us endless pain and keeping us from achieving the greatest value in our living.

At times we seem to forget the extent to which our present condition of well-being is dependent on new ideas acquired at an earlier period. Tradition, if not history, tells us that our whole modern factory system had its beginning in an idea that Arkwright chanced upon one day when startling his wife as she worked at the spinning wheel. The wheel was knocked over and, continuing to spin, suggested to Arkwright the idea of several spindles all driven by one wheel. For centuries on end it had required approximately six spinners for one weaver, as a spinner could spin but one thread at a time. Then in 1760 Arkwright brought forward his invention. Prices for woven fabrics dropped from 39 to 3 shillings per yard because of the reduction in required labor. The number of laborers needed was reduced at first six to one, then twenty-eight to one; later, much greater reduction occurred. The hand loom disappeared and the factory system was upon us. For the first time in history one man could do the work which formerly had required many.

Would those who oppose the research, discovery, and invention of the machine age have us go back to the days of homespun? We think not. Shall we abandon Whitney's cotton gin and bring back slavery? Most of us would say "No." Then why should we be content with haphazard financing of the most important activity of our civilization? We must have new knowledge and apply it to life if our civilization is to advance to the point where disease and poverty are eliminated and where there is that increment of wealth that gives to all relief from drudgery "and leaves the soul free a little."

We do not suffer today from lack of teaching or of teachers who understand the fundamentals of research. We do not suffer from lack of men trained and ready to carry on research. We do not suffer from lack of knowing how to proceed. But we are suffering, and that seriously, from the failure of many in authority to appreciate that in times of financial stringency money can be saved to least advantage by withdrawing the means that enable us to push forward into the new and unknown fields where lie the sources of all future wealth and progress.

In a previous paper we pointed out facts well known to every research man—namely, that (1) a minimum of five to seven years, on the average, is likely to be needed for bringing a research project from its first inception to its commercialization; (2) the amount of money required increases rapidly if the research proves successful and its industrial application is undertaken, and that the greater the success, the greater in all probability will be the need of money for development, manufacture, and sale.

What we would now emphasize is the necessity of continuity in our research program if we are to insure the financial gains we have a right to expect, if we are to provide the living conditions our people have a right to demand, and if we are to attain those higher things in life that can come only with health and freedom from drudgery.

Lawrence V. Redman

The loss from discontinuity of effort is twofold: (1) the loss of investment which results from premature cessation of effort, and (2) the loss due to postponement of achievement. Time once past can never be rewon by a nation any more than it can by an individual. Advancement in time of invention is the essence of progress. Those nations that have acquired much new knowledge in the past are today in the forefront of civilization. It is equally true that those nations that have neglected the acquisition of new knowledge have failed or are failing.

We can place no limit on the progress that new knowledge may bring. If as a people we are first to adopt a policy of stabilization of research for our industries, our universities, and our government, we cannot fail eventually to place this nation in the forefront of the nations of the world. But how is such stabilization to be brought about? Plainly it can come only through adoption of the policy of laying by, during a period of prosperity, funds to be employed during a period of depression.

In the long run, with continuity of a broad program of research we can be assured of satisfactory results. Of course, success for any one research project cannot be guaranteed any more than insurance can be safely conducted on the basis of one risk. But many risks make for such a high degree of certainty that research, like insurance, becomes one of the most stable of our institutions.

Perhaps it is this lack of certainty in the case of single research projects that has tended to make us timid even when we contemplate a broad program of research. But the past history of invention shows that, viewed as a whole, it has been an overwhelming economic success. There can be no doubt that modern organized research would show itself to be an even greater success. Nor is there any doubt that under intelligent control and consistent maintenance, a relatively small program of research may be depended upon to pay dividends. The business man has learned to apply the law of averages in his own field, and, if he has the facts, he will be led to acquire faith in the law of averages as applied to research. To this end a research into research as at present conducted would seem most desirable. Recent figures published on gold mining indicate that less than 50 per cent of all gold mines have ever paid a dividend, and less than 16 per cent have ever been a profitable investment to the owners. Yet we all think of gold mining as very real and profitable. If there could be compiled statistics to show what we spend in acquiring new knowledge as compared with the gain resulting from such new knowledge, it is safe to say we would be impressed by the size of the returns as compared to their cost. You are already objecting that we cannot evaluate the results of those researches that lead to the preservation of life and the promotion of health and happiness. These cannot be expressed in terms of money, yet they constitute one of the greatest arguments in favor of the stabilization of research as a national duty. But if the returns from what we may call our commercial researches could be compiled, we can have no doubt that the over-all results would show financial gain above that of any other legitimate type of investment.

Long-time financing is familiar enough to those who build edifices, roads, bridges, canals, or other public or private projects promising long terms of service. Some of our railroad bonds mature almost as far in the future as the discovery of America is in the past. But long-time financing of research is not yet a habit of mind with our financial men. Is it with us research men? Few of us but agree that the increment of knowledge is important; yet how important? Is it so vital that we would sacrifice anything short of the means to health and sustenance in order that it be not neglected? Perhaps that is the question we must decide for ourselves, and decide in the affirmative, before we can hope to be able to induce our executives to acquire enthusiasm in times like these for the great cause of stabilized research. But surely, if research is the most profitable of all human effort, we are not only justified but obligated to do everything in our power to see that the financing upon which it rests is of the most permanent form that can be devised. Fortunately at our universities research in the pure science is given, through endowment, large assurance of continuity. Now let intelligent, painstaking application of this fundamental knowledge to life's needs also be "endowed," and the funds for both be increased. Large dividends will be returned.

Whitehead has said: "The greatest invention of the nineteenth century was the invention of the method of invention." The "occasional genius or occasional lucky thought" were replaced by organized, systematic research. We venture the prediction that some day it will be said that the greatest invention of the twentieth century was the method of providing continuity of effort in research. With Adelbert Ames, we would employ surplus labor in "nonconsumable," wealth-producing, civilization-advancing activities, of which, to our mind, research is the outstanding example. Research is the heartbeat of modern civilization; it should become the instinct of national self-preservation. There would then be no need to preach stabilized research, or to plead for means to bring it about.

AMERICAN CONTEMPORARIES

Wilder D. Bancroft

WILDER D. BANCROFT

WILDER D. BANCROFT has just reached the age where he may be included in these thumb-nail sketches. Gaged by his looks, save for his recently gray hair, he would be taken for a much younger man, but on the basis of his published work he is nothing less than a Methuselah. Many a professor on retiring would feel that his duty in research and as a teacher had been fully performed by the study of a twentieth as many problems and the guidance of a twentieth as many graduate theses as those studied and guided by Bancroft.

Beside teaching and research he has given much time to the AMERICAN CHEMICAL SOCIETY. He was president in 1910, and as past president has been active in its councils ever since. He was president of the American Electrochemical Society in 1905 and 1919, and served as lieutenant-colonel in the Chemical Warfare Service during the war. For thirty-six years he has edited the *Journal of Physical Chemistry*. This was long a single-handed enterprise, founded and financed by himself because there was then no other American journal into which the articles he and his students were producing would fit.

A big active body, initially athletic (end on the Harvard football team), and kept in shape by plenty of golf, a big active mind, and a lot of personality mark this man who has been the outstanding professor of chemistry at Cornell for thirty-seven years. Thousands of Cornell chemists trained under him may have forgotten what facts he taught them, but few have forgotten what they learned about how to think, how to recognize a variable, and how to attack a problem.

Independence of thinking, the ability to appraise things for what they are rather than what others report them to be, is the legacy "Banty" has left to many college generations of students.

He was born of an old Boston family; his great-grandfather was a noted Unitarian minister and author, and served in the Revolution. His grandfather, George Bancroft, founded the Naval Academy at Annapolis, was minister to Great Britain and Germany, and wrote the "History of the United States." Wilder D.'s skill with the pen is hereditary. Whether or not it comes from his revolutionary forbear, he has independence. In fact, few people can be as independent as Banty has always been. He has been financially in such a position that, until his family became large, he did not draw his university salary, so he has never had to worry, and he is entirely incapable of worrying. Yet, no matter how obscure his origin might have been or what his financial status, one could never imagine Banty as the boot-licking or temporizing type of professor. In fact, he would probably be unhappy if everybody agreed with him. He doesn't mind being in the minority.

One summer on a Cornell chemists' boat ride, big straw hats of the farmer type were provided. Banty wore his on the campus for a week or so, until Mrs. Bancroft took it away from him. It wasn't what other professors were wearing just then, but it was a perfectly good hat and was handy. As long as it kept the sun off, it suited Banty just as well as a Panama.

He is not very much interested in some of the things the average professor cares for. Though he has been a full professor for some thirty years, and has a Leipzig Ph.D., he never uses either title, and always answers the phone, "Mr. Bancroft speaking." He turned down an election to Sigma Xi with a comment on its being a sort of mutual admiration society.

In 1923 he was given the honorary degree of D.Sc. from Cambridge University. He accepted this, but the story goes that underneath the academic gown was a vivid golf suit, so that after the ceremony there need be no delay in turning to something really important.

Striking sports costumes have always been a weakness with him. Back in 1901 van't Hoff visited the United States, and made a special trip to Ithaca to visit the then very young, but already world-prominent Cornell professor. In his diary van't Hoff describes this visit and comments equally upon his host's sports costume and his skilful handling of the reins on a trip to Taughhannock Falls by way of the lake road, then very far from improved. Although a sufficiently skilful driver of horses to impress van't Hoff, at least, Banty does not drive a car.

One's mental picture of him is as he enters the classroom with a bag full of bound journals which he dumps on the desk and from which he puts on the board tables of data and curves from various workers, which he knits together into a clear and definite story, but in which the chapters often show something quite different from what their original authors thought they meant. Many of his published papers, especially those in the *Journal of Physical Chemistry*, consist of pages of quotations from different authors who didn't get anywhere, with a few experiments aimed to unearth the previously neglected variables, and a few paragraphs of Bancroft fitting together the apparently discordant facts into an explanatory theory that does get somewhere. What the facts meant to those who observed them is nothing to Bancroft, what they mean to him is everything. He dislikes doing something that has already been satisfactorily done and prefers to start where the others left off. To this end he is an omnivorous reader and a marvelous rememberer. He can tell you the name of the worker, the journal in which the work was published, the year and quite close to the page, not only in regard to classic work but also to thousands of minor articles, especially those that stick out in his mind like a sore thumb because they do not fit into ordinarily accepted theory. Abstracts do not suffice him. At one time he needed to find out just exactly what the author of a Russian article said. Instead of getting the article translated, he learned Russian so he himself could study the article.

He is not at all interested in spending months on some precise experiment in order to chase down another decimal place in some constant. Too many things are still so discordant that they need to be straightened out by qualitative experiments before quantitative ones are in order. Thinking is much more important to Banty than is experimenting. He prefers to figure out a theory that can be tested and outline a few crucial experiments to test it rather than to flounder around with hundreds of experiments and then evolve the theory.

His comment on one of his students who was rated much higher by Banty than by his colleagues at Cornell was: "Yes, T. is lazy, but if you back him into a corner, he will think."

After Bancroft has thought and determined in his own mind what the facts are and what they mean, he is willing to tell the world about it in no uncertain terms, and it is a matter of supreme indifference to him whether anyone else has the same opinion. This holds whether the subject is one on which there is much expert opinion or not, and whether Banty has previously worked in that field or not.

Hence, to many experts whose toes have been stepped upon in his appraisal of their opinions, his name is anathema. But Banty has been right so many times that the chances of his being right when he is the only one holding an opinion are still such that, by and large, it's a fairly safe bet to gamble that the vast majority of his opinions will ultimately prove correct.

With all his positiveness, with his way of replying to adverse discussion (always striking and in later years often too bitingly sarcastic), and with a decided degree of intolerance for those who do not see things as he does, he has yet opened the pages of the *Journal of Physical Chemistry* to various articles far from orthodox and probably due to be exploded in time. Banty is as likely to explode these as anybody else when he gets around to it.

Some professors pick out a little field, and they and their students stay peaceably within its confines. A Texas ranch couldn't hold Banty, he'd always be sticking his nose over the line. He started out as an orthodox physical chemist, one of his early works being a book on the phase rule. Many salt and alloy systems were studied by him and his students, but he soon took electrochemistry under his wing and in notable articles on the "chemistry of electrochemistry" he straightened out many points then obscure. In this period he and his students worked out the foundations on which modern chromium plating is based.

The classic work of Sargent was partly carried out as a thesis and partly afterwards at Bancroft's expense. Banty tried to arouse commercial interest in chromium plating at that time, for he could see its many applications, but he was ahead of the times, and others later cashed in on the facts he had brought to light. When industry was ready to take the matter up, Banty's interest was somewhere else. During the electrochemical phase of his interests, he wanted a special generator set that would give high amperage with great flexibility in voltage for some special electrochemical work, but the bids were far above what the university could afford, so Banty made up the difference.

Among his outstanding contributions to physical chemistry has been the correlation of the scattered work in, and the development of a general theory of contact catalysis. The main points of his theory have been substantiated by the developments of the last fifteen years. Others have since tilled that field exhaustively, without straying much from it, and their names are now more closely connected with it in the minds of the younger generation, but Bancroft's contributions were fundamental and of lasting value.

Photography then came in for a good deal of his attention, and next he became interested in colloid chemistry, starting one of the first college courses on that subject in this country. He did pioneer work on emulsions, being the first to draw definite attention to the two possible types of emulsion and to deduce a working method of obtaining either type at will. Many commercial developments of the present day along the line of asphalt emulsions, for example, clearly trace their descent from the work of Bancroft and his collaborators at Cornell. Pedagogic methods occupied some thought, with his outline of "pandemic chemistry."

Then he made a few excursions into physics, with studies of the plasticity of clay and the work on "blue eyes and blue feathers." At the moment he is deep in the proteins and in physiological chemistry, having the time of his life in the work on insanity, asthma, and drug-addiction. These and myriads of other problems have occupied his attention from time to time. And today Bancroft can and does discuss any of them with as complete recollection of facts and theories as when each was his pet. His is no single-track mind.

With all his interest in science, his interest in athletics also continues unabated. He knows more about modern football than the average undergraduate does. He knows all the big league batting averages and slips away from a Chemical Society meeting for a ball game now and then. A colleague who slipped away with him one day says he'll never forget the yell Banty let out when Babe Ruth obligingly hit a home run.

Perhaps nobody has learned much tact from Banty, but at any rate nobody ever learned from him how to pussy-foot. His best friends will not deny that he has his faults, but his faults are those of strength, not of weakness. Without his positiveness and self-sufficiency, he would not be the personality he is, nor have made so deep an impression on his students.

Is it not in the order of things that a few investigators and educators of his type should be scattered through our universities to leaven the mass who teach only what everybody accepts, whether it is right or wrong, instead of what they have thought out for themselves?

To have watched a mind like his work, to have had his guidance, and perhaps to have gained some degree of his independence of thought are privileges that make any Cornellian who has worked under him proud to class himself as "one of Banty's men." H. W. GILLETT

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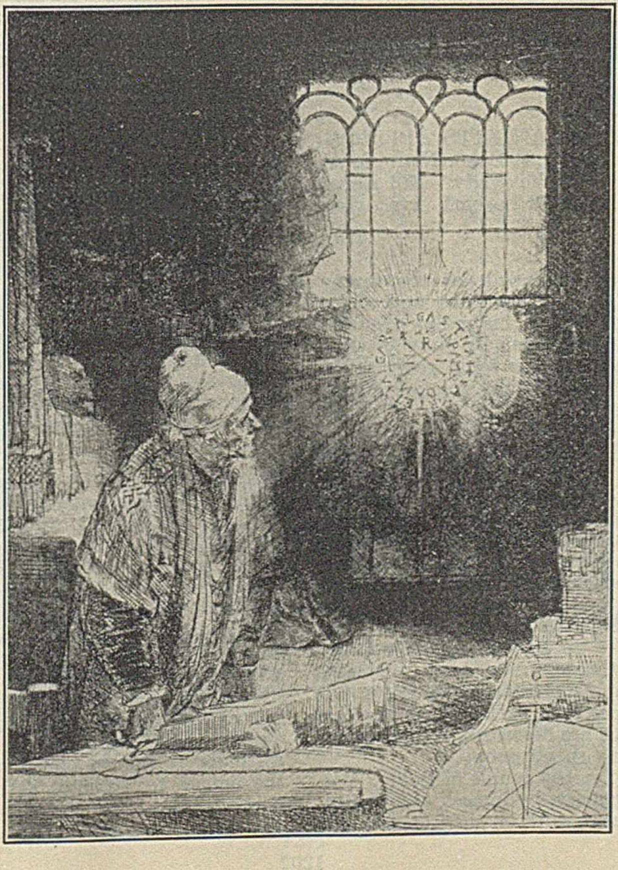
Dr. Faustus

by

Rembrandt van Ryn



While Goethe's Faust is based largely on legend, there seems to be some basis of fact in the story, in that Dr. Johann Faustus, a German astrologer, alchemist, and soothsayer, was active in South Germany during the first half of the 16th Century. A tower is still standing at the Abbey in Knittlingen in Wuerttemberg, in which Faustus is said to have carried on his alchemical experimentation.

(No. 21 of Percolator Series. The original is an engraving. See page 1173, this issue.)

BOOK REVIEWS

THE FREEZING, STORAGE AND TRANSPORT OF NEW ZEALAND LAMB. *By Ezer Griffiths, J. R. Vickery, and N. E. Holmes.* Department of Scientific and Industrial Research, Food Investigation Special Report No. 41. His Majesty's Stationery Office, London, 1932. Price, 7 s. 6 d.

This report presents in detail the results of a scientific study of the present methods employed in the cooling, freezing, storage, and transportation to England of New Zealand lamb and mutton. Eighteen freezing works were visited and the conditions in six of them analyzed. In addition, fifty-eight special lots of lambs, comprising eight hundred and nine carcasses, were followed all the way through the processes. The transport of the carcasses from the cold stores to the ship, the overseas transport, the transport from docks to London cold stores, and the cold stores in London were also thoroughly investigated. A great mass of data was recorded and analyzed.

The purpose of the investigations was to ascertain how far the conditions of freezing, storage, and transportation of New Zealand mutton and lamb could be modified so as to improve its "bloom" and general quality. Bloom is defined as the appearance of freshly killed meat.

It was found that the average loss of weight from prime carcasses during cooling, freezing, storage for 28 days in New Zealand, ocean transport, and storage for 28 days in Great Britain was 3.65 per cent. For lambs of second quality the loss was slightly greater. The average loss of weight for the trade as a whole is 3.95 per cent. This loss in weight is caused by evaporation of water from the superficial tissues of the carcasses, and thus these tissues become desiccated and lose their bloom. The longer carcasses are stored, the greater the loss of weight, and therefore of bloom.

The stockinets now used in covering lamb carcasses were found to be inadequate to protect the carcasses from serious desiccation and loss of bloom. The authors recommend wrapping carcasses in an odorless material of low permeability to aqueous vapor—e. g., several layers of waxed paper. Experiments carried out during the survey proved that such wrappings preserved the bloom.

This report is a valuable contribution to the literature on the freezing of meat and the transportation of the frozen product. The conclusions reached by the authors are logical and would have been predicted by a theoretical consideration of the problem.

Donald K. Tressler

CHEMICAL ANALYSIS BY X-RAYS AND ITS APPLICATIONS. *By Georg von Hevesy.* The G. F. Baker Nonresident Lectureship in Chemistry at Cornell University. 333 pages. McGraw-Hill Book Company, Inc., 370 Seventh Ave., New York, 1932. Price, $3.00.

In general, published lectures are intended for the musty oblivion of library shelves. Von Hevesy has done well under this burden in giving a running account of his major scientific contributions. Quantitative chemical analysis by x-ray spectroscopic methods serves as a background for some geochemical discussions and as an incidental theme in an account of the discovery and properties of hafnium.

The author speaks: "The great advantages of the x-ray method become especially conspicuous in the field of exact quantitative analyses where this method is, in most cases, of much greater use than the optical one." Two methods of x-ray analysis have been developed—one using fluorescent radiation, the other direct. In both instances determinations are made by comparison with an emission line of an element added in known concentration. If quantitative results are to be obtained, the selection of the reference line, conditions of excitation, and possible absorption effects must be carefully considered. The limiting detectable concentration of an element in mineral substances is about 0.01 per cent; the accuracy when moderate concentrations are considered can approach some parts per thousand, but is usually about 1 per cent. The art of carrying out analyses and the apparatus used are described in some detail after a cursory introduction to x-ray spectroscopy.

The finding of hafnium is rooted in the genius of Bohr. Von Hevesy gives an account of its discovery, by himself and Coster, followed by a summary of subsequent work on the isolation and the properties of its compounds. The most conspicuous property of the hafnium is its great chemical similarity to zirconium. This similarity, rather than rare occurrence, preserved the discovery of the element for a late day.

The last 60 pages (the third part) of the book treat of the chemical composition of the earth and of the cosmos. Clark's and Washington's data on terrestrial rocks, Merrill's and Farrington's on meteorites, and Russell's on the constitution of the solar atmosphere are discussed. The x-ray spectroscopic method was used in the determination of some minor constituents of meteorites and standard mixtures of central European intrusive rocks. A summary is given of the abundance of the elements in igneous rocks, and in meteoric stones and irons.

Sterling B. Hendricks

THE SCIENTIFIC PRINCIPLES OF PETROLEUM TECHNOLOGY. *By Leo Gurwitsch and Harold Moore.* 2nd edition. xii + 572 pages. D. Van Nostrand Company, Inc., 250 Fourth Ave., New York, 1932. Price, $8.00.

The new English edition of the well-known work by the late Leo Gurwitsch, translated and revised by Moore, includes a considerable amount of new information which brings the book well up to date. This information is selected to make the book more specifically adapted to the needs of the American petroleum technologists, which is very valuable, as the original work was based primarily on the experiences with Russian crudes.

With few exceptions, the text included in the first English translation is left intact, and additions are inserted in appropriate places without disturbing the integrity of the original work. Several new sections dealing with the power factor of insulating oils, tube still distillation, and hydrogenation of petroleum are introduced, adding to the value of the book, although the section on hydrogenation might have been presented in a more critical form.

It is to be regretted that the few omissions or misleading notations persist through the Russian, German, and English editions. Thus on page 223 the units chosen for expressing the electric conductivity of oils, as well as the temperature at which the measurements were made, are not given. The method of writing numerals in the form $2.5.10^{-15}$ is also misleading, as the same notation is used for separating the decimals and for indicating the multiplication sign. The total number of such omissions or of misprints is too small, however, to be of real inconvenience to the reader. A slightly more elaborate subject index appears desirable.

As in former editions, the tremendous amount of information on chemistry, physics, and refining of petroleum collected on comparatively few pages is astonishing; the logical order in their presentations, clearness of discussions, and proper selection of references makes the book invaluable both to beginners and to those with long experience in the petroleum industry.

V. Kalichevsky

ENZYCLÖPADIE DER TECHNISCHEN CHEMIE. BAND IX. SALPETER BIS TINONFARBSTOFFE. *By Fritz Ullmann.* 2nd revised edition. 835 pages. Urban and Schwarzenberg, Berlin and Vienna, 1932. Price, paper, 45 marks; bound, 54 marks.

Previous volumes of this series (of which there are to be 10 volumes) have already been reviewed [Ind. Eng. Chem., **21**, 393, 889 (1929); **22**, 200, 1024 (1930); **23**, 248, 973 (1931); **24**, 476 (1932)]. The present book is quite up to the standard of the previous volumes. Previous reviews have emphasized the importance of this exhaustive work, with its wealth of literature and patent citations. Among topics covered in this volume are: nitric acid, hydrochloric acid, oxygen, lubricants, sulfur, sulfur dioxide, sulfuric acid, sulfur dyes, silk, soaps, selenium, silver, silicon, starch, dust explosions, stearic acid, sterols, nitrogen, straw and straw pulp, strontium, sublimation, sulfonation, tobacco, tannins, tantalum, tellurium, temperature measurement, textile oils and soaps, thallium, and thorium. An index to the volume is included as a separate, which, with the indices to Volumes I–VII and VIII, furnishes a complete guide to all of the encyclopedia published so far. Volume X will contain a complete subject index.

C. J. West

MARKET REPORT—SEPTEMBER, 1932

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, SEPTEMBER 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals

Acetaldehyde, drums, lc-l., wks.	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.12
Adipic	lb.	.72
Linoleic	lb.	.16
Ammonium linoleate, drums	lb.	.11
Amyl furoate, 1-lb. tins	lb.	5.00
Aroclors	lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	1.00
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Crotonaldehyde, 50-gal. drums	lb.	.32
Dichloroethyl ether, 50-gal. drums	lb.	.06
Diethylene glycol, drums	lb.	.14
Monobutyl ether, drums	lb.	.24
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.50
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.30
Ethyl acetoacetate, 50-gal. drums	lb.	.65
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorocarbonate, carboys	lb.	.30
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Ethylene chlorhydrin, 40%, 10-gal. cbys.	lb.	.75
Dichloride, 50-gal. drums	lb.	.05
Glycol, 50-gal. drums	lb.	.25
Monobutyl ether, drums, wks.	lb.	.24
Monoethyl ether, drums, wks.	lb.	.17
Monoethyl ether acetate, drums, wks.	lb.	.19½
Monomethyl ether, drums	lb.	.21
Oxide, cyl.	lb.	2.00
Furfuramide (tech.), 100-lb. drums	lb.	.30
Furfuryl acetate, 1-lb. tins	lb.	5.00
Alcohol, tech., 100-lb. drums	lb.	.50
Furoic acid (tech.), 100-lb. drums	lb.	.50
Glyceryl phthallate	lb.	.26
Glycol stearate	lb.	.18
Isopropyl ether, drums	lb.	.10
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs.	lb.	1.15
Methyl acetate, drums	gal.	1.20
Cellosolve, *see* Ethylene glycol monomethyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Paraldehyde, 110–55 gal. drums	lb.	.20½
Phosphorus oxychloride, 175 cyl.	lb.	.20
Propyl furoate, 1-lb. tins	lb.	2.50
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.15
Distilled	lb.	.40
Tetrachloroethane, 50-gal. drums	lb.	.08
Trichloroethylene, 50-gal. drums	lb.	.10
Triethanolamine, 50-gal. drums	lb.	.40
Trihydroxyethylamine linoleate	lb.	.40
Trihydroxyethylamine stearate	lb.	.35
Vinyl chloride, 16-lb. cyl.	lb.	1.00
Zinc dithiofuroate, 100-lb. drums	lb.	1.00
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

Chemicals Previously Quoted

Acetanilide, U. S. P., powd., bbls.	lb.	.22
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks.	lb.	.10¼
Acetphenetidin, bbls.	lb.	1.25
Acid, acetic, 28%, c/l., bbls.	100 lbs.	2.75
56%, c/l., bbls.	100 lbs.	5.10
Glacial, c/l., bbls.	100 lbs.	9.14
Glacial, U. S. P., c/l., carboys	100 lbs.	9.64
Acetylsalicylic, bbls.	lb.	.75
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb.	.40
Boric, bbls.	lb.	.04
Butyric, 100% basis, cbys.	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.04½
Chromic, 99%, drums	lb.	.13
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.29
Cresylic, pale, drums	gal.	.45
Formic, 90%, cbys., N. Y.	lb.	.10¼
Gallic, U. S. P., bbls.	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.75
Lactic, 22%, dark, bbls.	lb.	.04
48%, light, bbls., wks.	lb.	.11
Mixed, tanks, wks.	N unit	.07
	S unit	.08
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	nom.
Nitric, C. P., cbys.	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic	lb.	1.45
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls., c/l.	lb.	.07½
Sulfanilic, 250-lb. bbls.	lb.	.14½
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.23
Tartaric, U. S. P., cryst., bbls.	lb.	.22½
Tungstic, kegs	lb.	1.40
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.56½
Amyl, from pentane, tanks	lb.	.176
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.123
Cologne spirit, bbls.	gal.	2.69
Denatured, No. 5, comp. denat., c/l., drums	gal.	.396*
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	1.00
Isopropyl, ref., drums	gal.	.60
Propyl, ref., drums	gal.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.57
Alpha-naphthylamine, bbls.	lb.	.32
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.30
Chrome, casks, wks.	100 lbs.	4.50
Potash, lump, bbls., wks.	100 lbs.	3.35
Soda, bbls., wks.	100 lbs.	3.45
Aluminum, metal, N. Y.	100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.15
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.25
Iron-free, bags, wks.	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks.	lb.	.05625
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.35
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.25
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls.	lb.	.08½
Oxalate, kegs	lb.	.22
Persulfate, cases	lb.	.20
Phosphate, dibasic, tech., bbls.	lb.	.08½
Sulfate, bulk, wks.	100 lbs.	1.05
Amyl acetate, tech., from pentane, tanks	lb.	.157
Aniline oil, drums	lb.	.14½
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.45
Antimony, metal	lb.	.05⅜
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.07½
Salt., dom., bbls.	lb.	.20
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Argols, red powder, bbls.	lb.	.07
Arsenic, metal, kegs	lb.	.27
Red, kegs, cases	lb.	.09⅜
White, c/l., kegs	lb.	.04
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	47.00
Chloride, bbls., wks.	lb.	.03¾
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05¼
Nitrate, casks	lb.	.07
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzidine base, bbls.	lb.	.65
Benzol, tanks, wks.	gal.	.20
Benzoyl chloride, drums	lb.	.40
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, drums	gal.	.75
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.22
Beta-naphthylamine, bbls.	lb.	.58
Bismuth, metal, cases	lb.	.90
Bismuth, nitrate, 25-lb. jars	lb.	.95
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.10
Blanc fixe, dry, bbls.	ton	65.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.018
Bordeaux mixture, bbls.	lb.	.11½
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butyl acetate, drums, c/l.	lb.	.159
Cadmium bromide, 50-lb. jars	lb.	1.40
Cadmium, metal, cases	lb.	.55

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* Delivered metropolitan area.

Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	2.40
Calcium acetate, bags	100 lbs.	2.50
Arsenate, bbls.	lb.	.05½
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	21.00
Cyanide, 100-lb. drums	lb.	.30
Nitrate, bags	ton	35.00
Phosphate, monobas., bbls.	lb.	.07½
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bags,	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Jap., slabs	lb.	.40
Carbazole, bbls.	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.051
Carbon black	lb.	.0275
Carbon dioxide, liq. cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.06¼
Casein, stand. gr., bbls.	lb.	.06½
Cellulose acetate, bbls.	lb.	.80
Cerium oxalate, kegs	lb.	.33
Charcoal, willow, powd., bbls.	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq., c/l., cyl.	lb.	.04
Chlorine, tanks	100 lbs.	1.55
Chlorobenzene, mono-, drums	lb.	.06
Chloroform, tech., drums	lb.	.15
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks.	gal.	.10
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	1.25
Cod-liver oil, bbls.	bbl.	30.00
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec.	100 lbs.	6.25
Copper carbonate, bbls., 52/54%	lb.	.15½
Chloride, bbls.	lb.	.22
Cyanide, drums	lb.	.39
Oxide, red, bbls.	lb.	.15½
Sulfate, c/l., bbls.	100 lbs.	3.00
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.17
Cyanamide, bulk, N. Y.	Ammonia unit	.97½
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls.	lb.	2.35
Dibutylphthalate, drums, wks.	lb.	.218
Diethylaniline, drums	lb.	.55
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.26
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls.	lb.	.13
Dinitronaphthalene, bbls.	lb.	.34
Dinitrophenol, bbls.	lb.	.23
Diphenylamine, bbls.	lb.	.34
Diphenylguanidine, bbls.	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot.	lb.	.80
Ether, conc., drums	lb.	.09
Ethyl acetate, tanks, c/l.	lb.	.09
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene dichloride	lb.	.05
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks.	lb.	.25
Feldspar, bulk	ton	6.50
Ferric chloride, tech., bbls.	lb.	.04½
Ferrous chloride, cryst., bbls.	lb.	.06
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls.	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls.	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, c. p., drums	lb.	.09¾
G salt, bbls.	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.46
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls.	lb.	.12
Iodine, crude, 200-lb. kgs.	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot.	lb.	6.00
Iridium, metal	oz.	160.00
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y.	100 lbs.	3.60
Lead acetate, bbls., white	lb.	.10½
Arsenate, bbls.	lb.	.08½
Oxide, litharge, bbls.	lb.	.06
Peroxide, drums	lb.	.20
Red, bbls.	lb.	.07
Sulfate, bbls.	lb.	.06¼
White, basic carb., bbls.	lb.	.07¼
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks.	ton	4.50
Lithopone, bbls.	lb.	.04½
Magnesite, crude	ton	32.00
Calcined, 500-lb. bbls., wks.	ton	40.00
Magnesium, metal, wks.	lb.	.30
Magnesium carbonate, bags	lb.	.05¼
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 50 lbs.	lb.	1.41
Mercury, flasks, 76 lbs.	flask	47.00
Meta-nitroaniline, bbls.	lb.	.67
Meta-phenylenediamine, bbls.	lb.	.80
Meta-tolylenediamine, bbls.	lb.	.67
Methanol, pure, synthetic, drums, wks.	gal.	.37½
Tanks, wks.	gal.	.35½
Methyl acetone, drums	gal.	.47
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls.	lb.	3.00
Naphtha, solvent, tanks	gal.	.26
Naphthalene, flake, bbls.	lb.	.03¾
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.10
Double, bbls.	lb.	.10
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.09½
China wood, bbls.	lb.	.05⅛
Coconut, Ceylon, tanks	lb.	.03¼
Cod, N. F., bbls.	gal.	.21
Corn, crude, tanks, mills	lb.	.03⅛
Cottonseed, crude, tanks	lb.	.03⅝
Lard, edible, bbls.	lb.	.09
Linseed, bbls.	lb.	.06
Menhaden, crude, tanks	gal.	.11½
Neat's-foot, pure, bbls.	lb.	.08
Oleo, No. 1, bbls.	lb.	.06⅛
Olive oil, denat., bbls.	gal.	.52
Foots, bbls.	lb.	.04⅝
Palm, Lagos, casks	lb.	.04
Peanut, crude, tanks	lb.	.03¾
Perilla, bbls.	lb.	.04½
Rapeseed, bbls., English	gal.	.36
Red, bbls.	lb.	.06½
Soy bean, crude, tanks	lb.	.03¼
Sperm, 38°, bbls.	gal.	.68
Whale, bbls., natural, winter	gal.	.56
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls.	lb.	.20
Palladium, metal	oz.	19.00
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.15½
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls.	lb.	.45
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.29
Para-phenylenediamine, bbls.	lb.	1.15
Para-toluidine, bbls.	lb.	.40
Paris Green, 250-lb. kegs	lb.	.23
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.80
Phenylethyl alcohol, 1-lb. bot.	lb.	3.75
Phosphorus, red, cases	lb.	.42
Phosphorus trichloride, cyl.	lb.	.18
Phthalic anhydride, bbls.	lb.	.15
Platinum, metal	oz.	37.50
Potash, caustic, drums	lb.	.06⅛
Potassium acetate, kegs	lb.	.28
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.08
Binoxalate, bbls.	lb.	.14
Bromate, cs.	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05
Chlorate, kegs	lb.	.08
Chloride	ton	34.55
Cyanide, cases	lb.	.50
Meta-bisulfite, bbls.	lb.	.10½
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.37½
Yellow, casks	lb.	.18½
Titanium oxalate, bbls.	lb.	.21
Pyridine, drums	gal.	.85
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P.	lb.	.13½
R salt, bbls.	lb.	.42
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	13.00
Saltpeter, gran., bbls.	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.21⅞
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.15
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.50
Sodium acetate, bbls.	lb	.05
Benzoate, bbls.	lb.	.42
Bicarbonate, bbls.	100 lbs.	1.85
Bichromate, casks	lb.	.05
Bisulfite, bbls.	lb.	.04
Bromide, bbls., U. S. P.	lb.	.31
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls.	lb.	.07
Metallic, drums, 12¼-lb. bricks	lb.	.19
Metasilicate, cryst.	100 lbs.	3.25
Metasilicate, gran., bbls.	100 lbs.	2.85
Naphthionate, bbls.	lb.	.52
Nitrate, crude, 200-lb. bags, N. Y.	100 lbs.	1.18
Nitrite, bbls.	lb.	.07
Perborate, bbls.	lb.	.17
Peroxide, cases	lb.	.21
Phosphate, trisodium	100 lbs.	3.20
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls.	lb.	.06
Stannate, drums	lb.	.18½
Sulfate, anhyd., bbls.	lb.	.02
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls.	lb.	.28
Thiosulfate, reg., cryst., bbls.	lb.	.02½
Tungstate, kegs	lb.	.60
Strontium carbonate, tech., bbls.	lb.	.07¼
Nitrate, bbls.	lb.	.09
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl.	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls.	lb.	.26½
Tin	lb.	.24½
Tin tetrachloride, anhydrous, drums, bbls.	lb.	.1735
Oxide, bbls.	lb.	.26½
Titanium dioxide, bbls., wks.	lb.	.17¼
Toluene, tanks	gal.	.30
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls.	lb.	.60
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.11
Whiting, bags	100 lbs.	1.00
Xylene, 10°, tanks, wks.	gal.	.26
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	3.45
Zinc ammonium chloride, bbls.	lb.	.05
Chloride, granulated, drums	lb.	.05⅝
Oxide, Amer., bbls.	lb.	.05¼
Stearate, bbls.	lb.	.16
Zinc dust, bbls., c/l.	lb.	.041