INDUSTRIAL & ENGINEERING CHEMISTRY

Published by the American Chemical Society

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

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Volume 16 SEPTEMBER 1, 1924 No. 9

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EDITORIALS

Data Needed on Education

THE American Institute of Chemical Engineers has given much attention to chemical engineering education, and has recently been engaged in preparing a recommended course of study, a standardized curriculum, for the beneficial guidance of institutions that offer professional training in chemical engineering. The conclusions of the institute may be expected to be received with respect, and their recognition and adoption by the leading universities and schools of technology will mark a forward step in the direction of chemico-educational reform. Even then, however, many advances will be necessary to place both chemical education and chemical engineering education in strong positions, comparable with, say, medical education.

The chemical profession has self but not legal existence, and there does not seem to be a need at present for the provision of licensure by statute of chemical practitioners and consultants. The profession can, however, stabilize and strengthen its body by the improvement of certain of its educational practices. It can collate statistics relating to chemical education. It can publish information regarding the number and qualifications of chemists as they complete their training. It can make available descriptive summaries of the character of chemical schools from the educational viewpoint. Would not particulars of these types throw an instructively helpful sidelight on the qualifications of the product coming from chemical schools? Certainly they would be of value in attempting to improve courses of instruction, methods of teaching, and procedures of laboratory administration.

There are a number of American institutions that have excellent undergraduate professional courses in chemistry and in chemical engineering. What are they and which ones are the best, are questions that are not answered in the literature of chemical pedagogy. Graduate instruction in chemistry is better known to the profession, because the various schools of importance and the specialties of their faculty members are recognized much more definitely. Perhaps the explanation of this condition is found in a statement of Henry S. Pritchett that "Every college and university covets the reputation of being a center of research. It is more anxious that its teachers should have the name of conducting scientific investigations than that they should be able to teach fruitfully and successfully."

Can the schools of chemistry and of chemical engineering be classified and graded according to teaching and research strength? Can an appraisal be made of their relative importance with respect to intellectual and physical equipment? Are we in a position to rank our professional schools along the general line followed by the medical and dental and legal professions? Would the chemical profession be benefited by this information, assuming its statistical accuracy?

It is as true today as in Daniel Webster's time that "Costly apparatus and splendid cabinets have no magical power to make scholars." It is also as true today as in the time of Berzelius that able lectures must be supplemented by thorough laboratory instruction and practice to train young men for the profession of chemistry. It is not thought, however, that the time has come when the chemical profession is able properly to evaluate its schools. It lacks the statistical ground work, and it does not have the authority that legislation has conferred on the medical and dental and legal professions. Otherwise such an investigation would be opportune. A large number of American educational institutions have been subjecting themselves to critical examination and they have been aided and abetted in this task by extramural criticism. Recently there has been a diligent stock taking, not only of the methods but also of the aims of education in general. These institutions are growing in size and in numbers. The rapid progress of science has multiplied many fold the possible numbers of subjects to be pursued and the extent to which each may be taught and investigated most advantageously.

Chemical science and chemical education have made remarkable progress in the United States during the last twenty-five years. The goal, however, is not yet attained and there will undoubtedly continue to be a broadening of scope and a shifting of emphasis. Laboratories and other equipment have been improved enormously during this period. Chemistry is rapidly becoming, not so much the training of the analyst, industrial chemist, and research man, as the most serious and important study of a branch of science, and it is calling to its support the allied sciences, physics and biology.

In this there is a call for service on the part of the SOCIETY. It can be rendered now under better auspices than formerly, and we recommend that our Division of Chemical Education consider the possibilities and perhaps go forward with a committee dominated by that division but upon which there shall be representatives of some of the other divisions and sections concerned. It appeals to us as a constructive piece of work which will not duplicate the efforts of the American Institute of Chemical Engineers.

Textile Education for Laymen

SEVERAL attempts have been made in the past to have the ultimate consumer, the public, take an intelligent interest in the selection and purchase of textiles. Since on the average a third of one's income is expended on textiles and other items of clothing, it seems reasonable to expect the buyer to be concerned with such questions as the relation of fibers, and the method of their construction into cloth, to wear. Several department stores have found laboratories to be an advantage in making their guarantee less of a liability, but it has been difficult really to interest the textile purchaser. The question of style causes many a decision to be made in favor of a less serviceable garment. In the days of petticoats one department store found that even where the results of physical tests and the analysis were available, an extra ruffle on a garment of inferior material would insure its sale in competition with a plainer one of superior silk.

Many a purchaser with some knowledge of materials has had cause to complain of higher prices for plainer garments than for those of the mode of the moment. The former, of better material, are made in smaller quantities; the latter need only last while styles are being changed.

Now comes another effort at education in the selection and conservation of textiles, which should be successful. The Department of Research of the Laundryowners National Association has issued a series of leaflets, the primary purpose of which is to relate some of the results of efforts to determine causes of failure in fabrics. The information given in the leaflets touches points with which every purchaser should be familiar, and while the assistance of the laboratory is necessary in running down some of the real causes of unsatisfactory service, when the consuming public knows that these things can be determined with certainty there is no reason why they should not demand this information from the distributor, who is in position to maintain or at least consult the chemical laboratory. The introductory leaflet states:

> On whose judgment do you rely when you purchase textiles? Are you able to detect fraud in textile construction? Can you recognize weaving imperfections that place a fabric among seconds? Are you able to trace the cause of the failure of a garment to its true source?

The relation of weaving to wear, the importance of knots in threads, the relation of threads of unequal size or weight to the strength of the fabric, the part played by short fibers, the question of shrinkage, the use of sizing or finish to hide defects, the importance of the proper application of dyes, are typical points discussed in these leaflets. Although intended for distribution by members of the Laundryowners National Association to their present and prospective patrons, the leaflets contain information which may be serviceable in the hands of many teachers and those interested in some examples of the everyday service of the chemical laboratory.

A Chemical Month

SEPTEMBER of this year holds in store an unusual treat for scientists, and particularly for chemists. Our annual meeting at Ithaca will be one of unusual importance, not only because of matters coming before the Council, such as the final report of Mr. Hoskins' committee on the classification of membership, but also because of the excellence of the scientific program. We are again to have the pleasure of hearing from distinguished fellow chemists from abroad, and there is now required only the enthusiastic attendance of large numbers to place the Ithaca meeting high among those which have been successful.

Beginning on September 17 the Franklin Institute will hold a memorable celebration. Besides being the centenary of the founding of the institute, the inauguration exercises of the Bartol Research Foundation are to be held. These exercises will be marked by addresses by men whose names are in themselves an attraction, as well as the subjects upon which they will speak. To mention those whom chemists will delight to hear would be to reprint the program which has been distributed. The meetings will be open to all who may care to hear the discussions and we trust that in the various audiences will be found a large number of members of the AMERICAN CHEMICAL SOCIETY.

One Hundred Million Pounds

ASK the average man when the largest single order for explosives was placed and he is fairly sure to say, "During the World War." At any rate, 100 per cent of the pacifists would so reply. Most people consider the manufacture of explosives primarily a war-time activity, and powder manufacturers have frequently been charged unjustly with fomenting international friction.

But the largest contract, one for one hundred million pounds, has just been awarded by the Government to the du Pont Company, the lowest bidders, and involves the preparation of one hundred million pounds of explosives to be used for the construction of highways, for agricultural purposes, and for other peaceful industrial pursuits.

This information should reach the general public and be emphasized, for it illustrates the point, so often made, that chemistry becomes a destructive agency only when so required in the defense of the nation.

Helium—Safety and Conservation

THE daily press carried some comments following our recent editorial on "Helium *vs.* Hydrogen," and one of the proponents of hydrogen, notwithstanding his official connection at the time with the Bureau of Aeronautics, United States Navy, went so far as to criticize the assumed action of the crew of the Dixmude. Without the details in possession of French officials, he ventured to state that that great dirigible was not destroyed because of the inflammability of hydrogen. His interest in commercial aviation is so evident that we need no further comment at this time.

Since then Dr. C. Leroy Meissinger of the United States Weather Bureau and Lieut. James T. Neely lost their lives when lightning struck their balloon. This adds another to an already long list of dirigibles and balloons filled with hydrogen and destroyed by fire or explosion.

It is true that many thousands of people have been carried safely in hydrogen-filled balloons, but why take unnecessary risks in times of peace when we know of something better? The Navy is steadfast for the use of helium in the Shenandoah, and in an editorial in the *New York Times* for June 6, Rear Admiral Moffett is quoted in the matter of costs which are usually cited by those who favor hydrogen. Admiral Moffett says, "When it is considered that it is possible to purify helium at a cost of approximately one dollar and a half per thousand and that on the other hand it is not safe nor practical to purify hydrogen, the conclusion is that the cost of forty dollars for helium would be as cheap in the end as hydrogen at fifteen dollars."

The ZR-3, a dirigible with a capacity less than 20 per cent greater than the Shenandoah, and being built in Germany as a part of the reparations, will doubtless be brought overseas with hydrogen. This will be at the property risk of the German Government, but we may be sure that once the United States Government assumes responsibility for this new giant, the gas compartments will be filled with helium.

There is a reason to believe that a cost of forty dollars per thousand cubic feet for helium will soon be attained. The possibility of purification has been demonstrated. The necessity of replacing hydrogen on the average twenty-two times per year gives a basis for the statement that the question of cost is no longer a consideration, granting for the sake of argument that it ever was. The wasteful practice of valving should soon be stopped in the Shenandoah, now that the condenser problem has been solved. One hundred and ten pounds of water can be recovered for each hundred pounds of gasoline burned. The solution of this heat transfer problem is discussed in this issue of INDUSTRIAL AND ENGINEERING CHEMISTRY, and some of the Shenandoah's engines have already been equipped with these condensers.

There is no intention of hampering the commercial development of dirigibles. We have reason to believe that commercial companies could develop their own sources of helium, and we are certain that one of the disasters which may at any moment overtake a hydrogen-filled gas bag would be sufficient, not only to make commercial development impossible, but sadly to retard our military program being developed as a defense measure. The military establishment in emergencies may be justified in occasionally risking observers and crew in hydrogen-filled ships, but the commercial operation of hydrogen-filled dirigibles will never be successful when the man in the street knows that safety is to be had only with helium.

The subject of helium will be brought prominently before Congress when it reconvenes in December by H. R. 5722 and Senate Bill 2166, both having to do with the conservation, production, and exploitation of helium gas. These bills aim first at the conservation of helium by authorizing the

Secretary of the Interior to acquire land or interest in land by purchase, lease, or condemnation where necessary, and to explore for, conserve, and extract helium gas, and give the Government the ownership and right to extract helium from all gas produced from public lands. Under these bills conservation would be effected largely by gaining possession of such geological formations as now hold the gas, and keeping it there imprisoned until needed. The bills also provide funds to erect plants to extract, purify, and supply helium to the Army and Navy, and also to lease to American citizens or American corporations under suitable regulations, any surplus helium not needed by the Government, moneys derived from this source being credited to a helium production account, with residual gas after helium extraction being sold for the benefit of the miscellaneous receipts of the Treasury. The bills also forbid the exportation of helium from the United States or its possessions without express permission from the Secretary of the Interior. They further endeavor to combine the activities of the Army and Navy with those of the Department of the Interior in carrying out a constructive helium program.

The bills do not interfere with the private development of helium, and their enactment would not create a condition in any way harmful to commercial aeronautics. We are in accord with the spirit of these bills, and chemists, appreciating the importance of this element, are sympathetic toward any program designed to effect conservation through scientific development and efficient use.

Travel of Scientists

AT THE Washington meeting the Council passed resolutions favoring more liberal regulations and laws governing the attendance of scientific workers in Government departments upon scientific conventions and congresses. These resolutions were sent to the several departments involved and have met in most instances with sympathetic reception. At least two of the great Government departments have stated that they will continue to send scientific workers to conventions and congresses whenever possible under the limitations of available appropriations and where it is clear that these expenditures are made in the public interest. We quote from one of the official responses:

> I am very much pleased to note the action of your Society and that of other associations and trust that your efforts will result in a more universal understanding of the benefits to be derived from this system. We have, in expressing the matter to Congressional committees, stated that it is impossible for the Department to maintain national leadership if its representatives are not present at the conferences in which policies and programs of action are being worked out, and we have found an almost universal appreciation and support of the sentiment.

The present practice which greatly limits the attendance of scientific men upon these meetings is said to have originated, as nearly all restrictions do, in an abuse of privileges. The story is that some years ago two members of the Washington police force made a junket at Government expense which so aroused some members of Congress that restrictions were put in force.

The practice of allowing only those scientists to attend meetings who have papers upon the program is not always satisfactory. Some have even thought that it has led to the presentation of summaries without introduction of new results or the reports of uncompleted work, whereas results might have been better had the paper been delayed until the data were complete. Often procedure upon a piece of uncompleted research may be influenced directly by one of those formal or informal discussions such as characterize our meetings.

The extent of research under Government auspices and the variety of topics in hand is such that no scientific meeting is complete without a reasonable representation from the Government laboratories. We hope ways and means may be found to increase the number who can attend.

We have frequently emphasized the returns possible in the case of corporations paying expenses of their scientists to such meetings, and these same arguments hold true not only in the case of Government employees but also where institutions of learning are involved. One of the best ways of inducing narrowness is to confine a scientist to his laboratory or his study and keep him out of contact with his fellows with whom he has a common interest.

Chemistry Not Warlike

IN THEIR effort to give full credit to the part played by chemistry during the Great War, our daily, weekly, and monthly press has succeeded in giving the science a reputation which it does not deserve. Chemistry becomes destructive only of those things which threaten our lives and when called upon to act in self-defense.

The *Harvard Alumni Bulletin* in a recent number comments editorially upon chemistry and medicine with special reference to "Chemistry in the Service of Medicine," a pamphlet issued by the Committee to Extend the National Service of Harvard University. As the editorial points out, "One of the minor consequences of the war has been that in the minds of many people the work of chemists is associated with destructive discoveries and inventions. The idea that laboratory experiments are concerned to a large extent with an effort to increase the deadliness of poison gas and the power of high explosives is prevalent. Chemists are looked upon as persons who are in cold blood preparing weapons with which mankind may eventually exterminate itself." The pamphlet discusses typical problems in the solution of which chemistry has been important, and indicates some of the accomplishments that may be expected if research is adequately supported in future.

The presence in this country of a former expert in the Chemical Division of the British Army, who believes he has a method for the eradication of the famous cotton boll weevil, brings to mind another example of the peace-time application of knowledge gained in chemical warfare service.

Still another is the use of chloropicrin to displace heat in smothering silkworm cocoons, the process being superior as far as cost is concerned and easier to control than heat. The silk obtainable from cocoons smothered by chloropicrin differs in no way as regards elasticity, tenacity, and ease of degumming from that obtained from cocoons killed by heat.

A further illustration may be taken from the extensive work performed by our Chemical Warfare Service on the protection of marine piling and other structures from the toredo borer, which in one harbor in a single year recently did damage estimated at nineteen million dollars. The fight against the borer, in progress for many years, has, until now, met with indifferent success. It is doubtful whether such preparations as have shown themselves highly effective in large-scale trials would have been developed without the acquisition of that great mass of special toxicological information which has been brought together at Edgewood.

With these and many other accomplishments to the credit of peace-time activities of the chemists in the Chemical Warfare Service, it seems a pity that the name of that corps was not chosen to avoid placing arguments on the lips of those who see only the word "warfare," and do not comprehend its real chemical service. Had the Medical Corps been called the Medical Warfare Service, we wonder what stories the pacifists might have devised. It is probably too late to make a change in the name of the Chemical Warfare Service, but it is never too late to have the public understand the real nature of its work and the real importance of its information.

Heat Transfer in the Condensation of Water from Engine Exhaust Gas[1,2]

By Robert F. Kohr and Lucinthia Butler

Bureau of Standards, Washington, D. C.

Extended use of gas-filled airships by the United States Army Air Service has emphasized the necessity of developing some means of compensating for the loss of weight due to fuel consumption during flight, in order that excessive waste of lifting gas may be avoided. "Valving" or releasing lifting gas in order to maintain static equilibrium is in any case extremely wasteful, and must be avoided if helium is to be used.

The exhaust from a gasoline engine contains more than a pound of water per pound of gasoline burned, owing to the combination of hydrogen in the fuel with the oxygen of the air. The Bureau of Standards has devised apparatus to condense a large part of this water, thus making it possible continually to compensate during flight for the weight of fuel burned. The apparatus weighs about 1.5 pounds per horsepower of the engine served, and this weight can be wholly compensated for by a corresponding decrease in the weight of ballast previously carried.

THE work on which this paper is based was done at the request and with the support of the United States Army Air Service. It was occasioned largely by the proposed use of helium as a lifting gas in lighter-than-air craft. On account of its noncombustible nature, helium is exceedingly important from the military standpoint, and is in fact a virtual military monopoly, inasmuch as nearly all the known world supply is found in this country.

There has always been a great loss of lifting gas in airships during extended flights, due to the necessity of maintaining static equilibrium by valving gas when the total load has been decreased by consumption of fuel. This waste might be tolerated when hydrogen is used, but must be nearly eliminated before a gas so rare and expensive as helium can be put into general use.

The problem then, is that of maintaining a constant total load in order that change of load may not have to be compensated for by change of lift. To this end a survey of the possible means was made and resulted in the adoption of the method indicated in the title of this paper, condensation of water from engine exhaust gas.

The exhaust from a gasoline engine contains about 1.4 pounds of water per pound of fuel burned, and to compensate wholly for the loss of fuel weight it is necessary only to cool the exhaust products sufficiently and separate and collect the condensed water.

Various cooling systems were considered, but the method finally adopted was that of direct air cooling by passing the exhaust gas through long, thin-walled pipes, whose outer surfaces were exposed to the air flowing past the ship. In order to prevent the escape of entrained moisture, the gas leaving the cooling tubes was passed through a baffle type separator.

Two condensers of this type were designed, built, and subjected to ground test. The first of these was later installed on the army Airship D-3 and given a flying test of over 50 hours. The performance closely approximated that expected from theoretical considerations. Similar apparatus is to be used as service equipment on all new army ships intended for long-distance flying.

The Model I condenser installed on the D-3 is shown in Fig. 1 suspended between the envelope and car. It is approximately 21 feet long, weighs, installed, about 450 pounds, and comprises over 3000 feet of 1-inch aluminium tubing.

Theory of Water Recovery

In reviewing the theory involved in the process of obtaining water from the engine exhaust gas, it may be well, in order to avoid confusion, first to discuss the nomenclature used.

Reference is made to the chart, Fig. 2, in which vertical distances represent weights of the quantities indicated.

The fuel burned is, of course, the basis upon which the other quantities are determined. The total water in the exhaust gas is the sum of water of combustion and the moisture entering with the carburetor air. This quantity depends upon the kind of fuel and, to a small extent, upon the mixture ratio (air fuel) and relative humidity.

Since the amount of water lost as vapor depends upon the final temperature of the exhaust gas, and since, in an air-cooled system, the limit of cooling is the air temperature itself, it at once becomes apparent that the recoverable water is the total minus the vapor necessary to saturate the gaseous exhaust products at air temperature.

The designed recovery is, of course, limited by the recoverable water as determined by an assumed air temperature. It may be arbitrarily placed at any value less than that of the recoverable water, but would not ordinarily be less than the fuel burned.

Since the designed recovery is based upon a designed final exhaust temperature, it is evident that error in design assumptions or changes in flying speed or air temperatures will change this final tempera-

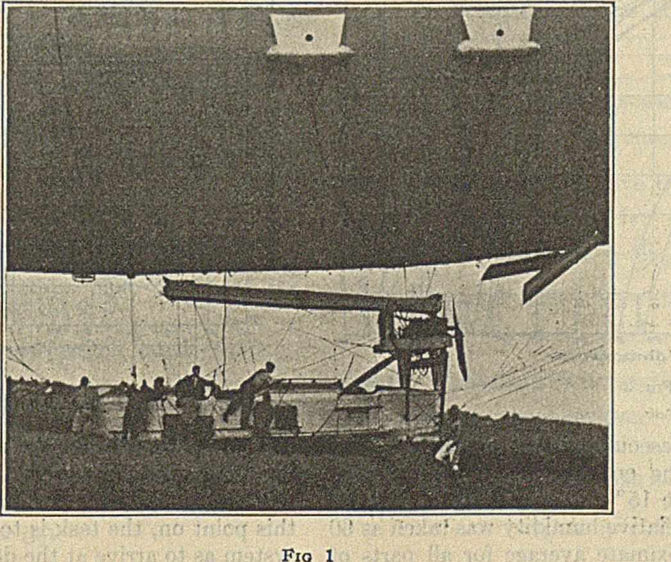

Fig 1

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] Published by permission of the Director, U. S. Bureau of Standards.

ture and therefore the amount of water actually condensed. The water condensed may be either greater or less than the designed recovery, but is represented as showing a loss.

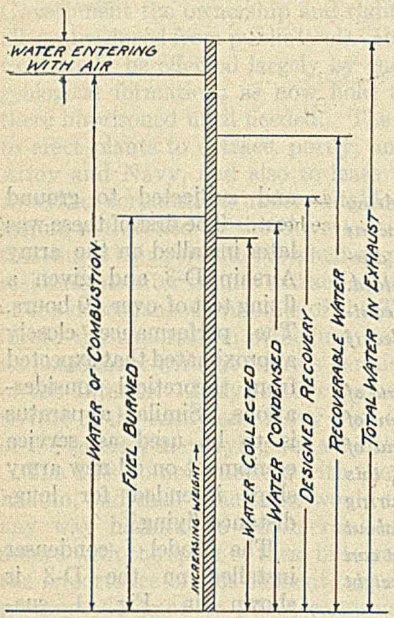

Fig. 2

In the collection of the water condensed, leaks of any kind, as well as faulty separation of entrained moisture, will lower the quantity available as ballast. The water collected is therefore always less than that actually condensed.

The quantities shown, when expressed as per cent, are based upon the weight of fuel burned.

The design of the condensing apparatus is dependent upon a large number of variables, which may be best taken up as they appear.

It is at once apparent that the water condensed is dependent upon the composition of the exhaust gas and its final temperature. The first of these is readily determined when the chemical composition of the fuel, ratio of air to fuel, and relative humidity and temperature of the air are known. The final exhaust temperature, however, is a function of the length, diameter, spacing, and number of condenser tubes, mass flow and initial temperature of exhaust gas, and the velocity and temperature of the air flowing past the tubes.

The influence of different fuels is shown in Fig. 3, in which the water condensed is plotted against final exhaust temperature for each of the fuels considered. These curves were obtained by adding the water of combustion to the water entering with the carburetor air, and subtracting the weight of vapor necessary to saturate the gaseous exhaust products at the temperatures indicated. The entering air temperature in each case was assumed to be 15° C. lower than that of the cooled exhaust gas, and its relative humidity was taken as 60 per cent, which is an approximate average for all parts of this country for the whole year, for altitudes less than 5000 feet. As a basis of comparison of the different fuels, their chemically correct air-fuel ratios were used.

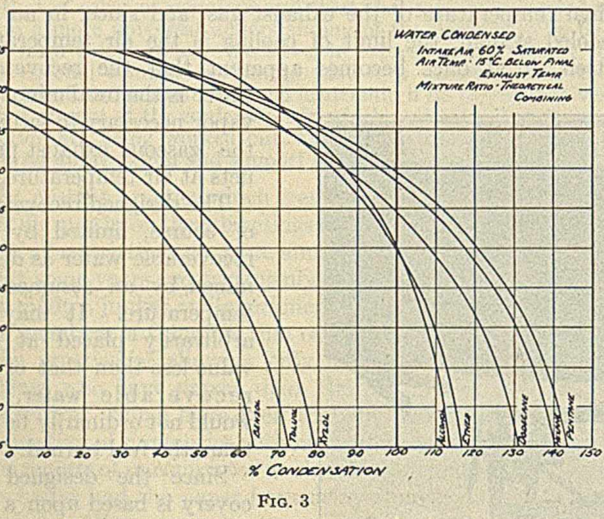

Fig. 3

Since it is improbable that any fuel having exactly the composition of one of those shown in Fig. 3 will ever be put into service use, this figure is supplemented by Fig. 4, showing the final temperature to which the exhaust gas must be cooled in order to condense 1 pound of water per pound of hydrocarbon fuel burned. This curve was derived by plotting the points where curves such as those of Fig. 3 cross the 100 per cent condensation line.

All the curves thus far shown are based on the theoretical combining mixture ratios of air to fuel, which correspond to extremely lean carburetor settings and give the economy so vitally important in the operation of airships. Some multicylinder engines are unable to operate on mixtures quite as lean as those shown, but since the leaner mixtures are less advantageous as regards water recovery, the curves are based on the worst expected condition and should be on the safe side.

The effect of mixture ratio upon water condensed is shown in Fig. 5. The fuel in this case was assumed to be gasoline having a 15 per cent hydrogen content, which closely approximates the fuel now in service use. Fig. 6 shows the effect of mixture ratio upon the final temperature to which the exhaust gas must be cooled in order to condense 1 pound of water per pound of gasoline burned.

Since the humidity is uncontrolled, it is possible that for special cases some value other than the average one of 60 per cent should be applied. The curves of Fig. 7 indicate the limits for the humidity range between 0 and 100 per cent. It will be seen that at a temperature corresponding to 100 per cent condensation with saturated air, the decrease due to a change to dry air is about 29 per cent. The points plotted in this figure are average values obtained during a 90-hour endurance test of the Model I condenser. These points represent actual water collected, and it will be readily recognized that faulty separation of entrained moisture or any leakage of either exhaust gas or water would lower the apparent condensation (water collected).

It is obvious from the foregoing paragraphs and curves that it is a relatively simple matter to determine a desirable final exhaust temperature, having assumed the kind of fuel, mixture ratio, air temperature, and relative humidity. From this point on, the task is to so select and arrange the cooling system as to arrive at the desired final temperature.

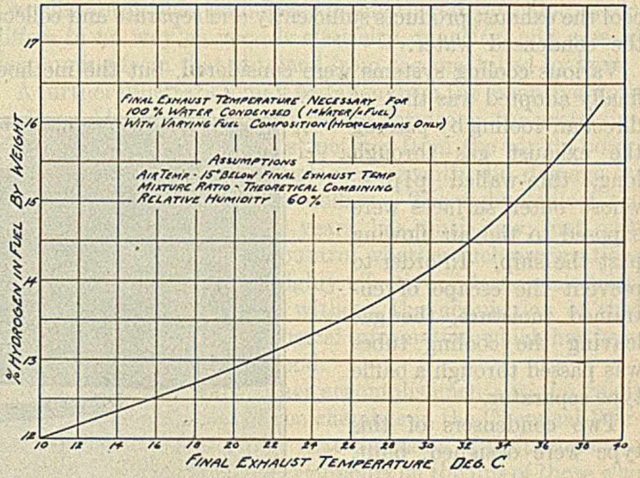

Fig. 4

HEAT TRANSFER

In an apparatus consisting of a bank of tubes parallel to the direction of flow of the cooling air stream, it is evident that the conditions of heat transfer are different for those tubes at the center of the bank and those in the outer rows.

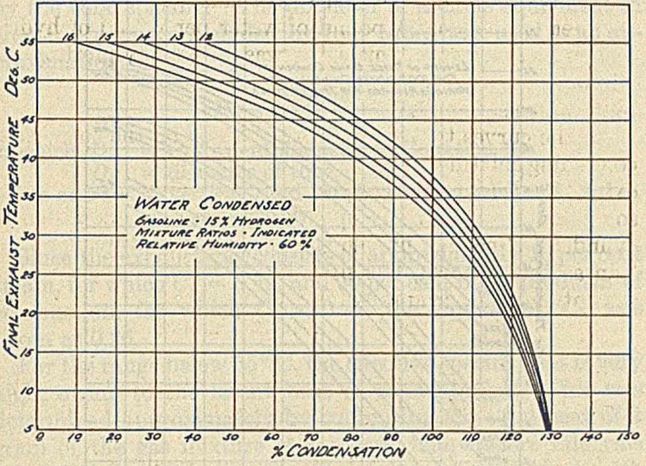

Fig. 5

For the purpose of design computations one tube at the center of the bank is considered. Inasmuch as the outer tubes are better cooled, this admittedly inaccurate method is at least on the safe side. The amount of cooling air flowing past each pipe is determined by the spacing of the tubes.

The equations for heat transfer which are the basis of the design of the exhaust cooling system have been derived under the following assumptions: (*a*) the surface temperature of the pipe is the same inside and out at any given point in the length of the pipe and is uniform around the circumference; (*b*) the cooling air flows with uniform velocity in a direction parallel to the axis of the pipe, is turbulent, and of temperature, density, pressure, and humidity characterizing normal atmospheric conditions.

In a given length of pipe for steady conditions, the heat given up by the passing exhaust gas is equal to that taken up by the pipe wall, which is equal to that dissipated by the pipe wall, and is equal, in turn, to that taken up by the external air stream. The loss of heat from the gas to the wall per element of length dx at any point along the pipe is

$$-M_hC_h\frac{d\Theta_h}{dx}dx \text{ or } -H_h\frac{d\Theta_h}{dx}dx$$

where M_h = mass of exhaust gas passing any point along the pipe, grams per second

C_h = specific heat of the gas at constant pressure, $\frac{\text{calories}}{\text{grams} \times {}^\circ\text{C.}}$

$H_h = M_hC_h$ = heat capacity of the mass of exhaust gas which passes any point in unit time in $\frac{\text{calories}}{\text{seconds} \times {}^\circ\text{C.}}$

Θ_h = temperature of exhaust gas, ° C.

x = coördinate along length of pipe, positive in the direction of exhaust gas flow

$\frac{d\Theta_h}{dx}$ = change in temperature per unit length of pipe

$\frac{d\Theta_h}{dx}dx$ = change in temperature per element of length

The sign is negative since the total heat of the exhaust decreases as x increases.

The heat taken up by the pipe wall per element of length is

$$q_h\,p\,dx\,(\Theta_h - \Theta_w)$$

where q_h = coefficient of surface heat transfer between exhaust gas and pipe wall, $\frac{\text{calories}}{\text{seconds} \times {}^\circ\text{C.} \times \text{sq. cm.}}$

p = perimeter of pipe, cm.

$p\,dx$ = element of surface area, sq. cm.

Θ_w = temperature of wall, ° C.

Similarly, the heat dissipated by the pipe wall is

$$q_c\cdot p\,dx\,(\Theta_w - \Theta_c)$$

and that heat taken up by the external air stream

$$H_c\frac{d\Theta_c}{dx}dx$$

where q_c = coefficient of surface heat transfer between pipe wall and air stream, $\frac{\text{calories}}{\text{seconds} \times {}^\circ\text{C.} \times \text{sq. cm.}}$

$H_c = M_cC_c$ = heat capacity of the mass of air stream which passes any point in unit time, $\frac{\text{calories}}{\text{seconds} \times {}^\circ\text{C.}}$

M_c = mass flow of air past any point along the pipe, grams per second

C_c = specific heat of air at constant pressure, $\frac{\text{calories}}{\text{grams} \times {}^\circ\text{C.}}$

Θ_c = temperature of air stream, ° C.

The conditions stated above then give the three equations

$$-H_h\frac{d\Theta_h}{dx}dx = q_h\,p\,dx\,(\Theta_h - \Theta_w) \tag{1}$$

$$H_c\frac{d\Theta_c}{dx}dx = q_c\,p\,dx\,(\Theta_w - \Theta_c) \tag{2}$$

$$q_h\,(\Theta_h - \Theta_w) = q_c\,(\Theta_w - \Theta_c) \tag{3}$$

Combining these eliminates one variable, Θ_w, and leaves two simultaneous differential equations in Θ_h, Θ_c, and x.

$$-\frac{H_h}{p\,q_h}\frac{d\Theta_h}{dx} + \frac{H_c}{p\,q_c}\frac{d\Theta_c}{dx} = \Theta_h - \Theta_c \tag{4}$$

$$H_h\frac{d\Theta_h}{dx} + H_c\frac{d\Theta_c}{dx} = 0 \tag{5}$$

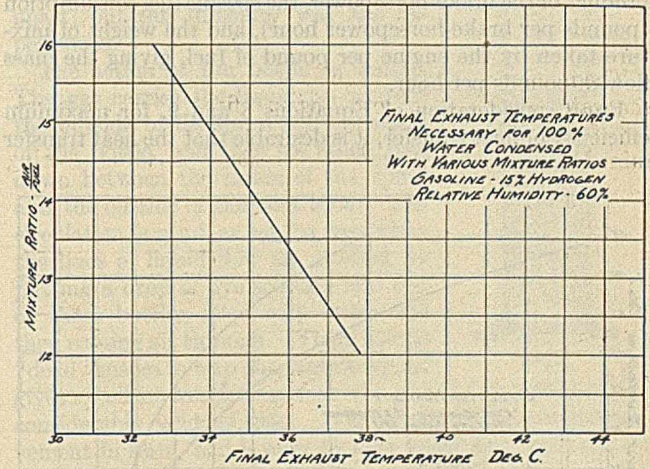

Fig. 6

These can be solved to give Θ_h and Θ_c as functions of x.

$$\Theta_h = Ae^{nx} + B \tag{6}$$

$$\Theta_c = -A\frac{H_h}{H_c}e^{nx} + B \tag{7}$$

where e = base of natural logarithms

$$n = -p\,\frac{q_hq_c}{q_h + q_c}\left(\frac{1}{H_h} + \frac{1}{H_c}\right)$$

A and B = constants of integration

To eliminate these constants the following end conditions are applied:

For counterflow of exhaust gas and air

$$\left.\begin{array}{l}\Theta_h = T_a \\ \Theta_c = t_b\end{array}\right\} \text{ when } x = 0$$

$$\left.\begin{aligned}\Theta_h &= T_b\\ \Theta_c &= t_a\end{aligned}\right\}\text{ when } x = L$$

For parallel flow

$$\left.\begin{aligned}\Theta_h &= T_a\\ \Theta_c &= t_a\end{aligned}\right\}\text{ when } x = 0$$

$$\left.\begin{aligned}\Theta_h &= T_b\\ \Theta_c &= t_b\end{aligned}\right\}\text{ when } x = L$$

where T_a = initial exhaust temperature, ° C.
T_b = final exhaust temperature, ° C.
t_a = initial air temperature, ° C.
t_b = final air temperature, ° C.
L = length of pipe, cm.

The resulting equations arranged in a form convenient for design work are:

For counterflow

$$\log_e \frac{T_a - t_b}{T_b - t_a} = p\,\frac{q_h q_c}{q_h + q_c}\left(\frac{1}{H_h} - \frac{1}{H_c}\right) L \qquad (8)$$

For parallel flow

$$\log_e \frac{T_a - t_a}{T_b - t_b} = p\,\frac{q_h q_c}{q_h + q_c}\left(\frac{1}{H_h} + \frac{1}{H_c}\right) L \qquad (9)$$

The values for q_h and q_c are obtained from the Lanchester-Stanton relation[3] combined with Lees' equation for skin friction

$$q = C_p m\left[0.0765\left(\frac{\mu}{mD}\right)^{0.35} + 0.0009\right] \qquad (10)$$

in which
C_p = specific heat at constant pressure
μ = viscosity, poises
m = mass flow, $\dfrac{\text{grams}}{\text{seconds} \times \text{sq. cm.}}$
D = diameter of tube, cm.

In working toward a satisfactory heat-dissipating apparatus the first determination necessary is the total rate of mass flow of exhaust gas coming from the engine. This will be the product of the brake-horsepower, the specific fuel consumption (pounds per brake-horsepower hour), and the weight of mixture taken by the engine per pound of fuel, giving the mass flow in pounds per hour.

From consideration of Equations 8 and 9, for maximum efficiency of heat transfer, it is desirable that the heat transfer coefficients, and hence the mass flows per unit cross-sectional area, be approximately the same inside and outside the tube. Then, having a known flying speed and air density, the resultant mass flow would be the rate of flow for exhaust gas most effective for cooling.

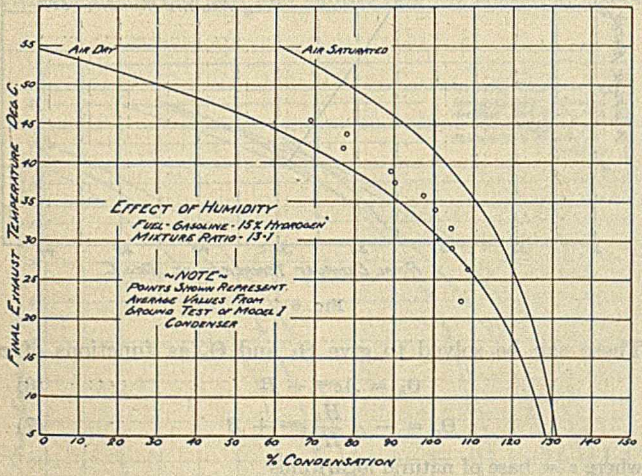

Fig. 7

The density of the exhaust gas changes by a factor of 3 as the temperature drops from 650° to 30° C., so that for a given mass flow the velocity at the hot end is three times that at the cold end. Thus, for an air speed of 45 miles per hour, the average cruising speed for airships now in service, the corresponding velocity at the hot end would be 135 miles per hour, which threatened difficulties due to back pressure. A compromise resulted in taking 0.017 pound per second per square inch (1.195 grams per second per square centimeter) as the desirable mass flow inside the pipes.

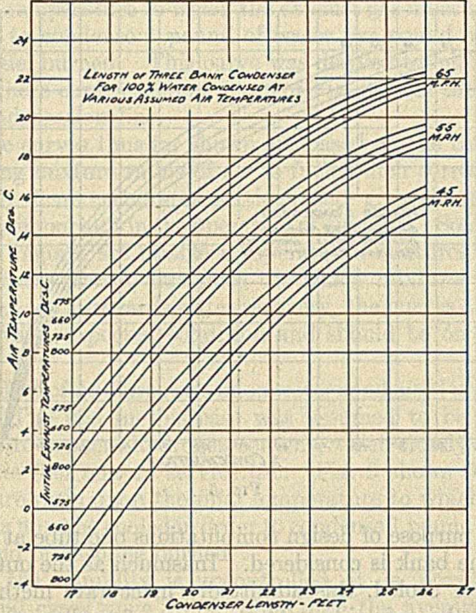

Fig. 8

The selection of the most advantageous size of tubes must of necessity be a compromise between heat transfer efficiency and mechanical considerations. The effectiveness of the apparatus will be found (Equation 10) to be increased as the diameter of the tubes is decreased, whereas the smaller the tubes, the greater will be the exhaust back pressure and liability to clogging, and the less the mechanical strength of the tubes, both as self-supporting beams and as long columns.

An indication of the relative resistance to flow with increase or decrease of pipe size may easily be obtained, but for the purpose of this work it is safe to let the limiting factor in reducing tube diameter be the mechanical strength necessary in a structure of the type contemplated. Soon after the beginning of the design work on the full air-cooled type of water recovery apparatus, a tube of 1-inch diameter was assumed and the strength of thin tubes of this size was computed. This choice of dimensions has been vindicated by the ground and flying tests, since tubes of this diameter and the thinnest walls commercially obtainable have proved amply strong, while the back pressure is nearly at the allowable limit. In this paper, therefore, only tubing of circular section, 1 inch in diameter, is considered.

Having the assumed tube size, the known total mass flow and advantageous mass flow per unit area, the total number of tubes and mass flow per tube are easily computed.

Inasmuch as the Lanchester-Stanton equation for film coefficients is applicable strictly only to smooth, round pipes, it is evident that it cannot be expected to give exact results when used to determine the heat transfer from the outside of the tubes to the air stream. However, as no more reliable method was at hand, this equation was applied, after first computing the diameter of a round pipe equivalent in cross-

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[3] Great Britain Committee for Aeronautics, *Tech. Rept.* **1912-13**, p. 45; *Bur. Standards, Tech. Paper* **211**, p. 320.

sectional area to the space included by four adjacent tubes. The results later obtained seemed to justify the use of the equation in this way.

In solving Equation 10 for q_c, the mass flow of air, m, is determined by the air density, flying speed, and spacing and number of tubes, while D_c has a value also determined by the tube spacing. The diameter of a circle equivalent in area to the space included by four tubes was used as an approximation.

$$D_c = \sqrt{\frac{4ab}{\pi} - D_h^2}$$

in which D_c = equivalent diameter in Equation 10
D_h = diameter of tube
a and b = vertical and transverse spacing of tubes, respectively

Since the exhaust gas consists of approximately 10 per cent steam, for which $C_p = 0.45$, and 90 per cent other products of combustion, for which $C_p = 0.24$, the equivalent C_h was taken as 0.26.

For the range below 55° C. the effective specific heat is very high, owing to the latent heat of condensation. This was determined approximately by computing the total heat of 1 gram of the gas mixture at frequent temperature intervals below 55° C. and finding the rate of change of total heat with temperature. This rate of change was taken as the effective specific heat with a mean value of 2.83 in the range 55° to 45° C. and 1.92 in the range 45° to 35° C., or 2.20 for the entire range 55° to 35° C. The figure 45° C. for the exhaust temperature at the end of the second condenser bank was secured by successive approximations, and is used only to determine the effective specific heats over the ranges indicated. These values were checked by a more rigorous mathematical determination, which can well be omitted here.

The viscosity of the gas changes considerably with temperature, but an average value of μ over the range 600° to 55° C. was taken as 2.4×10^{-4} poises, the viscosity of air at 150° C. For the range below 55° C. it was assumed the effect of the condensing vapor was negligible and the value 2.0×10^{-4} poises for the viscosity of air was used. For the air flowing outside the tubes, $\mu = 1.85 \times 10^{-4}$.

Thus, we have constant values for the variables in Equation 10, so that q_h and q_c, and consequently $\frac{q_h q_c}{q_h + q_c}$ may be taken as constant for each range above and below the condensation point.

For a three-bank condenser of the general form of Model II, it is impossible to compute the necessary L directly, on account of the changing functions of the variables during parallel and counterflow as well as the change of C_p with temperature of the exhaust gas. The most convenient method is to assume an over-all length for the condenser and solve Equation 8 or 9 for each section given. It is, of course, necessary to measure or assume the temperature of the exhaust gas received by the condenser as well as the air temperature.

It will be found that an equation in two variables will be left in each case, but that one of these can be eliminated by solving simultaneously with the equation expressing the fact that the heat lost by the exhaust is equal to the heat taken up by the air.

$$(T_a - T_b)\ H_h = (t_b - t_a)\ H_c$$

The curves of Fig. 8 show air temperature plotted against necessary length of a three-bank condenser for three air speeds and four initial exhaust temperatures. These summarize the effect of changes in the most important variables on heat transfer, for a constant final exhaust temperature of 32° C. This figure represents the conditions necessary for the condensation of 1 pound of water per pound of gasoline burned.

A New Spiral Gas-Washing Bottle[1]

By L. H. Milligan

NORTON CO., WORCESTER, MASS.

IN AN apparatus for analyzing gaseous mixtures of oxides of nitrogen it was necessary to have a gas-absorption bottle that would contain a known volume of liquid through which the gases could be passed, give excellent contact between the gas and the liquid so that complete absorption would result, circulate the liquid thoroughly so that all the liquid would be brought into contact with the gas, not trap air or gas at any point, and be all glass because the gases were corrosive. Requirements of moderate ruggedness and accessibility for washing out completely also had to be met. Any bottle that satisfies all these conditions is an almost perfect gas-washing bottle for general laboratory purposes.

The spiral gas-washing bottle designed for this use by the writer while working at Cornell University is shown in Fig. 1. There are three essential parts: B is a gas inlet tube sealed through a ground-glass stopper. C is a cylindrical tube open at both ends, the walls of which have been pressed in the form of a spiral. This slides on and off over the inlet tube, but is held in position, when the bottle is assembled as shown in the figure, by the turned-up end of the inlet tube. A is the cylindrical outside bottle; the spiral fits this fairly closely and the top of the bottle is closed by the ground-glass stopper of the inlet tube.

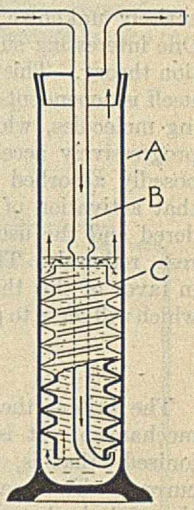

FIG. 1

This bottle is easy to make and is moderately rugged. At first it was feared that the spiral would tend to break off the end of the inlet tube by falling against it or by being jerked against it when the bottle is taken apart; but this difficulty was not experienced.

The action of the bottle is simple. The gas carries the liquid up between the outside of the spiral and the inside of the bottle, and then the liquid goes down between the inside of the spiral and the outside of the inlet tube. The circulation is good, as can be seen when the lines of liquid flow are studied by putting a drop of dye solution into one of these bottles filled with water and then passing air through. There are no "dead" spaces to trap gas, and the spiral gives excellent contact between the gas and the liquid for a considerable period of time. The bottle is compact and convenient in form, and is easy to take apart and wash out for quantitative work. The opening at the top of the spiral is elliptical, so that when gas bubbles tend to lift the spiral it is brought to rest against the little bulb at the center of the inlet tube. When the bottle is taken apart it is possible to slide the spiral off over the end of the inlet tube. This feature makes it easy to pack the bottle for shipment, or possible to replace a broken spiral without getting a new bottle.

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[1] Received June 25, 1924.

Gas Hazards in Street Manholes

A study of gas hazards in street manholes has been completed by engineers attached to the Pittsburgh Experiment Station of the Bureau of Mines. Examinations were made of gases found in street manholes of Pittsburgh and Philadelphia to determine the health and explosion hazards of such gases, particularly from the appearance of natural gas, manufactured gas, or other inflammable substances getting into the manholes.

A Suggested Mechanism for Antiknock Action[1]

By G. L. Wendt and F. V. Grimm

Standard Oil Co. (Indiana), Whiting, Ind.

Midgley's development of tetraethyl lead as an antiknock catalyst in the automotive engine has not yet produced a satisfactory interpretation of the mechanism of this negative gaseous catalysis. This paper suggests tentatively that the explosive flame is propagated by the emission of electrons from the reacting molecules, in that the advance of these electrons before the flame front ionizes and activates the unburned molecules, causing detonation at high temperatures and pressures. On this hypothesis the function of the antiknock is to absorb electrons and to promote the recombination of ions previous to combustion, thus reducing the normal acceleration of the combustion rate.

The experiments described show that tetraethyl lead and other antiknock compounds do actually have a marked effect in recombining gaseous ions at ordinary pressures and temperatures while the knock inducers similarly tested have no effect. Attempts to reduce the rate of combustion by the application of magnetic and electrostatic fields were unsuccessful.

The great economic promise involved in the possibility of general use of high-compression automobile engines makes the recent development of antiknock compounds by the General Motors Research Corporation one of primary interest to the automotive and petroleum industries. Midgley[2] has shown that the presence of as little as 1 molecule of tetraethyl lead in over 200,000 molecules of a combustible mixture of kerosene and air exerts a marked effect in the suppression of detonation. This pronounced negative action by a gaseous catalyst is a new phenomenon, the mechanism of which is still entirely unknown, though of vital importance to industry. One interesting suggestion for it is based on Perrin's radiation theory. This assumes that the propagation of the flame itself is dependent on an activating radiation from the reacting molecules, which travels ahead of the flame front and progressively accelerates the flame. This radiation is supposedly absorbed by the screen of antiknock molecules so that activation of unburned hydrocarbon molecules is hindered and the usual acceleration of the rate of flame progress reduced. There is as yet no experimental evidence in favor of this theory, and the minute amount of catalyst which will serve to prevent detonation is a serious obstacle to it.

THEORETICAL

The writers, therefore, wish to suggest an entirely different mechanism. It is well known that all flames are highly ionized—that is, they are excellent carriers of an electric current. This means that the energy released in the reaction of the hydrocarbon with oxygen serves in part to liberate electrons from the reacting molecules. The advance of electrons propelled at high velocity from the flame front undoubtedly ionizes the molecules in the gaseous region just ahead of the flame. This ionization is tentatively regarded as the essential activation and the factor directly responsible for the increased acceleration of the flame. At high temperatures and high pressures, such as always obtain when detonation is excessive, the velocity of the liberated electrons is high and their energy is readily absorbed by the combustible gas. The rate of flame propagation therefore becomes extremely high. It is, then, the function of the antiknock molecules or, more particularly, the lead atoms present in the commonest example of antiknock, to attract these electrons, thus forming highly charged lead ions and preventing the former ready ionization of the unburned hydrocarbon. Furthermore, the lead ion would have another function. Not only does it reduce the number of available electrons but also it attracts the positively charged hydrocarbon ions to it and by neutralization restores them momentarily to an inactive state.

On this conception a minute quantity of lead could easily exert a marked reduction in the acceleration of the flame rate. Furthermore, the effectiveness of an antiknock compound should be proportional to the number of lead atoms which it furnishes per unit of vapor volume. This last has been established by Midgley. Finally, the power thus to absorb electrons should be possessed in the greatest degree by the elements in the lower right-hand corner of the Mendelejeff periodic table. These atoms have unsaturated exterior electron rings and all of them assume a negative charge with ease. The heavier atoms, however, are markedly more effective than the lighter ones, so that iodine has the desired negative action while chlorine is actually positive and accelerates the flame. Pentavalent antimony induces a knock, while the trivalent form is antiknock—a fact which again is in accord with the electronic point of view. The heavy elements farther to the left show a similar dependence on conditions, mercury being a knock inducer at the high pressures of the automotive cylinder while it is an antiknock in combustion at atmospheric pressure.

While, therefore, the known phenomena of detonation and antiknock are in accord with the suggested mechanism, it is extremely difficult experimentally to demonstrate such a mechanism under the conditions at which detonation takes place. One consequence of the hypothesis suggested, however, is relatively easy to verify. If the foregoing mechanism is correct, then it would be supposed that tetraethyl lead vapors added to an ionized but not burning gas at ordinary temperatures and pressures should result in a measurable decrease in the number of ions present, owing to the action of tetraethyl lead molecules in attracting electrons and in serving to recombine the molecular ions. The experiment here described completely verified this prediction. The vapors of the lead compound do have a strong action in recombining the ions of gas, thus presumably reducing the potential activity of the gas molecules and hence the rate at which combustion would proceed without further stimulating influence.

EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. Air drawn from the room was first dried by calcium chloride and soda lime and then passed over a reasonably constant electric arc in order to ionize it. It is difficult to obtain a constant source of ionization. Light both from a carbon arc and from a mercury arc was used, but without success, owing to fluctuations in the current. Ionization by a spark obtained from a

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[1] Presented under the title "A Theory of the Mechanism of the Action of Antiknock Compounds" before the Division of Petroleum Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] *J. Soc. Automotive Eng.*, **10**, 7, 374, 451 (1922); **11**, 247 (1922); **12**, 367, 458 (1923); This Journal, **14**, 589, 849, 894 (1922); **15**, 421 (1923).

small induction coil was also unsatisfactory. A small Thordarson wireless transformer, operating on 110 volts in the primary and furnishing a voltage ratio of 100 to 1, was quite satisfactory provided the particular design of electrodes shown in the figure was used. The electrodes entered the tube inclined at an angle of about 45 degrees and after approaching each other to within 5 mm. were bent away at an angle of about 45 degrees from the horizontal so as to form a V. The current of air passing over the arc, which normally rests at the point of nearest approach of the electrodes to each other, swept the arc slightly upwards so as to increase its length in case of excessive heat evolution from fluctuations in the electric current, thus tending to equalize the energy liberated. In this way the ionization could be kept constant within 10 per cent. Having been ionized, the air passed through a coil immersed in cold water in order to reduce its temperature and to prevent it from subsequently evaporating more of the hydrocarbon than it was able to carry completely through the system. Next the air passed through a long, narrow capillary to increase its linear velocity and to prevent the possible dangerous back diffusion of hydrocarbon vapors to the vicinity of the arc. The air then passed over a horizontal surface of hydrocarbon fuel, either gasoline or benzene. The latter was more satisfactory because of its more constant volatility. This surface had an area of about 1 × 10 cm. It was kept constant by regulating the height of the liquid from the reservoir by means of the stopcock. By this time the ionized air was essentially saturated with hydrocarbon vapor and passed directly through a tube into the brass chamber in which its conductivity was measured.

The ionization was measured at two points in a brass tube 5 cm. in diameter, by means of two insulated electrodes supported in the axis of the tube 35 cm. apart. The electrodes were first supported by and insulated from the brass tube by means of buttons of elementary sulfur. This is a very convenient and effective insulator and serves very well for almost every such purpose, but it rapidly becomes conducting when exposed to the vapors of tetraethyl lead. The sulfur insulators were therefore satisfactorily replaced by clear transparent amber. The tip of the electrode extending through the amber button was so placed as to make contact with a flat spring connected to the gold leaf system of an ordinary electroscope which could thus be interchangeably placed on either of the two electrodes. The leaf and the electrode were charged by means of a 500-volt battery of small dry cells. After passing through this tube the air went on through a sensitive flowmeter by means of which the air supply could be regulated and kept constant, and finally was discharged into a large metallic can, which served to equalize small variations in the suction line, and thence to a fairly constant steam suction pump.

Measurements of the conductivity of the gas were made after constant conditions had been established. Because of variations in both the air stream and the arc, it was necessary for a large number of readings to be taken to obtain a reliable figure for each conductivity. For this reason, the electroscope was placed on electrode No. 1 and five measurements of the rate of fall of the leaf were taken; the electroscope was then transferred to the second electrode for five readings and then replaced on the first electrode, the interchange being repeated four or five times so that twenty or twenty-five individual readings were made for each electrode. These individual figures are not here reproduced, but the average of all readings is given with the mean percentage deviation of the twenty or twenty-five measurements used in obtaining the average value as recorded in Table I. The conductivity at the second electrode was, of course, always less than at the first, owing to the natural recombination of

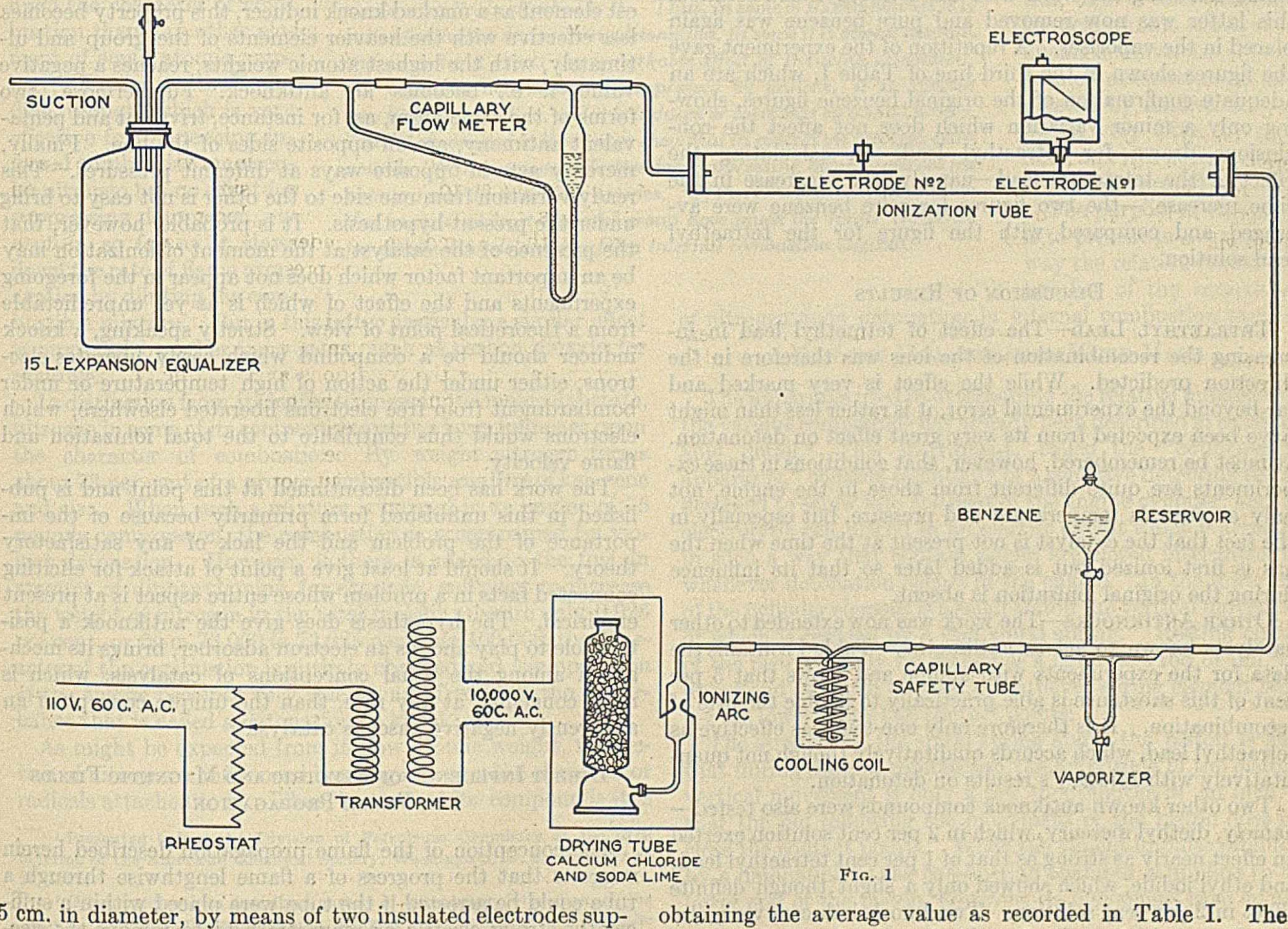

Fig. 1

the ions during the several seconds which elapsed while the ionized air passed from the first electrode to the second. Table I shows that with pure benzene the time required for the fall of the gold leaf between two definite points on the electroscope scale was more than four times as long at the second electrode as at the first. The number of ions present at the second electrode is therefore less than one-fourth of the number present at the first.

TABLE I—TIME OF DISCHARGE FOR BENZENE VAPOR–AIR MIXTURE AS AFFECTED BY TETRAETHYL LEAD AND ANILINE

	Time of Discharge					
	First electrode		Second electrode			
	Seconds	Mean deviation Per cent	Seconds	Mean deviation Per cent	Time increase between electrodes Per cent	Increase in time increase due to antiknock Per cent
Benzene	17.2	±3.5	74.3	±7.3	432	
Benzene + 1% tetraethyl lead	15.6	±7.0	266.0	±4.7	1705	370
Benzene (check)	17.0	±3.0	81.5	±4.2	480	
Benzene	13.1	±5	52.7	±19.8	400	
Benzene + 5% aniline	22.9	±8.7	162.6	±7.9	710	180
Benzene (check) (with trace of aniline remaining)	17.8	±2.3	65.0	±11.7	368	

The benzene was withdrawn from the vaporizer and replaced by a 1 per cent solution of tetraethyl lead in benzene. The measurements were then repeated in precisely the same manner as before. Table I shows that with this quantity of the negative catalyst present the time required for the leaf to fall at the second electrode was seventeen times that required at first. In other words, the conductivity was only one-seventeenth of its original value. Since the conductivity fell to less than one-fourth without the catalyst, the effect of the latter was clearly to decrease the number of ions from about one-fourth to one-seventeenth, which is an increase of 370 per cent in the rate of recombination of the ions.

In order to make sure that conditions in the tube had not changed during the work with the tetraethyl lead solution, this latter was now removed and pure benzene was again placed in the vaporizer. A repetition of the experiment gave the figures shown in the third line of Table I, which are an adequate confirmation of the original benzene figures, showing only a minor variation which does not affect the conclusions drawn for tetraethyl lead. In calculating the effect of the tetraethyl lead—namely, the "increase in the time increase"—the two figures for pure benzene were averaged and compared with the figure for the tetraethyl lead solution.

DISCUSSION OF RESULTS

TETRAETHYL LEAD—The effect of tetraethyl lead in increasing the recombination of the ions was therefore in the direction predicted. While the effect is very marked and far beyond the experimental error, it is rather less than might have been expected from its very great effect on detonation. It must be remembered, however, that conditions in these experiments are quite different from those in the engine, not only as regards temperature and pressure, but especially in the fact that the catalyst is not present at the time when the gas is first ionized but is added later so that its influence during the original ionization is absent.

OTHER ANTIKNOCKS—The work was now extended to other catalysts known to act as antiknocks. Table I contains the data for the experiments with aniline and shows that 5 per cent of this substance is able practically to double the rate of recombination. It is therefore only one-tenth as effective as tetraethyl lead, which accords qualitatively though not quantitatively with Midgley's results on detonation.

Two other known antiknock compounds were also tested—namely, diethyl mercury, which in 2 per cent solution exerted an effect nearly as strong as that of 1 per cent tetraethyl lead; and ethyl iodide, which showed only a slight though definite effect in 2 per cent solution. Two knock inducers were also tested—namely, bromine and dibromethane. These showed no effect whatever.

The foregoing work raises no experimental obstacles to the mechanism suggested. All the known antiknock compounds mentioned were shown to be effective in removing ions from the gas. At the time when this work was done, diethyl mercury was stated to be a knock inducer, and that fact was then considered to be a serious obstacle to the hypothesis, inasmuch as in these experiments this compound acted like the antiknock compounds. This fact, however, led Midgley to reëxamine diethyl mercury, with the result[3] that diethyl mercury was confirmed as a knock inducer in the automotive engine but was shown to be an antiknock in explosions at atmospheric pressure, this being the pressure here used.

UNSOLVED PROBLEMS

The question of knock inducing is not well covered by the mechanism suggested and should be solved by further experimental work on the basis of the present hypothesis. The simple mechanism proposed can hardly account for knock inducing, and yet Midgley has presented facts which argue strongly that the two effects are fundamentally the same. In any group of the periodic system, starting with the lightest element as a marked knock inducer, this property becomes less effective with the heavier elements of the group and ultimately, with the highest atomic weights, reaches a negative value—i. e., becomes an antiknock. Furthermore, two forms of the same atom, as, for instance, trivalent and pentavalent antimony, are on opposite sides of the line. Finally, mercury acts in opposite ways at different pressures. This ready variation from one side to the other is not easy to bring under the present hypothesis. It is probable, however, that the presence of the catalyst at the moment of ionization may be an important factor which does not appear in the foregoing experiments and the effect of which is as yet unpredictable from a theoretical point of view. Strictly speaking, a knock inducer should be a compound which easily liberates electrons, either under the action of high temperature or under bombardment from free electrons liberated elsewhere, which electrons would thus contribute to the total ionization and flame velocity.

The work has been discontinued at this point and is published in this unfinished form primarily because of the importance of the problem and the lack of any satisfactory theory. It should at least give a point of attack for eliciting connected facts in a problem whose entire aspect is at present empirical. The hypothesis does give the antiknock a positive role to play and, as an electron adsorber, brings its mechanism among the usual conceptions of catalysis, which is more congenial, at any rate, than the unique concept of an apparently negative gaseous catalyst.

DIRECT INFLUENCE OF ELECTRIC AND MAGNETIC FIELDS ON FLAME PROPAGATION

The conception of the flame propagation described herein suggests that the progress of a flame lengthwise through a tube could be arrested if the tube were placed within a sufficiently strong electric or magnetic field to remove the elec-

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[3] Discussion of this paper at the Washington Meeting, A. C. S.

trons instantly, thus preventing their advance ahead of the flame front. Attempts to produce this effect, however, were unsuccessful. Lind[4] made the same attempt about twelve years ago, though the work was not published until after the writers' work was completed. Lind was unable to show any effect on the velocity of a hydrogen-oxygen explosion in a brass tube fitted with an axial electrode charged by means of a Wimshurst machine.

The present attempt involved the explosion of an acetylene-air mixture in the ratio of 1:7.14, which is the best ratio to give carbon monoxide gas and the most likely to detonate. Detonation in a 1-meter Pyrex tube was, in fact, very marked when this mixture was fired by an ordinary automobile spark plug, but no decrease in the detonation could be observed when the tube was fitted with a long axial brass electrode charged to ±500 volts by means of a battery of dry cells. Similarly, there was no effect when the tube was placed within a solenoid 7 inches long and containing 500 turns of copper wire with a field strength of 2000 ampere turns. Finally, with a solenoid 2.5 feet long with 1500 turns of wire and carrying 7.5 amperes, hence a field strength of 11,000 ampere turns, no effect was noted, whichever polarity was used. Neither did a strong horseshoe magnet with an iron core so placed that two poles were on opposite sides of the glass tube at various distances from the spark plug show any effect. While these experiments were failures, it was hardly to be expected that the attainable fields would be sufficient to affect decisively the velocity or the number of electrons in the flame, especially when no exact measurements were made and the only criteria of the effect were the visual and audial judgments of the violence of detonation.

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[4] *J. Phys. Chem.*, **28**, 57 (1924).

Relative Effects of Some Nitrogen Compounds upon Detonation in Engines[1]

By T. A. Boyd

General Motors Research Corp., Dayton, Ohio

Nitrogen in some of its compounds exerts a greater influence upon the character of combustion than any other element of small atomic number. The action of nitrogen is influenced in a large way by the elements or radicals attached to it. Thus, in some of its compounds it is quite effective for suppressing detonation, in some it is almost neutral, and in some it exerts the remarkable effect of inducing detonation. For example, detonation is suppressed by aniline, it is affected very little by pyridine, and it is induced or increased by propyl nitrite. The data presented in this paper show that in general the nitrogen compounds which are most effective for suppressing detonations are the primary and the secondary amines. Of these the aryl amines or those that contain at least one aryl group have much the larger influence for eliminating detonation from internal combustion engines.

NITROGEN in some of its compounds exerts a greater influence upon the character of combustion than any other element of small atomic number.[2] Unlike molecular iodine, though, which is very effective for influencing internal combustion, molecular nitrogen has no effect for suppressing detonation, except in so far as it slows down the rate of flame propagation by diluting the combustible mixture. But in this latter particular a similar effect is produced by other inert gases, such as carbon dioxide for example.

In distinction from its ineffectiveness in the molecular state, nitrogen in some of its compounds exerts a large influence upon the character of combustion. By weight nitrogen forms about 73 per cent of a proper combustible mixture of kerosene and air. When such a mixture is burned in an engine of 75 pounds compression, the combustion is accompanied by violent detonation. However, if there is added to the fuel an amount of diphenylamine, for example, sufficient to increase the weight of nitrogen in the total fuel-air mixture only 0.025 per cent, or from 73,000 to 73,025 parts per 100,000, the character of the combustion is entirely changed and the operation of the engine becomes very smooth and free from the disturbance that is called a detonation or knock.

As might be expected from its low atomic weight, the action of nitrogen is influenced in a large way by the elements or radicals attached to it. Thus, in some of its compounds it is quite effective for suppressing detonation, in some it is apparently almost neutral, and in some it exerts the remarkable effect of inducing detonation. For example, detonation is suppressed by aniline, it is affected very little by pyridine, and it is induced or increased by propyl nitrite.

The purpose of this paper is to present in a systematic way the relative effects of a number of the compounds of nitrogen upon detonation in internal combustion engines.

How the Measurements Were Made

The apparatus used in determining the relative influences of the various compounds has already been described in considerable detail.[3] This instrument, called the "bouncing-pin apparatus," consists essentially of a sensitive detecting device designed to screw into the heat of the engine cylinder, and an electrolytic cell placed in an electric circuit which is arranged in such a way that contact points are closed intermittently whenever detonation occurs in the engine. In the lower end of the cylinder element is a small piston the vertical movement of which is resisted by a stiff spiral spring. Resting on top of the piston simply by gravity is a light steel rod or pin, the upper end of which touches a cantilever spring element bearing the lower of the two contact points.

The strength of the spiral spring above the piston is such that during normal combustion the amplitude of the piston's vertical movement is only a few thousandths of an inch, so that the pin following the movement of the piston does not close the contact points. When the violent impulse produced by a detonation in the combustion chamber is applied to the lower end of the piston, however, its movement is so sudden

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[1] Presented before the Division of Petroleum Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] Other publications describing means of influencing detonation, or the "knock," in automotive engines are: Midgley and Boyd, *J. Soc. Automotive Eng.*, **10**, 7 (1922); *Ibid.*, **10**, 451 (1922); This Journal, **14**, 589, 849, 894 (1922); Midgley, *Ibid.*, **15**, 421 (1923).

[3] Midgley and Boyd, *J. Soc. Automotive Eng.*, **10**, 7 (1922); This Journal, **14**, 589, 894 (1922).

that the pin is thrown upward and free from the piston, thereby closing the electric circuit at the contact points and causing a generation of gas in the electrolytic cell. The elements bearing the contact points are springs; and, since the more violent the detonation the greater the impulse given to the pin, the length of time the contacts are closed is a function of the intensity of detonation. The amount of gas generated in the cell, in turn, is proportional to the length of time the circuit is closed. And so the volume of gas evolved in the electrolytic cell, which is arranged to measure it automatically, is a function of the intensity of detonation.

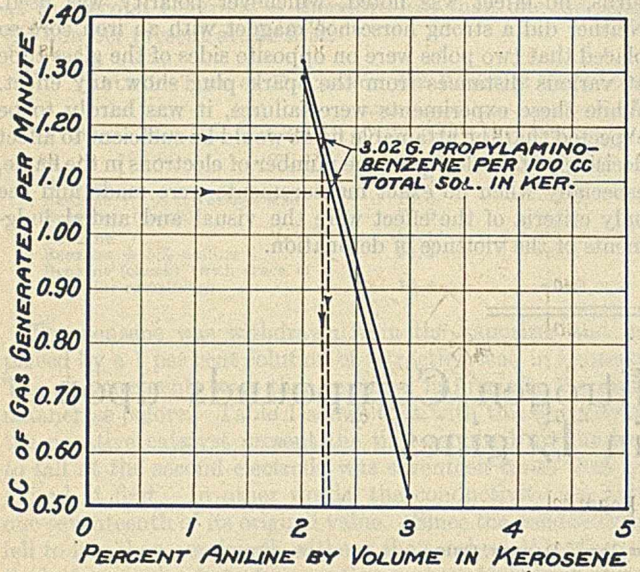

Fig. 1—Comparison of Propylaminobenzene with Aniline

Propylaminobenzene		Aniline
3.02 grams	=	2.28 grams
0.0224 mol	=	0.0245 mol
1 mol	=	1.10 mols

The observations reported in this paper were made on a small, single-cylinder, air-cooled engine. Kerosene was used as fuel, and in all the measurements aniline in concentrations of 1 to 3 per cent by volume in the fuel was employed as the standard of effect in suppressing detonation. In such concentrations aniline is readily soluble in kerosene at ordinary temperatures, so that no binding material of high solvent action was needed to carry it into solution. In one or two cases, however, where the material whose effect was being compared with that of aniline was not sufficiently soluble in kerosene alone, a mixture of absolute alcohol and kerosene was used as fuel, and the compression of the engine was raised in order to give knocking conditions. The standard aniline was of course always dissolved in the same fuel as the compound under test.

Table I—Influence of Some Groups Attached to the Atom on the Antiknock Effect of Nitrogen

Compound	Formula	Reciprocal of mols required to give antiknock effect equivalent to 1 mol of aniline[a]	Source of Compound
Ammonia	NH_3	0.09 (negative)	
Ethylamine	$C_2H_5NH_2$	0.20	Eastman
Diethylamine	$(C_2H_5)_2NH$	0.495	
Triethylamine	$(C_2H_5)_3N$	0.14	
Diethylaniline	$C_6H_5N(C_2H_5)_2$	0.24	General Motors Research
Ethyldiphenylamine	$C_2H_5N(C_6H_5)_2$	0.58	
Triphenylamine	$(C_6H_5)_3N$	0.09	
Diphenylamine	$(C_6H_5)_2NH$	1.5	Eastman
Phenylamine (aniline)	$C_6H_5NH_2$	1.0	du Pont

[a] Based on concentrations of aniline up to 3 per cent by volume in kerosene.

The method of making the measurements can best be described by giving a specific example. A comparison of the effect of propylaminobenzene with that of aniline may be used for this purpose. First, it was roughly determined that about 3 parts of propylaminobenzene and 97 parts kerosene by volume gave about the proper amount of detonation in the engine—that is, it gave a knock of such intensity that somewhat less than 1.25 cc. of gas was generated in the electrolytic cell in 1 minute. This value was known to lie between that for 2 parts and that for 3 parts of aniline, which was the compound used as a standard of effect, in the same fuel.

A number of 1-minute runs were then made, the fuel being successively 3 parts aniline and 97 parts kerosene by volume, 3.02 grams propylaminobenzene in 100 cc. total mixture with kerosene, and 2 parts aniline and 98 parts kerosene. For each run the volume of gas generated and the power output of the engine were recorded, the latter simply as a check on the engine operation. This set of runs was then repeated in the reverse order. All the values for the volumes of gas generated in the electrolytic cell during the runs on each fuel were then averaged and the data so obtained were plotted on coördinate paper in the manner illustrated in Fig. 1 in which the results of two determinations like that described are shown. The amount of aniline to which 3.02 grams of propylaminobenzene are equivalent was obtained simply by projecting its value in gas generated horizontally to the corresponding aniline curve and vertically to the abscissa scale, where the aniline equivalent was read directly. These numbers were then averaged and converted to the molecular basis, as is shown by the tabulation under Fig. 1.

Results

The results of the determinations, or the data on which this paper is based, are tabulated in Tables I and II, and shown graphically in Figs. 2 and 3. The most striking thing about these charts is the way in which the curves of effect rise and fall with the different elements or radicals attached to the nitrogen atom.

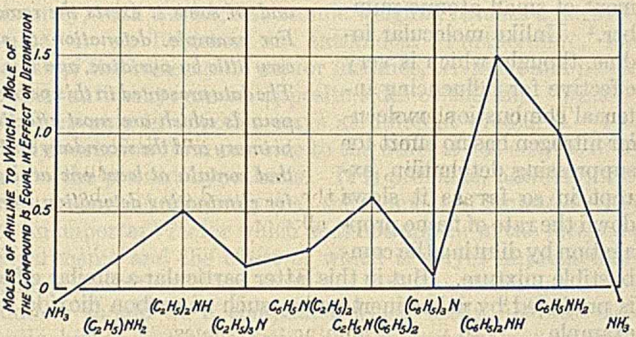

Fig. 2—Influence of the Groups Attached to the Atom on the Antiknock Effect of Nitrogen

These interesting facts may be noted about the data in Fig. 2:

(1) The curve has minimum points when the atoms or radicals attached to the nitrogen atom are all alike. Thus, minimum effects on detonation are shown by NH_3, $(C_2H_5)_3N$, and $(C_6H_5)_3N$.

(2) The curve has maximum points at diethylamine and at diphenylamine, both secondary amines, the intermediate maximum point being at ethyldiphenylamine, a tertiary amine. The superior effect of the phenyl radical for influencing the antiknock action of nitrogen is illustrated by the values for diethylamine and diphenylamine, the latter being three times as great as the former.

(3) Two of the intermediate points on the curve are at primary amines, ethylamine and aniline, the other being at the tertiary amine, phenyldiethylamine (diethylaniline). The compound at this last intermediate point differs from that at the adjacent maximum point by having two alkyl groups and one aryl group, instead of two aryl groups and one alkyl group. The greater effect of the aryl than the alkyl radicals for influencing the antiknock value of nitrogen is illustrated here also in the relative values for ethylamine and aniline, the latter of which is much more effective than the former.

Further data on the influence of the atoms or radicals attached to nitrogen on its effect upon detonating combustion are plotted in Fig. 3, which shows the relative antiknock values of a number of derivatives of aniline. Although the diagram is self-explanatory, mention may be made of the following points: Replacing one of the hydrogen atoms of the amine group by an organic radical increases the effectiveness in the cases of the methyl, ethyl, and phenyl radicals. Thus, methylaniline is 40 per cent more effective molecularly than aniline, and diphenylamine is 10 per cent more effective than methylaniline; but when an alkyl radical larger than ethyl is substituted in the amine group the antiknock effect is lowered.

TABLE II—EFFECTS ON THE ANTIKNOCK VALUE OF ANILINE OF SUBSTITUTING VARIOUS ORGANIC RADICALS FOR HYDROGEN IN THE RING AND IN THE AMINE GROUP

COMPOUND	FORMULA	Reciprocal of mols required to give anti-knock effect equivalent to 1 mol of aniline[a]	SOURCE OF COMPOUND
Aniline	$C_6H_5NH_2$	1.0	du Pont
Toluidine	$CH_3C_6H_4NH_2$	1.22[b]	Eastman
m-Xylidine	$(CH_3)_2C_6H_3NH_2$	1.4	du Pont
Cumidine	$(CH_3)_3C_6H_2NH_2$	1.51	
Ethylaminobenzene	$C_2H_5C_6H_4NH_2$	1.14	General Motors Research
n-Propylaminobenzene	$C_3H_7C_6H_4NH_2$	1.10	
n-Butylaminobenzene	$C_4H_9C_6H_4NH_2$	1.11	
Amylaminobenzene	$C_5H_{11}C_6H_4NH_2$	1.15	
Aminodiphenyl	$C_6H_5C_6H_4NH_2$	1.14	
Monomethylaniline	$C_6H_5NHCH_3$	1.4	Eastman
Monoethylaniline	$C_6H_5NHC_2H_5$	1.02	du Pont
Mono-*n*-propylaniline	$C_6H_5NHC_3H_7$	0.75	Eastman
Mono-*n*-butylaniline	$C_6H_5NHC_4H_9$	0.52	
Mono-iso-amylaniline	$C_6H_5NHC_5H_{11}$	0.248	General Motors Research
Diphenylamine	$C_6H_5NHC_6H_5$	1.5	Eastman
Dimethylaniline	$C_6H_5N(CH_3)_2$	0.21	Baker
Diethylaniline	$C_6H_5N(C_2H_5)_2$	0.24	Eastman
Di-*n*-propylaniline	$C_6H_5N(C_3H_7)_2$	0.27	

[a] Based on concentrations of aniline up to 3 per cent by volume in kerosene.

[b] Average of *o*, *m*, and *p* values.

The low values for the dialkyl anilines are worthy of note; but, as may be seen from Fig. 2, the dialkylanilines are more effective than triethylamine, or even than triphenylamine, compounds in which the nitrogen atom is bonded to only one type of organic radical.

The alkylaminobenzenes exhibit a peculiar type of function. The curve shows not only the dropping off from the maximum at methylaminobenzene (toluidine) that characterizes the monoalkylanilines, but also a later increase in molecular effectiveness as the size of the alkyl radical attached to the ring becomes larger. The alkylaminobenzenes from the ethyl to the amyl were prepared by nitrating and reducing the corresponding alkylbenzenes. The compounds so obtained, and which theoretically should consist largely of the para isomer, were used in determining the values shown. In this fact may lie the explanation for the peculiar shape of the alkylaminobenzene curve, because *p*-toluidine is about one-sixth more effective for eliminating detonation than *o*-toluidine or *m*-toluidine, both of which are of about equal effectiveness. So it appears that the relative percentages of the para isomer present in the various alkylaminobenzenes used would exert a considerable influence on the shape of the curve.

TABLE III—NITROGEN COMPARED WITH SOME OTHER ELEMENTS IN EFFECT UPON COMBUSTION

ELEMENT	COMPOUND	Reciprocal of mols required to give an antiknock effect equivalent to 1 mol of aniline
Nitrogen	$(C_2H_5)_3N$	0.14
	$(C_6H_5)_2NH$	1.5
Selenium	$(C_2H_5)_2Se$	6.9
Tellurium	$(C_2H_5)_2Te$	26.8
Lead	$(C_2H_5)_4Pb$	120.0

COMPARISON OF NITROGEN WITH SOME OTHER ELEMENTS

The effects of nitrogen compounds for suppressing detonation are small in comparison with those of similar compounds of some of the elements described in previous publications.[2] Some comparative values illustrating this point are tabulated in Table III. From these data it may be seen that, even in diphenylamine, one of the best of its compounds reported, nitrogen is only about one-eighteenth as effective molecularly as diethyl telluride and only about one-eightieth as effective as tetraethyl lead.

NEARLY NEUTRAL NITROGEN COMPOUNDS AND THOSE THAT INDUCE DETONATION

Some organic nitrogen compounds have very little effect upon the character of combustion. Thus, such materials as pyridine, quinoline, piperidine, phenylhydrazine, acetamide, and organic cyanides have little importance because, relatively speaking, the influence they exert upon detonation is extremely small. But when nitrogen is bonded into organic compounds with oxygen, such as nitrates and nitrites, the resulting materials are inducers of detonation, the former being more effective than the latter. The alkyl compounds of this class exert a much greater disturbing influence upon combustion than the corresponding aryl compounds. For example, isopropyl nitrite is very much more effective than nitrobenzene for inducing detonation. One mol of isopropyl nitrite is equivalent in effect upon combustion to the inverse of the detonation-suppressing influence of over 10 mols of aniline, but the detonation-inducing effect of nitrobenzene is very small. Nitric acid, and even some inorganic nitrates, can also cause detonation in internal combustion engines.

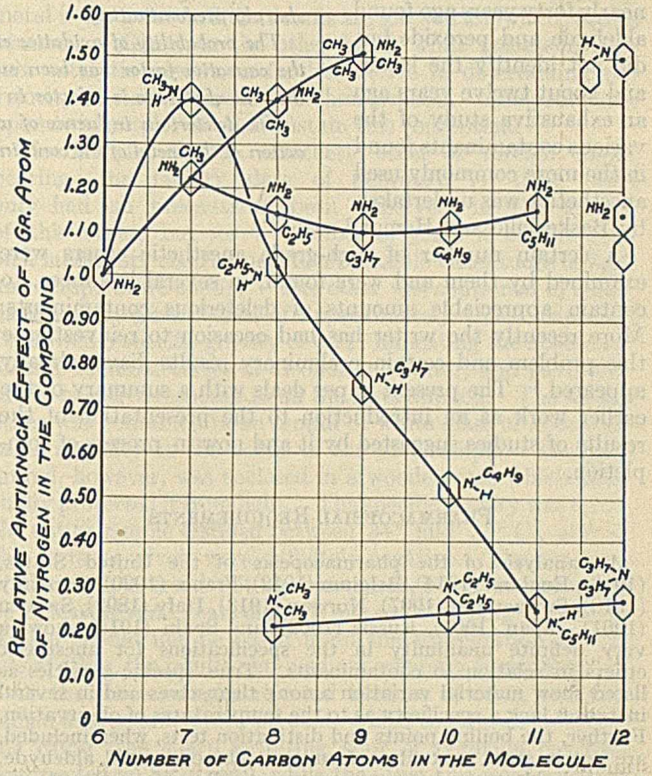

FIG. 3—INFLUENCE ON ANTIKNOCK EFFECT OF ANILINE OF SUBSTITUTING VARIOUS ORGANIC RADICALS FOR HYDROGEN IN THE RING AND IN THE AMINE GROUP

Naturally, the compounds that have a desirable influence upon the combustion are those which eliminate or suppress the detonation characterizing the burning of most petroleum hydrocarbons when the initial compression to which the fuel-air mixture is subjected is an economical one. The data presented in this paper show that in general the nitrogen compounds which are most effective for this purpose are the primary and the secondary amines; and of these the aryl amines, or those that contain at least one aryl group, have much the larger influence for eliminating detonation from internal combustion engines.

The More Common Impurities of Anesthetic Ether[1]

By A. W. Rowe

Evans Memorial, Boston, Mass.

Simple tests for the examination of the purity of anesthetic ether have been selected. One hundred ethers have been subjected to these tests and thirty-four of these have been found to be seriously contaminated.

Peroxide and aldehyde are the chief contaminants, the former sharply predominating.

The probability of oxidative changes subsequent to preparation as the causative factor has been suggested, and evidence is offered that the time of storage is a factor in determining oxidation.

The deleterious influence of water and alcohol and the catalytic action of the metal of the container are briefly discussed.

THE deleterious effects of storage on the purity of anesthetic ether have received comment by several writers. Warden[2] nearly forty years ago found aldehyde and peroxide but did not identify the latter, and about twelve years ago an exhaustive study of the various contaminants found in the more commonly used anesthetics was undertaken by Baskerville and Hamor.[3]

A certain number of high-grade anesthetic ethers were examined by them and were found, in several instances, to contain appreciable amounts of deleterious contaminants. More recently the writer has had occasion to reinvestigate this problem and certain preliminary results have already appeared.[4] The present paper deals with a summary of the earlier work as an introduction to the presentation of the results of studies suggested by it and now in process of completion.

Pharmacopeial Requirements

An analysis of the pharmacopeias of the United States, (1916), England (1914), Belgium (1912), France (1920), Germany (1910), Switzerland (1907), Norway (1913), Italy (1892), Sweden (1901), Japan (1901), Russia (1902), and Spain (1915) shows a very definite unanimity in the specifications for anesthetic ethers in relation to contaminants. True, specific gravities as listed show material variation among themselves and in several instances lack a specificity as to the temperatures of observation. Further, the boiling points and distillation tests, when included, are not in strict mutual conformity. The odor, acid, aldehyde, and peroxide tests, however, are practically universal and uniform. Of the two latter a positive aldehyde test is one of exclusion in all the countries except Japan, while the peroxide test is omitted only by Japan and Spain. Germany, Norway, Sweden, Japan, and Russia specify glass containers.

Tests for Purity

The preliminary studies already cited dealt primarily with the establishment of a few simple, dependable tests covering the points mentioned, and these may be briefly reviewed as an introduction to the body of the paper.

The specific gravity was determined by the Westphal balance, the earlier determinations being checked by pycnometric measurements. The ether was contained in a silvered, cylindrical Dewar flask and the density determined by a carefully standardized Westphal balance. Temperatures were carefully recorded. Owing to the prevailing laboratory temperature, all measurements were referred to a basis of specific gravity at 25°/25° C. To avoid delay in the measurement—a thermally homogeneous ether is essential—the temperature coefficient of the specific gravity was determined by a series of careful pycnometric measurements, at different temperatures, and was found to be 0.0008 per degree. (Corrections for temperature at no time exceeded ±0.002.) On this basis of temperature comparison, the density of pure ether approximates 0.711, and as water and alcohol represent the two common impurities, an upper limit of 0.714 was set to embrace allowable amounts of these two substances. The hygroscopicity of anhydrous ether is a complicating factor and determines this somewhat liberal specific gravity range.

The boiling point and distillation tests are usually considered together. The former test is nearly valueless, as water and alcohol exercise opposite effects on the boiling point. The difficulty of carrying out the distillation test in such manner as to exclude error makes it time-consuming if properly performed, and worthless if carelessly carried out. In many of the later determinations the test was omitted.

In the earlier samples acidity was titrated by the modified Vulpius[5] technic, but the amounts found were so small that the standard qualitative litmus paper test was substituted.

The odor test is easily performed and is surprisingly informative concerning the possible presence of the higher alcohols and their products, free acids and peroxides.

The aldehyde test is one of the two fundamental exclusion tests. The test selected was the standard potassium hydroxide method, the time being 6 hours. A white turbidity may be caused by alcohol; brown or yellow coloration indicates the formation of aldehyde resin.

The peroxide test is the second one for basic exclusion and is the test for the most commonly found deleterious contaminant. Following the recommendation of Baskerville and Hamor, cadmium and potassium iodide in 10 per cent aqueous solution are used as the reagent and the requirement is placed at freedom from liberation of iodine within 1 hour.

Note.—The various requirements outside of the United States usually specify potassium iodide alone, but as this is notably subject to the influence of atmospheric oxygen when in acid solution, the foregoing technic seems to offer the greater accuracy and to be the fairer criterion.

Results

The present report comprises results obtained from the examination of 100 samples of anesthetic ether, gathered from widely divergent sources over a period of nearly three years, and representing quantities of material well in excess of 10 tons.

The tabulated results are divided into three series: The first of 25 samples was tested prior to the first report, the second of 50 samples contained many lots sent direct from the factory; and the third comprised a series of 25 samples the majority of which were obtained direct and so not subject to the vicissitudes of storage. In all, 66 ethers complied with the standards of the Pharmacopeia and 34 did not. An analysis of the rejections is compiled in Table I.

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[1] Received April 19, 1924. Presented in part before the National Anesthesia Research Society Congress, Columbus, Ohio, October 31, 1922.

[2] *Am. J. Pharm.*, **57**, 148 (1895).

[3] This Journal, **3**, 301, 378 (1911).

[4] *The Modern Hospital*, **17** (1922). *Current Res. anaes. analg.*, **2**, 104 (1923).

[5] *Chem. Ztg.*, **11**, 1246 (1887); *J. Soc. Chem. Ind.*, **6**, 750 (1887).

TABLE I—ANALYSIS OF CAUSES OF REJECTION OF ETHER SAMPLES

		NUMBER REJECTED			
CONTAMINANT		Series 1	Series 2	Series 3	Total
Aldehyde and peroxide		1	3	0	4
Aldehyde		3	0	0	3
Peroxide		8	10	5	23
Acid		1[a]	2	0	3[a]
Odor		0	1	2[a]	3[a]
Totals	Number	12[b]	16	6[b]	34[b]
	Per cent	48	32	24	34

[a] Also contained peroxide.
[b] Correcting for samples counted twice.

The first inference to be drawn from the results is that one-third of a series of 100 ether samples have been rejected because of failure to comply with the U. S. P. specifications. The second lies in the relative results of the three series, in which there is apparently an inverse proportion between the number of rejected lots and the presumptive period of storage. In other words, there seems to be a clear indication that the ether, after being placed in the container, undergoes certain deleterious changes.

Further analysis of the table shows that aldehyde and peroxide are the dominant contaminants, with the latter a factor in over two-thirds of the samples. An interesting confirmation of this conclusion is found in the results of a series of analyses made at the Royal Victoria Hospital of Montreal. Of 14 samples drawn from three different sources, 3, or 21 per cent, were rejected because of the presence of peroxide. Odor and acid tests were uniformly negative. Five of the samples showed turbidity and a white separate referable to alcohol, but in none of them was there the brown discoloration of aldehyde resin. Two samples showed high specific gravities but were otherwise satisfactory.

In the writer's opinion the presence of aldehyde alone indicates an ether contaminated at the time of placing in the containers; those containing peroxide alone, ethers which have probably undergone deterioration during storage. Where both are present the aldehyde probably represents a second phase in the oxidation of the ether or the alcohol, although it may conceivably be due to an initial contamination.

The term "peroxide" is used for its nonspecificity, although the recent work of Clover[6] has done much to clear up the question of ether oxidation. Clover regards the first oxidative step as the formation of an ether peroxide and to this latter body assigns what seems to be a probable formula. This by decomposition could go to form aldehyde directly, while alcohol and water might be among the other products. In the presence of acid, hydrogen peroxide would be formed, and in the opinion of Clover the presence of hydrogen peroxide is to be regarded as indicative of secondary rather than primary oxidation.

A detailed discussion of the oxidative changes is to be the subject of a shortly forthcoming paper. A few general considerations are pertinent to the present discussion, however.

The three substances normally present in the majority of high-grade anesthetic ethers are alcohol, water, and air. The statement is usually made that alcohol is included to prevent the undue cooling effects obtained by the evaporation of an alcohol-free ether. Two problems—first, the possible prevention of contamination by the presence of alcohol; and second, the removal of contaminants by means of alcohol—were studied a number of years ago by Thoms.[7] He concluded that alcohol neither prevented contamination nor removed contaminants. Susceptible as it is to oxidation, it forms a very evident potential source of aldehyde. Its exclusion should improve the keeping power of the ether, and the objection to an alcohol-free ether previously cited could be met by the addition of definite amounts of pure alcohol prior to use.

Water is a powerful catalytic agent for certain types of reaction. Further, in the presence of oxygen and many of the metals it tends spontaneously to produce hydrogen peroxide, a powerful oxidizing agent. Its boiling point is relatively high compared with that of ether and if its inclusion is for the purpose of moistening the ether vapor the end is hardly attained. The substitution of a water bottle through which the ether vapor is bubbled gives a far more efficient saturation and removes another source of potential contamination.

Air cannot be entirely excluded, although the sealing of containers of ether at the boiling point of the liquid and with the container practically full would cut down the concentration of the active agent. That this offers mechanical difficulties is obvious. The current practice in this country is to market ether in metal containers and with an appreciable air space. The number of chemical reactions catalyzed by metal is too great and the details are too well known to require comment. Glass, on the other hand, while possessing certain catalytic powers, is far less active in determining the velocity of oxidation reactions than is metal. Analyses made upon two samples of ether sustain this contention.

The first lot was an anesthetic ether of foreign make, bearing the factory date of February 7, 1910. Not only had no precautions been observed in the storage of this ether, but for a number of years it had reposed on a laboratory shelf subject to all possible vicissitudes of light and temperature change. The ether was contained in small, dark amber, glass bottles of approximately 150cc. capacity. It showed a specific gravity of 0.711 indicating the absence of all but minimal traces of alcohol and water, and gave definitely negative response to all the tests applied. The second ether was contained in an ampul of white glass of about the same capacity as the bottle of the first sample. The glass ampul, however, was enclosed in a wooden case which effectually protected it from light. The specific gravity was 0.711, the entire sample distilled between 34° and 35° C., and all the tests as given were definitely negative. The exact age of the sample could not be ascertained, but it was known to be at least several years old. While too sweeping a generalization should not be based upon the examination of two lots of ether, the results obtained are certainly suggestive.

Of the three samples rejected because of odor, one contained a large amount of peroxide which could well have been the cause (the sharp irritating odor of peroxide has been commented on by others), while the other two were contaminated by appreciable amounts of higher alcohols (fusel oil) or their oxidation products. Of the three samples showing acid reaction, one contained free hydrochloric acid with appreciable amounts of a metallic chloride—in other words, soldering fluid. (The odor here was sharp and irritating, but as this came from so patently foreign a cause, it is not included in the tabulation.) Of the two remaining, one also had peroxide in liberal amount and presumably represented a later stadium in the oxidation, while no clue to origin was given by the analysis of the other.

ACKNOWLEDGMENT

The author takes pleasure in expressing his thanks to Marion D. Alcott and Endora Mortimer, for their assistance in making many of the analyses; to Drs. D. H. Arnott and R. C. Kingswood for the analyses made at the Royal Victoria Hospital of Montreal; and to Drs. F. L. Richardson, Samuel Johnston, and E. A. Tyler for their coöperation with regard to the samples of old ether contained in glass.

Celluloid films so thin that 254,000 of them could be packed into a space an inch thick have been produced by the Bureau of Standards. They were made by dissolving the celluloid in amyl acetate and dropping the solution on a clean water surface, allowing the acetate to evaporate. These films are intended for use in connection with some X-ray studies the Bureau of Standards is undertaking.

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[6] *J. Am. Chem. Soc.*, **44**, 1107 (1922).

[7] *Pharm. Gesell.*, Berlin, **1894**.

Mercury Poisoning from Electric Furnaces[1,2]

By Louis Jordan and W. P. Barrows

Bureau of Standards, Washington, D. C.

Four cases of subacute or chronic mercurial poisoning[3] were found among men operating high-frequency induction furnaces. One case terminated fatally; two of the other three cases were quite serious.

A survey of laboratory conditions during operation of the furnaces indicated the escape of mercury vapor from the mercury discharge gaps of the high-frequency converters. The concentration of mercury vapor in the air beside the furnace during operation was as high as 0.7 mg. per cubic meter, a concentration sufficient to cause mercury poisoning if daily exposure continued for several months or longer. Another source of possible poisoning existed in the frequent cleaning of the mercury and repairs necessary in the original type of discharge gap.

A new type of discharge gap having stationary electrodes, mercury-sealed discharge chambers, and operating in an atmosphere of hydrogen, was installed and enclosed in a separate compartment fitted with a forced-draft hood. Under these conditions the escape of mercury from the discharge gap could not be detected. Repairs to the gap are infrequent and the necessity of cleaning the mercury is practically eliminated in the present equipment.

Four cases of subacute or chronic mercury poisoning were recently experienced in a metallurgical research laboratory among men operating high-frequency induction furnaces. The conditions under which these cases of mercurialism developed may exist in other research laboratories and possibly in a small number of industrial plants. The insidious nature of the development of chronic mercurialism, as well as the serious and sometimes fatal results of continued or repeated exposure to very small amounts of mercury vapor, are clearly shown in the cases under consideration.

It should be understood that the record of this experience with mercury poisoning is in no way made as an indictment of the high-frequency induction furnace, since work with this furnace subsequent to its recognition as the cause of the poisoning indicates that with proper precautions it can be operated with entire safety. It should also be stated that, so far as is known, the instance given in the report is the only case of serious mercury poisoning among the users of over sixty installations of high-frequency furnaces. Nevertheless, the seriousness of the cases experienced in these laboratories warrants careful attention to protection against the possible danger.

Metallic Mercury a Source of Danger

The dangers that lie in the frequent handling of mercury or the continued exposure to mercury vapor, even at ordinary room temperatures, are indicated by data given and cases described by Kober and Hayhurst.[4] In spite of such records of the poisonous nature of mercury, its frequent use in chemical and physical laboratories without any recognized ill effects has probably in many instances led to a certain amount of disregard for the possible danger.

Volatilization of Mercury—Kober and Hayhurst state that the greatest danger to those who work with mercury lies in the fact that it will volatilize at room temperature. Glaser[5] gives the loss by volatilization of mercury at room temperature as 0.002 mg. per sq. cm. of surface per hour, increasing from 0.016 to 0.727 mg. as the temperature rises from 30° to 100° C. Kober and Hayhurst, quoting Renk, give the concentration of mercury in the air at various heights above a mercury surface of 0.5 square meter. These figures indicate the presence of 0.85 mg. of mercury per cubic meter of air at 10° C. and 1 meter above the mercury surface. The same authors quote Hertz as giving practically the same value for the concentration of mercury vapor in air at 20° C. These concentrations given by Renk and by Hertz are as great as those found to have caused the poisoning resulting from the operation of high-frequency induction furnaces.

Absorption of Mercury through the Skin—It is also said that mercury can be taken into the body by absorption through the pores of the skin. A number of cases of poisoning have been reported among dentists, which were probably due to a practice of rubbing amalgams in the palm of the hand. Teleky[6] tells of an examination by Schulte of the urine of fifteen dentists and technical assistants. Schulte invariably found traces of mercury. Teleky also cites Edsall as describing the cases of two dentists who contracted mercurial poisoning from working up amalgams in the palms of their hands.

In the course of an investigation of dental amalgams at the Bureau of Standards some years ago, one of the men engaged in the work had occasion to prepare a considerable number of amalgams following the usual practice of dentists of working the mixture of solid alloy and mercury to a plastic condition in the palm of the hand. The man states that shortly after working in this manner for several weeks small red areas appeared on his back and left side. They were at first diagnosed by a physician as ringworm and so treated without any apparent effect. The physician later decided that his original diagnosis was not correct. No further medical treatment was given and the blotches disappeared in a short time. This was very probably a symptom of mercury absorption which had been caused by the work with dental amalgams.

Mercury in High-Frequency Converters

Obviously the most dangerous condition of work with mercury obtains when it is necessary to heat the metal to a point where vaporization is rapid. This is actually done in operating the present type of high-frequency induction furnaces whose power is supplied by an oscillatory-current, high-frequency converter embodying a mercury discharge gap.[7]

Two high-frequency furnaces have been used quite continuously for several years in the metallurgical chemistry laboratories of the Bureau of Standards. The two furnaces are in separate rooms. The smaller furnace, rated as a 10-kw.

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[1] Received June 24, 1924.

[2] Published by permission of the Director, U. S. Bureau of Standards.

[3] Turner, "Mercurial Poisoning," *Treasury Dept., Public Health Rpts.*, **39**, 329 (1924).

[4] "Industrial Health," **1924**. P. Blakiston's Son & Co., Philadelphia, Pa.

[5] "Zur Elektroanalyse des Quecksilbers," *Z. Electrochem.*, **9**, 11 (1903).

[6] Kober and Hayhurst, *op. cit.*, p. 485.

[7] Northrup, *Trans. Am. Electrochem. Soc.*, **25**, 69 (1919). The original type of mercury discharge gap with stationary electrodes and operating in alcohol vapor is described on pages 128 and 133 of this article. A more recent form of discharge gap with movable electrodes and operating in hydrogen is described in *Chem. Met. Eng.*, **29**, 932 (1923).

installation, was purchased in 1918. The larger furnace, having a 20-kw. converter, was secured in 1921.

At the time of its purchase the older furnace was equipped with the original form of discharge gap with stationary electrodes. It was operated with this form of gap until shortly after the installation of the second furnace. At that time the gap was remodeled and made of the same type as the gap supplied with the newer furnace—namely, with movable electrodes. During the operation of these gaps, ethyl alcohol was dropped into the discharge gap pot. All gaps were fitted with cork gaskets between the cover and the pot of the gap, and those with movable electrodes had tightly fitting openings or asbestos-packed stuffing boxes through which the electrodes moved, and electrical insulators passing through the gap cover had asbestos gaskets or packing.

Possible Escape of Mercury Vapor. In spite of these precautions for making the gap tight, vapors could always escape, as evidenced by the odor of alcohol vapors as soon as the furnaces began to operate. Some means for the escape of alcohol vapor had to be provided, since alcohol was allowed to drop into the gap continuously during operation. For this purpose a small spring valve for the release of pressure within the gap was provided in the cover. On starting up the furnaces, slight explosions sometimes occurred inside the gap due to alcohol on the mercury surface remaining from a previous run. Such explosions sometimes blew out portions of the gasket and, as appears very probable in the light of subsequent experiences, permitted the escape of large amounts of mercury vapor if the damage to the gasket was not detected and repaired at once. With a gap of this construction, which allowed continual escape of alcohol vapor, it is not surprising that mercury vapor also had means of escape.

Dangers in Cleaning and Repair of Gap. The mercury in these gaps rapidly fouled, in spite of the alcohol vapor atmosphere, and frequent cleaning was required. Breakdown of electrical insulation and wearing and breaking of graphite electrode tips also made it necessary frequently to open the gap and make repairs. The furnace operator on such occasions was exposed to danger of mercury absorption from getting on his hands or clothing the finely divided mercury that condensed in a thick layer on the inside of the gap, as well as from stirring up and inhaling this fine dust, unless all cleaning and repair work was done while wearing gloves and under a well-ventilated hood.

Obviously, in the long-continued operation of a high-frequency converter of the type described, there may exist opportunities both of inhaling mercury vapor and of absorbing metallic mercury through the skin.

POISONING AMONG FURNACE OPERATORS

In the latter part of July, 1923, one of the men, designated as "A," who had frequently operated the induction furnaces for the past three years, quite rapidly developed alarming symptoms—diarrhea, rapid loss of weight, very marked pallor, and great weakness. "A" was sent by his physicians to a hospital for rest and observation. The case was at first diagnosed as ulcerations of the intestine, and later as pulmonary and intestinal tuberculosis accompanied by anemia. After many examinations and questioning as to possible causes of his condition, the possibility of some form of metal poisoning was suggested. "A" stated that frequently he had experienced headaches after operating the induction furnace, and recalled that after one or two periods of unusually frequent and continued operation of the furnace he had experienced a feeling of general illness. He was sent to a tuberculosis sanatorium late in September. In spite of all possible care and medical attention no improvement could be brought about, and he died early in February, 1924. The abnormal intestinal activity, continuing almost to the last, and the anemic condition resulting in complete exhaustion were the most serious aspects of the case.

While tuberculosis was presumably the immediate cause of "A's" death, the similarity of his condition and symptoms at the beginning of his sickness to the symptoms shown by the remaining furnace operators in their physical examinations, coupled with the fact that "A" had been exposed for several years to the conditions which were later shown to have caused mercury poisoning in all the other furnace operators, make it quite certain that he was also suffering from mercurialism. The symptoms common to both the case of "A" and that of the remaining men suffering from mercury poisoning were a striking paleness, diarrhea, marked deterioration in the condition of the teeth, and headache following any continued operation of induction furnaces.

The final stages of chronic mercury poisoning are said to be hemorrhages in various parts of the body and death from anemia, septic inflammation, or exhaustion. This description follows very closely the last stages of "A's" sickness.

SURVEY OF LABORATORY CONDITIONS—At the first suggestion of metal poisoning in the diagnosis of "A's" case, attention was directed towards the mercury discharge gap of the induction furnace. The assistance of the United States Public Health Service was requested in the study of conditions existing in the laboratories during the operation of the furnaces and in the examination of other men working under similar conditions. Dr. J. A. Turner, of the Office of Industrial Hygiene and Sanitation, was assigned to the study. His report[8] of the investigation will merely be summarized here.

Determinations of mercury were made on dust samples collected at various points in the room in which high-frequency furnaces were operated; determinations were made of mercury vapor in the laboratory air during the operation of furnaces; and thorough physical examinations were made of all men working with or near the furnaces.

Diffusion of Mercury through Furnace Room. The dust samples were collected at points where accidental spilling of mercury was most improbable. A sample taken at a distance of 15 feet from the furnace, brushed from a narrow ledge above the sink and out of reach from the floor, contained 1.0 per cent of mercury. A sample taken at only 7 feet from the furnace contained 3.0 per cent of mercury. Inside the cage of the converter at places near the spark gap were deposits of fine gray powder which on rubbing showed small mercury globules.

Concentration of Mercury Vapor in Laboratory Air. Attempts were made to determine the amount of mercury vapor in the air during the operation of the furnaces. The first tests were made drawing the air through a glass tube packed with gold leaf and glass wool and determining the increase in weight of the tube. After subtraction of the value obtained from several blank runs when the furnace was not operating, these tests showed a small gain in weight which was equivalent to 0.5 mg. of mercury per cubic meter of air for the 10-kw. furnace, and 0.4 mg. for the 20-kw. furnace. This test was, however, a rather crude determination for the very small amount of mercury apparently present and no evidence of mercury could be detected in the appearance of the gold leaf after the test.

The method used for all subsequent tests was based on that described by Lloyd and Gardner,[9] a colorimetric method which is in effect a reversal of the Nessler method for determining ammonia. In place of the usual Nessler solution a solution containing ammonium chloride, potassium hy-

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[8] *Public Health Rpts.*, **39**, 329 (1924).

[9] *J. Soc. Chem. Ind.*, **31**, 1109 (1912).

droxide, and potassium iodide is added to the unknown solution containing mercuric chloride. A brown coloration is produced, which is matched with small amounts of a standard mercuric chloride solution. The method of washing air samples in a dilute aqua regia solution contained in a Palmer dust machine is described in detail in Dr. Turner's report.[8] Tests by this method made during the operation of the 10-kw. furnace indicated the presence of 0.7 mg. of mercury per cubic meter of air, an amount somewhat greater than that shown by the gold-leaf method. Similar samples of air taken when the furnace was not operating showed no mercury. The determination of the mercury in the aqua regia solution is very accurate. The completeness of the removal of mercury from the air passing through the aqua regia in the Palmer machine was not checked up, but this procedure certainly gives a result indicating a minimum probable value and is more direct than the gold-leaf method.

The examination of dust samples from places as distant as 15 feet from the mercury discharge gap proved that mercury vapor had been present in the laboratory and had diffused to a very considerable distance. The determinations of mercury vapor in the laboratory air during the operation of the induction furnace, and the entire absence of mercury if the furnace was not operating, proved that the source of the trouble was in the discharge gap of the high-frequency converter.

Physical Examination of Furnace Operators—At the time of the study of the laboratory conditions during operation of the furnaces in question, one of the men most concerned with the induction furnaces was seriously ill (case "A" described above). All the seven men remaining in the section were carefully examined. Two of these men, recent employees, had been exposed to mercury to a very slight extent, if at all, and showed no symptoms of poisoning. Two more had operated the furnaces some time previous to their examination. Their histories showed that they had experienced symptoms of mercury poisoning when operating the furnaces frequently, but for the past three or four years they had been but little exposed. The remaining three men, who were operating furnaces at the time of the examination, all showed definite symptoms of mercury poisoning.

The details of the examinations and histories of all these men are given by Dr. Turner.[8] The conclusions of his report indicate that the presence of mercury vapor in the laboratory air in a concentration of 0.7 mg. per cubic meter might result in the daily absorption of 0.77 to 1.29 mg. of mercury, and that this amount will produce symptoms of poisoning. Symptoms of chronic mercurialism are described as a copper-colored discoloration of the mucous membrane of the pharynx, swollen gums, superficial erosions of the mucous membrane of the gums and buccal mucous membrane, perialveolar abscesses, and occasional increased flow of saliva. Tenderness of the gums and teeth, increased intestinal activity occasionally developing into diarrhea, gastrointestinal disturbances, and neuralgic pains in various joints were also reported.

In addition to the symptoms of poisoning described in the *Public Health Reports*, it may be said that two of the men most seriously affected often had exhibited abnormal irritability or excitability, and one man had noted the appearance of eruptions and red blotches on his skin. Both these symptoms are said to be characteristic of chronic mercury poisoning. The effects of the poisoning on the teeth were very noticeable in all three of the men regularly operating the furnaces. In the case of the man longest exposed, the loss of eight teeth from loosening and abscessing resulted.

The survey of laboratory conditions during the operation of the high-frequency furnaces and the symptoms and histories of the four men regularly working with these furnaces left no doubt of the existence of an exceedingly dangerous state of affairs. The subsequent death of the man whose illness first called attention to the existence of chronic mercurialism among the furnace operators all too clearly emphasized the necessity of extreme precautions.

Elimination of Danger

New Type of Discharge Gap—A short time previous to the recognition of the existence of mercurial poisoning from the high-frequency furnace, specifications and drawings for a mercury discharge gap somewhat different from the usual type had been furnished the bureau. This gap had been developed to eliminate the frequent cleaning and repairs necessary in the old type gap. This new gap had stationary electrodes, was operated in an atmosphere of hydrogen, and the mercury in the discharge chamber was apparently very efficiently enclosed by means of water-cooled mercury seals. This design seemed to give promise of eliminating both of the dangers of the old gap—that is, eliminating the frequent cleaning and repairs as well as the escape of any vapors from the discharge chambers. Gaps of this new type were installed in both furnaces. The exit hydrogen from the gap was washed by bubbling through the water and finally led either directly outside the building through a window casing or discharged into a ventilating flue of a laboratory hood. A very fine gray powder of mercury collected in the bottom of the bubble tube in which this exit hydrogen was washed, showing that mercury was present in the hydrogen flowing out of the spark gap. This exit hydrogen, therefore, must not be allowed to escape into the air of the furnace room.

Tests were then made of the mercury content of the air during the operation of the 20-kw. furnace equipped with the new type hydrogen gap. These tests were made with the Palmer dust machine in the same manner as those previously described. They showed that mercury vapor was present in the air during the operation of the furnace in amounts slightly over 0.35 mg. per cubic meter of air,[10] still a dangerous concentration. In these tests, again, a control run when the furnace was not operating showed no mercury vapor in the air.

Ventilating Hood and Enclosed Gap—It was not easy to see how the spark gap itself could be constructed so as to keep the mercury in the discharge chambers more tightly enclosed. Indeed it was hard to believe that the mercury detected in the air could have come from the spark gap. Nevertheless, three separate tests showed over 0.35 mg. per cubic meter with the furnace operating and none when the furnace was not operating. Therefore, as a further measure of safety, the section of the converter-protecting cage in which the spark gap stands was completely boxed in with hard asbestos board, and a small sheet-steel hood connected to a forced-draft ventilating flue was inserted through the top of this enclosing box. The hood was set close down above the spark gap, leaving only a few inches clearance of the electrical leads to the gap. A sliding glass window was put in one side of the enclosing box to permit observation of the gap and also to allow an opening into the enclosed chamber so that at all times there should be a positive flow of air from the laboratory into the enclosed chamber, and thence to the ventilating flue.

Finally, determinations were made of the mercury content of the air beside both 10-kw. and 20-kw. furnaces operating under the last-described conditions. The amounts of mercury detected under these conditions were so small as to be below the limit of accuracy of the analytical method. The apparent mercury content of the air during operation of the furnaces in four determinations was approximately 0.035 mg. per cubic meter. However, the control determinations,

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[10] Turner, *loc. cit.*, p. 335.

when the furnace was not operating, indicated practically the same concentration of mercury. There was, moreover, a small blank correction from the reagents used in the analytical method. This blank was so small as not to permit any satisfactory estimate of its apparent mercury equivalent, and no correction on this account was made in the results of these final tests.

The results showed that, within the limits of accuracy of the methods of sampling and analysis used, no mercury was escaping from the high-frequency induction furnaces as operated during these final tests. A trace of mercury vapor may have been present in the laboratory air irrespective of whether the furnaces were operating or not, but any so present was probably considerably less than 0.035 mg. per cubic meter.

The recommendation made by the U. S. Public Health Service in the final conclusion of its report[11] on the study of the old type of discharge gap is fully confirmed—namely,

The problem of the prevention of mercurial poisoning in laboratories and industrial establishments can best be solved by enclosing all apparatus in which mercury is used and by conveying the fumes away from the worker's face so that it will be impossible for him to inhale them.

Cleaning and Repairing Gap—The fouling of the mercury in the hydrogen gap is very slight in comparison with the old type of alcohol gap. The necessity of cleaning the mercury is thus practically eliminated. Replacements and repairs are required very infrequently. When, however, it does become necessary for any reason to open the mercury chambers of the gap, the furnace operator is protected from dust and vapors by the forced ventilation and the constant flow of air into the compartment enclosing the gap. The furnace operator should wear rubber gloves at all times when handling parts of the mercury chambers of the gap. Thus the second source of danger of mercury poisoning which existed in the old form of discharge gap is reduced to a minimum in the present equipment.

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[11] Turner, *op. cit.*, p. 341.

By-Product Coke Cell Structure[1]

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THE nature of the cell structure of coke has always been considered an important property of coke. In 1917, Ramsburg and Sperr[2] showed several pictures of cut longitudinal sections of cokes made from mixed coals regularly coked at different by-product coke plants throughout the United States. The relationship of cell structure to porosity data was studied and "standards for gaging cell structure" were proposed. The present paper is a continuation of the earlier work, except that the present study is confined to coke cell structure of unmixed coals or to mixed coals that are very similar.

Method for Preparing Coke Sections

The apparatus for cutting coke is shown by Fig. 1. The motor is an ordinary dustproof grinding type motor of 1/6 horsepower and 1750 r. p. m. The cutting wheel is known in the trade as an "elastic" cutting-off wheel (abrasive particles set in a bond of organic materials). The specifications for the wheel which have proved very satisfactory for cutting coke are:

Type of wheel........	Elastic
Diameter, 10 inches...	Thickness, 1/16 inch
Bore................	Dependent on diameter of motor shaft, which usually would be 1/2 inch
Face A, Grade 5, Grain 24	

No attempt was made to develop an entirely new apparatus, but standard material which was readily obtainable was used. A 1/4-horsepower motor would probably be more satisfactory, but less than 1/6 horsepower would be too small. Connection to an exhaust fan should be provided to take care of the coke dust while cutting. The usual safety guards should be installed.

Fig. 1—Apparatus for Cutting Coke

The coke pieces are fed by hand, and with the apparatus described it is possible to cut on the average approximately twelve pieces in an hour, depending on the hardness of the coke. A mechanical feed may be used, but account would have to be taken of the fractures of the coke pieces. In general, these would not permit firm clamping to a feed device without breaking up the piece of coke.

Selection of Coke—At least three representative coke pieces, which show the usual wall and inner end effects, should be cut longitudinally. This method will show the cell structure for the entire length of the piece. The coke

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[1] Presented under the title "Coke Cell Structure" before the Section of Gas and Fuel at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] *J. Franklin Inst.*, **183**, 391 (1917).

pieces should be fairly dry before cutting, and the cut surfaces should be thoroughly blown out with compressed air to get rid of any dust which, due to the cutting force, may be firmly packed in the cells.

Pictures of Cut Sections—A camera with 8 × 10-inch plates or films is the most satisfactory for taking the pictures of the cut sections of the coke. For purposes of comparison all coke sections are taken actual size. This is possible with an 8 × 10-inch plate, as nearly all by-product coke pieces are shorter than 10 inches. Usually it is possible to take two sections of coke on one plate by mounting the sections on artists' modeling clay (Plasticene). Care should be taken that the sections are mounted so that they will be parallel to the focusing plate in all directions. The pictures may be taken in ordinary daylight, but much better results are obtained by mounting two 500-watt electric lights with suitable reflectors—one on each side of the lens at a distance of about 15 to 18 inches from the center of the coke surfaces. The pictures should be printed on glossy paper in order to bring out the maximum detail.

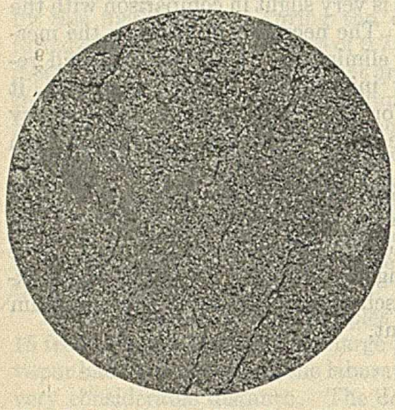
Fig. 2—Coke from Big Seam Coal, Jefferson County, Ala.

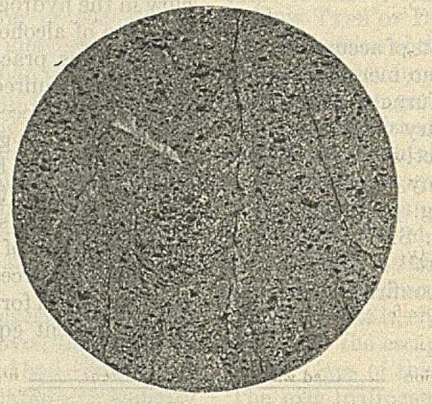
Fig. 3—Coke from Washed Nova Scotia Coal, Canada

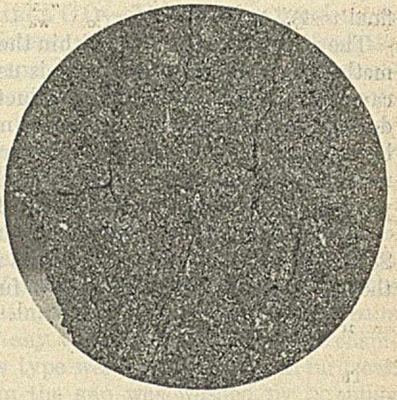
Fig. 4—Coke from No. 6 Seam, Franklin County, Ill.

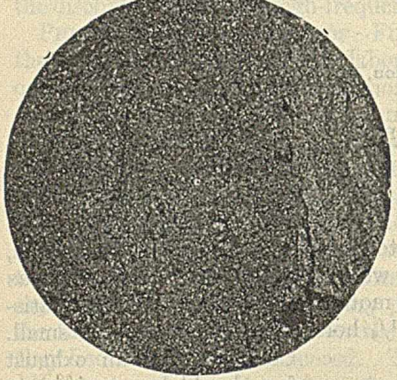
Fig. 5—Coke from No. 4 Seam, Sullivan County, Ind.

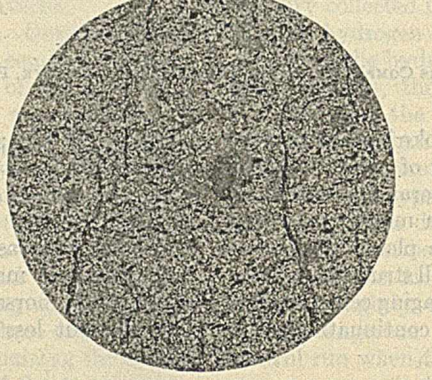
Fig. 6—Coke from Harlan Seam, Harlan County, Ky.

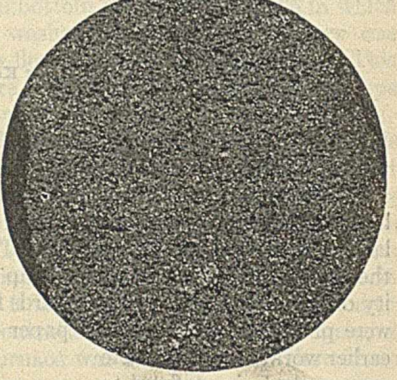
Fig. 7—Coke from Pittsburgh Seam Coal, Washington County, Pa.

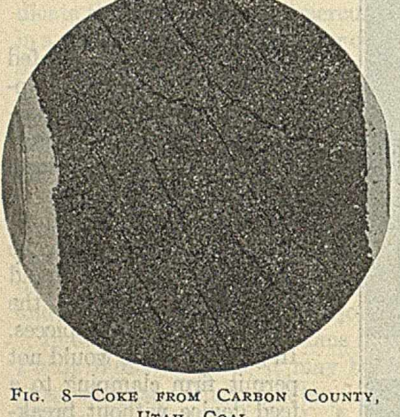
Fig. 8—Coke from Carbon County, Utah, Coal

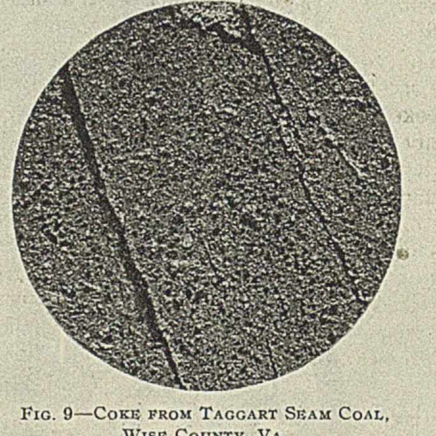
Fig. 9—Coke from Taggart Seam Coal, Wise County, Va.

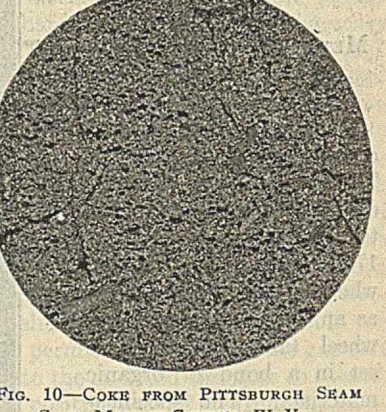
Fig. 10—Coke from Pittsburgh Seam Coal, Marion County, W. Va

Coke Porosity Data

Twenty cokes have been selected to show the range of porosity values which may be encountered in by-product coking of American coals. These are shown in the table. Cokes 1, 5, 6, 7, 8, 9, 10, 11, 12, 13, 18, 19, and 20 were made on 12-hour coking time in Becker ovens having a 14-inch average width. All were coked under regular plant conditions with the exception of Nos. 19 and 20 (cokes from low volatile coals), which were coked in special steel boxes in

COKE POROSITY DATA

				Coal Characteristics					Coke Porosity Data		
						Coal sieve test					
State	County	Seam	Coke No.	Moisture Per cent	Volatile matter Per cent	On 1/4 in. Per cent	On 1/8 in. Per cent	Through 1/8 in. Per cent	Apparent specific gravity	True specific gravity	Porosity Per cent
Ala.	Walker	Black Creek—washed	1	7.7	36	12	22	66	0.83	1.89	56.1
Ala.	Jefferson	Big Seam—washed	2 (Fig. 2)	4.9	28	57	17	26	0.98	1.82	46.2
Canada	Nova Scotia	Mixed Coal-washed	3 (Fig. 3)	11.0	34	53	13	34	0.85	1.93	56.0
Colo.	Las Animas	Mixed Coal—washed	4	9.1	32	80% through 3/4 in.			1.02	1.93	47.2
Ill.	Williamson	No. 6	5	5.0	35	3	12	85	0.79	1.91	58.6
Ill.	Franklin	No. 6	6 (Fig. 4)	5.3	36.5	4	18	78	0.75	1.78	57.9
Ind.	Sullivan	No. 4	7 (Fig. 5)	9.0	39.5	2	9	89	0.92	1.93	52.3
Ky.	Harlan	Harlan	8 (Fig. 6)	2.0	37	9	24	67	0.885	1.80	50.8
Pa.	Allegheny	Freeport	9	3.2	34	82% through 1/8 in.			0.97	1.96	50.5
Pa.	Fayette	B	10	2.6	25	4	15	81	0.89	1.99	55.3
Pa.	Fayette	Pittsburgh	11	2.4	32.5	1 1/4 in. and under			1.09	1.94	43.8
Pa.	Washington	Pittsburgh	12 (Fig. 7)	4.8	34.5	19	24	57	0.91	1.87	51.3
Utah	Carbon	....	13 (Fig. 8)	5.5	41.5	12	18	70	0.905	1.79	49.4
Va.	Wise	Taggart	14 (Fig. 9)	3.0	35	70% through 1/8 in.			0.85	1.84	53.8
Wash.	Pierce	Mixed Coal—washed	15	3.7	31.5	82.5% through 1/8 in.			1.00	1.85	45.9
W. Va.	Fayette	No. 2 Gas	16	3.2	34	7	22	71	1.00	1.91	47.6
W. Va.	Marion	Pittsburgh	17 (Fig. 10)	2.3	35.5	1 1/4 in. and under			0.93	1.79	48.0
W. Va.	Monongalia	Pittsburgh	18 (Fig. 11)	3.3	36.5	7	17	76	1.24	2.02	38.6
W. Va.	McDowell	Pocahontas No. 3	19 (Fig. 12)	1.8	17	30	23	47	0.955	1.95	51.0
W. Va.	Raleigh	Beckley	20	1.2	22	33	24	43	0.95	2.00	52.5

Note.—For Cokes 1, 4, 5, 6, 14, 15, 16, true specific gravity was made on 200 mesh, boiling 1/2 hour without suction with benzene as liquid; and apparent specific gravity was by "Bottle Method—Using 1-inch Cubes." See the "Gas Chemists' Handbook," **1922**, p. 55.

For other cokes, the porosity determination was made according to "Tentative Method of Test for Volume of Cell Space of Lump Coke," A. S. T. M. Serial Designation D-167-23T, **1923**.

The method in use at the time the cokes in question were tested was employed. Benzene tends in most cases to give slightly lower values for true specific gravity than water; but the differences, according to data available, are not consistent, as in some cases both benzene and water give the same values. [Rose, THIS JOURNAL, **14**, 1047 (1922); and Selvig and Parker, *Chem. Met. Eng.*, **28**, 547 (1923).] The use of 1-inch cubes in place of full-length coke pieces according to the A. S. T. M. method may give slightly different values for the apparent specific gravity. However, several comparisons were made with the "1-inch cube" and the "A. S. T. M." methods, and both methods gave practically the same per cent porosity, provided that the coke actually used in the apparent specific gravity determination was pulverized for the true specific gravity determination.

a Becker oven under as nearly regular plant conditions as possible. The rest of the cokes were made in Koppers ovens at various plants. The average oven width was approximately 18.5 inches and the coking time varied between 16.5 and 19 hours, with exception of Cokes 14, 16, and 17, which were coked on 22.5-hour coking time. The table also gives some of the characteristics of the coals from which these cokes were made. It will be noted that the variation in porosity data is really quite large.

Apparent specific gravity.........	0.75 to 1.24
True specific gravity.............	1.79 to 2.02
Per cent porosity.................	38.6 to 58.6

A value of 1.10 is more representative of the upper limit for apparent specific gravity as the high value of 1.24 was obtained for only one out of a large number of cokes tested, and is really an abnormally high value, although included to show the extreme range of values found. If the upper limit for apparent specific gravity is 1.10 the range for porosity would be from about 43 to 58.6 per cent for the set of values in the table.

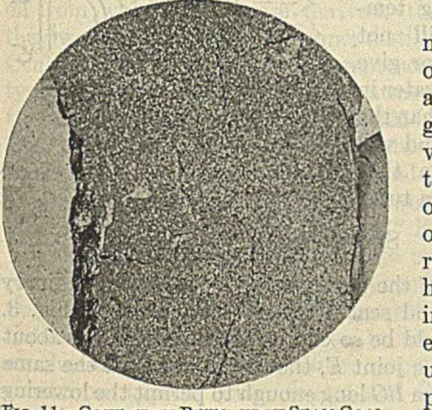

FIG. 11—COKE FROM PITTSBURGH SEAM COAL, MONONGALIA COUNTY, W. VA.

COKE CELL STRUCTURE PICTURES

Eleven of the cokes described in the table have been selected to show the general character of coke structure (Figs. 2 to 12, inclusive).[3] These figure numbers are also indicated for comparison with porosity values.

COMPARISON OF COKE CELL STRUCTURE[4] AND THE POROSITY DATA—On comparing the pictures of the cell structure with the corresponding porosity data, it will be noted that in some cases there is very good agreement while in others there is apparently wide disagreement. The cell structure in Fig. 11 shows very "dense," and this agrees with the low porosity value for this coke. Fig. 4 (Illinois coke) also appears to have "dense" cell structure, but the porosity value is among the highest of the entire series. On closer examination of the cell structure of the Illinois cokes, it will be seen that the cokes consist of a large number of very small cells with very thin cell walls and are really "finely porous" instead of being "dense;" the total volume of cell space is large.

By comparing the picture of a cut section with its corresponding porosity, it can readily be seen that some description of the cell structure is necessary for proper interpretation of the porosity data. Ramsburg and Sperr proposed standards for gaging cell structure based on average size of cells which were assigned numbers 1 to 4, inclusive, No. 1 being the smallest size cell structure and No. 4 the largest. In the study of various coke sections, the thickness of the cell walls should also be included.

It would be hard to make a clear-cut classification of coke according to cell structure; yet, in the study of various coke sections, four divisions suggest themselves:

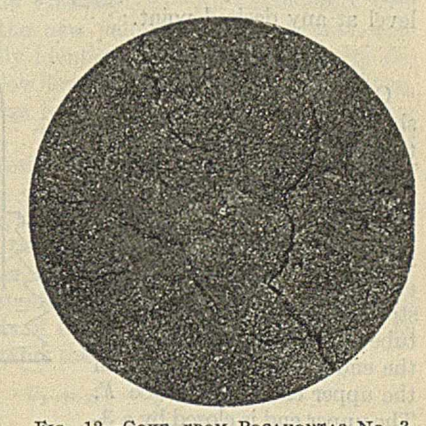

FIG. 12—COKE FROM POCAHONTAS NO. 3 SEAM, MCDOWELL COUNTY, W. VA.

1—*Very small cells with very thin cell walls.* Cokes from Illinois No. 6 Seam, Utah, and low volatile coking coals come under this heading. It is very surprising that cokes from coals so widely different as low volatile and Illinois coals should have similar type of cell structure.

2—*Large cells with thin cell walls.* Cokes from many Kentucky, Alabama Black Creek Seam, many West Virginia and Nova Scotia coking coals would answer this description. Coke from Indiana No. 4 Seam coking coals would also belong here, although it is not usually considered such good coking coal as the other coals mentioned. The cell walls are not nearly so thin as in Class 1.

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[3] All pictures of sections of coke were selected from the portion between 1.5 and 3.5 inches from the wall end of the coke piece, and show the cell structure actual size.

[4] Thau, *Chem. Met. Eng.*, **30**, 222, 306 (1924), showed interesting pictures of coke including pictures of cut sections, together with a few porosity values.

3—*Small to medium cells with fairly thick cell walls.* Cokes from many Pittsburgh seam and some Alabama, Colorado, and Washington coking coals would be placed in this class.

4—*Large cells with fairly thick cell walls.* Cokes from some Pittsburgh and Freeport seam coals would come under this class. However, thick cell walls of this class of structure are often "finely porous."

Two Forms of a Constant Water-Level Device[1]

By H. D. Wilde, Jr.

University of Texas, Austin, Texas

In some work recently done at this laboratory, several water baths made of enameled iron vessels were used. A device for maintaining the water-level constant by replacing the water lost through evaporation was desired, but the common form of the device, shown in Fig. 1, has several objections. In the first place, in order to attach this device to the bath, a hole must be made in the side of the vessel, which injures the lining of the vessel and renders it unfit for other purposes.

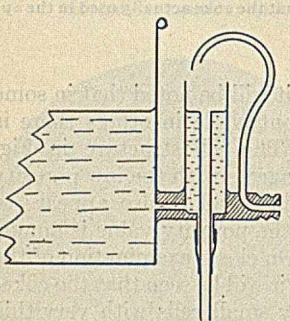
Fig. 1

In the second place, when the device is once attached to the vessel, it cannot be easily removed. In the third place, though the overflow tube is movable, after the bath has been used for some time the rubber tubing that fastens it to the device usually gets hard and sticks tenaciously to the overflow tube; it is then difficult to change the adjustment to maintain the water level at a new height.

Two forms of such a device were developed which have the following advantages over the common form: They are easily made from materials found in any laboratory; they do not require a hole in the side of the bath, and therefore they do not injure the vessel and may be used with glass or stoneware vessels; they may be readily changed from one vessel to another; and they are easily adjusted to maintain the water level at any desired point.

First Form

One form of this device is shown in Fig. 2. In principle this is but a modification of the common form shown in Fig. 1. It consists of a glass tube, *F*, about 3 cm. in diameter and 15 cm. long. The lower end is closed by a 1-hole rubber stopper through which the glass tube *CE* is so inserted that the end *C* is about 4 cm. from the upper end of the tube *F*. The upper end is closed by a 3-hole rubber stopper. Through one hole is inserted a short inverted U tube, *A*, which serves as an inlet for the water; through a second hole is inserted the long inverted U tube *B*, which serves as a siphon between the bath and the tube *F;* while the third hole serves as a vent to the atmosphere. The holes in the stoppers should be so arranged that the end of the inlet *A* will not be directly above the overflow *E*.

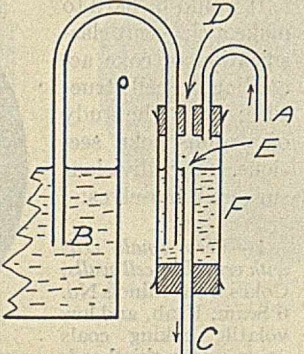

Fig. 2

The device is held in a clamp so that the arm *B* is within the water bath. The height of the device is so adjusted that the level of the overflow *E* is slightly above the level at which the water within the bath is to be maintained. Since the water in the arm of the siphon over the bath is warmer than the water in the other arm, the level in the bath will be slightly lower than the level of the overflow tube, but the difference will be so small as to be negligible. A small stream of water is sent through the inlet tube *A*, and the overflow tube *C* is connected with the drain by means of a rubber tube. The siphon tube may be filled with water by pinching the rubber tube below *C* and closing the vent *D*. If the water level in the bath is below the level of *E*, water will flow through the siphon into the bath until the level rises to the height of *E*. After that, all the water entering through *A* will overflow at *E* and discharge into the drain. If the level of the water in the bath rises above the level of *E*, water will flow out of the bath through the siphon and overflow *E*. Although the water in the bath is at the boiling temperature, steam will not form in the siphon or give any trouble. The water in the siphon is cooler than the water in the bath and will condense any steam that may enter the siphon tube.

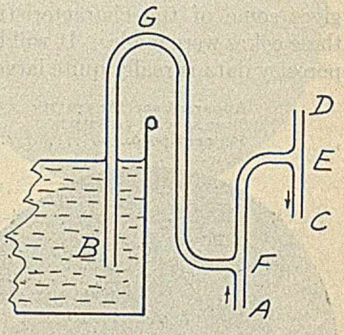

Fig. 3

Second Form

The second form of the device is made entirely of ordinary glass tubing, bent and sealed together as shown in Fig. 3. The dimensions should be so chosen that the joint *F* is about 10 cm. lower than the joint *E*, the end *B* at about the same level as *F*, and the arm *BG* long enough to permit the lowering of the device to such an extent that *E* will be at the lowest level at which the water is to be maintained.

The device should be held in a clamp so that the arm *BG* is within the bath and the device adjusted so that the level of the overflow *E* is slightly above the level at which the water is to be maintained within the bath. A small stream of water is sent through the inlet *A* and the overflow tube *C* connected to the drain. If the vent *D* is closed and the rubber tube below *C* is pinched, the siphon *BG* will be filled with water. The device is then ready for operation.

Both of these devices, when once adjusted, require no further attention, and are very satisfactory.

The Canadian Carbonate Company, Ltd., has bought Canadian rights for the patent of the United States Industrial Alcohol Company for the absorption and purification of carbon dioxide, as produced in alcohol manufacture. The patent will be operated in Montreal and Calgary.

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[1] Received April 24, 1924.

Viscosity-Temperature Curves of Fractions of Typical American Crude Oils[1,2]

Second Paper

By F. W. Lane and E. W. Dean

Bureau of Mines, Petroleum Division, Chemical Section, Washington, D. C.

Some time ago the Bureau of Mines undertook an investigation for the purpose of obtaining information relative to the variation of viscosity with temperature for a rather wide range of petroleum products of known origin and of accurately determined physical properties. Part of these data was presented by the authors in a previous article.[3] *Results of the remaining work are given in the present paper together with a revision of the previous data. A method of rectifying the temperature-viscosity curves is also discussed, and the possibility of its practical utilization is pointed out.*

THE following crude oils were selected for the tests: (1), (2), (3) one sample each of Pennsylvania, Wyoming, and California crude, as heretofore described;[3] (4) a sample of crude petroleum from Bigheart field, Osage County, Oklahoma, which was regarded as representative of Midcontinent oils; (5) a sample of crude petroleum from Sour Lake field. This oil was considered representative of the Gulf Coast production. These samples were analyzed according to the procedure adopted by the Bureau of Mines,[4] and the results for Oils 4 and 5 appear in Table I. Similar analyses for the other crudes have already been reported.[3]

Viscosity determinations were made on each individual fraction, distilled at atmospheric pressure between the limits of 100° to 125° C. (212° to 257° F.), 125° to 150° C. (257° to 302° F.), etc., up to 250° to 275° C. (482° to 527° F.), and on all "vacuum" fractions distilled at 40 mm. absolute pressure. The identity of these fractions will be made clear by reference to the analytical data of Table I. The fractions are hereinafter designated by letters and numbers indicating the crude oil from which they were derived, the pressure at which they were distilled, and the upper distillation limit, in degrees Centigrade. Thus, "T-A-225" represents a fraction from the typical Texas crude, distilled at atmospheric pressure, between the temperatures of 200° and 225° C. (392° and 437° F.). The abbreviation "O-V-250" indicates that this particular fraction was distilled from the typical Oklahoma crude, at an absolute pressure of 40 mm., between temperature limits of 225° and 250° C. (437° and 482° F.).

It has been thought worth while to present in this paper a revision of the viscosity data previously published on fractions prepared from typical Pennsylvania, Wyoming, and California crudes. The revision in no respect changes the conclusions drawn in the earlier paper. Data for oils derived from typical Midcontinent and Gulf Coast crudes are also given. In addition, the following special oils were dealt with:

(1) "P-R," the residuum from the distillation of the Pennsylvania crude.
(2) "P-Mixt," a mixture of "P-R" and the fraction "P-V-225."
(3) "P-C-Mixt," a mixture of "P-R" and the California fraction "C-V-250."
(4) "O-R," the residuum from the distillation of the Oklahoma crude.

Viscosity determinations were made on the various fractions of oil produced in the analytical distillation of the crude (Table I). The results of this work, expressed in terms of kinematic viscosity, are given in full in Table II. The specific gravity of each oil at 15.6° C. (60° F.) is given in Table I, and it is therefore possible to convert the given figures into absolute viscosity by making use of the petroleum expansion tables published by the Bureau of Standards[5] and the equation[6]

$$\mu = V_k d$$

where μ = absolute viscosity in poises
V_k = kinematic viscosity
d = density of oil at temperature of determination

In Table III are given the Saybolt Universal viscosities of the heavier fractions for kinematic viscosities greater than 0.0142. Transformations were made from Table II by the use of the equation recommended by the Bureau of Standards

$$V_k = 0.00216t_s - \frac{1.80}{t_s}$$

in which V_k = the kinematic viscosity
t_s = the Saybolt Universal viscosity

Experimental

The oils used were prepared by distilling the crude petroleum as described by Bureau of Mines.[4] The first paper[3] contained a very brief outline of this method, as well as a description of the Ostwald viscometers used, and the method employed in filling them. The same apparatus and method of operation have been retained in the new work herein reported.

Standardization of Viscometers—All viscometers were restandardized, and the new values of the constants were found to be practically identical with those previously determined. The four slow flowing viscometers, having the long, fine capillaries and large bulbs, were calibrated with water at three temperatures. The other instruments could not be standardized satisfactorily with this liquid, because of the very short efflux times obtained. It was possible, however, to choose an oil which, at 50° C. (122° F.), showed a suitable rate of flow, both in the slow flowing viscometers, already calibrated against water, and in all the remaining instruments. The values of the constants for the latter were therefore based on the water constants of the slow flowing viscometers. In computing these constants the general equation

$$V_k = At - \frac{B}{t}$$

was abbreviated to $V_k = At$, in which V_k = the kinematic viscosity, t = the efflux time, and A = the viscometer constant to be determined. With the rate of flow adopted in the present work, the kinetic energy correction, represented by the term $\frac{B}{t}$, was shown to be negligible.

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[1] Presented before the Section of Petroleum Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. Received June 5, 1924.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] This Journal, 13, 779 (1921).

[4] Dean, Hill, Smith, and Jacobs, *Bur. Mines, Bull.* 207.

[5] *Bur. Standards, Circ.* 57.

[6] *Bur. Standards, Tech. Paper* 100, p. 7.

TABLE I—ANALYSES OF TYPICAL CRUDE OILS FROM THE MIDCONTINENT AND GULF COAST FIELDS BY BUREAU OF MINES METHOD[a]

Sample 625

Oklahoma Bigheart Field Osage County
Specific gravity, 0.846 A. P. I. gravity, 35.8°
Per cent sulfur, 0.19 Per cent water, 0.1

Distillation, Bureau of Mines Hempel Method

Air distillation, barometer, 738 mm. First drop, 54° C. (129° F.)

Temperature ° C.	Temperature ° F.	Per cent cut	Sum Per cent	Specific gravity cut	° A. P. I. cut	Cloud test ° F.
Up to 50	Up to 122					
50 - 75	122–167	0.9	0.9	0.719	65.3	
75 -100	167–212	3.5	4.4			
100–125	212–257	5.4	9.8	0.738	60.2	
125–150	257–302	5.6	15.4	0.758	55.2	
150–175	302–347	6.3	21.7	0.778	50.4	
175–200	347–392	5.0	26.7	0.796	46.3	
200–225	392–437	6.4	33.1	0.814	42.3	
225–250	437–482	6.0	39.1	0.828	39.4	
250–275	482–527	7.0	46.0	0.841	36.8	
Vacuum distillation at 40 mm.						
Up to 200	Up to 392	5.7	5.7	0.857	33.6	16
200–225	392–437	6.9	12.6	0.867	31.7	28
225–250	437–482	6.4	19.0	0.876	30.0	46
250–275	482–527	5.3	24.3	0.886	28.2	66
275–300	527–572	6.2	30.5	0.892	27.1	81

Carbon residue of residuum, 5.3 per cent

Sample 725

Texas Sour Lake Field Hardin County
Specific gravity, 0.941 A. P. I. gravity, 18.9°
Per cent sulfur, 0.655 Per cent water, 1.1

Distillation, Bureau of Mines Hempel Method

Temperature ° C.	Temperature ° F.	Air distillation Per cent cut	Air distillation Sum Per cent	Specific gravity cut	° A. P. I. cut
Up to 50	Up to 122				
50 - 75	122–167				
75 -100	167–212				
100–125	212–257	0.8	0.8	0.778	50.4
125–150	257–302	0.7	1.5		
150–175	302–347	1.2	2.7	0.801	45.2
175–200	347–392	1.9	4.6	0.832	38.6
200–225	392–437	3.6	8.2	0.858	33.4
225–250	437–482	6.3	14.5	0.880	29.3
250–275	482–527	9.1	23.6	0.901	25.6
Vacuum distillation at 40 mm.					
Up to 200	Up to 392	6.8	6.8	0.924	21.6
200–225	392–437	7.8	14.6	0.942	18.7
225–250	437–482	7.6	22.2	0.953	17.0
250–275	482–527	7.5	29.7	0.963	15.4
275–300	527–572	8.2	37.9	0.967	14.8

Carbon residue of residuum, 7.2 per cent

[a] For the analysis of typical Pennsylvania, Wyoming, and California crudes see previous paper. The method of analysis is described in *Bur. Mines, Bull.* **207.**

FILLING THE VISCOMETERS—The mechanical details of filling the viscometers were discussed in the previous paper.[3] One aspect of this phase of the work may well be reëmphasized here. In the ordinary use of the Ostwald type of viscometer, it is customary to introduce a given volume of oil at the temperature at which the viscosity determination is made. In the present work such a procedure would be impracticable both on account of the nature of the liquids used and because of the large number of refillings that would be required. The viscometers may be filled at any suitable temperature, and the efflux time determined at any other temperature, provided a correction is made to compensate for the change in head brought about by the change in volume of the oil. In the present work it has been found convenient to fill the viscometers at 25° C. (77° F.) and, in a few instances where the oils were very viscous, at 100° C. (212° F.). The determination of the correction, or "filling factors," to be used in correcting viscosity determinations made at temperatures other than at which filling was done, was accomplished as follows: The efflux time was determined twice for a given oil at 100° C. (212° F.), the viscometers having been filled first at 25° C. (77° F.) and then at 100° C. (212° F.). The ratio (1.018) of the values so obtained is the filling factor at 100° C. (212° F.) when the filling is made at 25° C. (77° F.). Under the same conditions the filling factor at 25° C. is 1.000. It was shown, furthermore, that the change of this factor with temperature may be represented adequately by a straight line, and hence the correction, or filling factor, to be used at any of the experimental temperatures may be read from the straight line connecting the two points just mentioned. It was found that a single set of filling factors could be used for all viscometers, the mean deviation from the average values being only 0.3 per cent. Filling factors have been redetermined in the present work and are given in Table IV.

Other miscellaneous operating details were given in the previous paper.

CALCULATION OF RESULTS—The equation for calculating the results is

$$V_k = \frac{At}{f}$$

where V_k = kinematic viscosity
t = efflux time in seconds
f = filling factor, properly chosen for the temperature of operation
A = viscometer constant

DISCUSSION OF RESULTS

Table II gives the experimental results in terms of kinematic viscosity. Corresponding Saybolt Universal values are given in Table III. Fig. 1 shows graphically the temperature-viscosity data for certain fractions derived from the typical Pennsylvania, California, and Texas crude oils. It will be noted that in general, the Pennsylvania oils show the least rapid change of viscosity for a given change in temperature, the California oils are intermediate in this respect, while the fractions from the Texas crude show the greatest change of viscosity for a given temperature increment. Furthermore, it will be observed that the most impressive differences appear in the higher fractions, while the temperature-viscosity characteristics of the lighter oils are quite

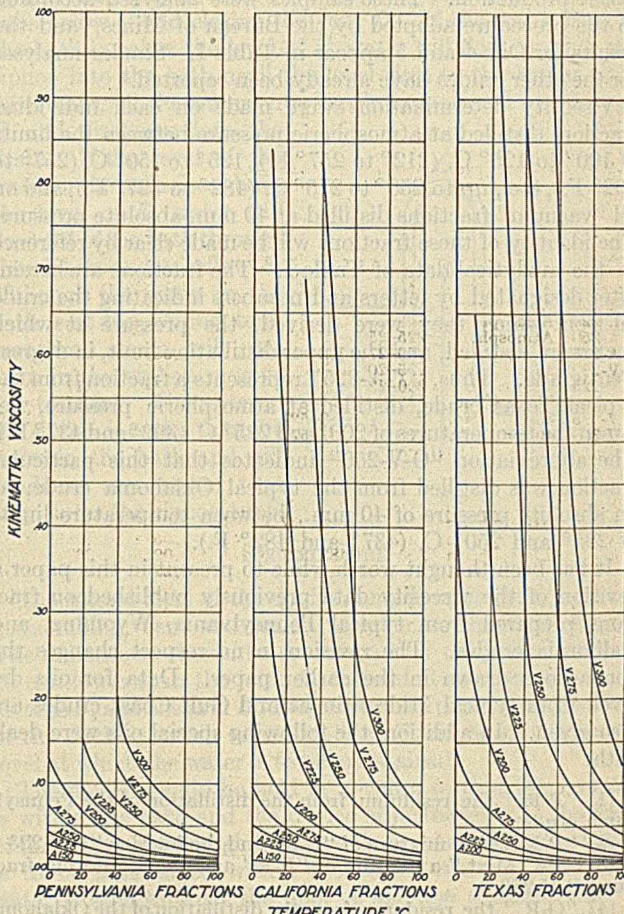

FIG. 1—VISCOSITY-TEMPERATURE CURVES OF CERTAIN FRACTIONS DERIVED FROM PENNSYLVANIA, CALIFORNIA, AND GULF COAST CRUDE PETROLEUM

Table II—Kinematic Viscosities of a Series of Products Derived from Five Typical American Crude Oils

Designation of Product	Description of Product: Pressure under which distilled	Description of Product: Temperature limits of cuts ° C.	° F.	Kinematic Viscosities Determined at Indicated Temperatures: 0° C. 32° F.	10° C. 50° F.	20° C. 68° F.	30° C. 86° F.	40° C. 104° F.	50° C. 122° F.	60° C. 140° F.	80° C. 176° F.	100° C. 212° F.	Kinematic Viscosities Calculated or Interpolated for Indicated Temperature: 37.8° C. 100° F.	54.4° C. 130° F.	98.9° C. 210° F.
A—Pennsylvania crude															
P-A-125	Atmospheric	100–125	212–257	0.00894	0.00787	0.00706	0.00643	0.00590	0.00536	0.00499	0.00443	...	...	...	...
P-A-150	Atmospheric	125–150	257–302	0.0113	0.00973	0.00871	0.00778	0.00702	0.00640	0.00591	0.00509	0.00448	...	...	...
P-A-175	Atmospheric	150–175	302–347	0.0143	0.0122	0.0106	0.00944	0.00842	0.00758	0.00689	0.00600	0.00531	...	...	...
P-A-200	Atmospheric	175–200	347–392	0.0203	0.0168	0.0142	0.0123	0.0109	0.00953	0.00857	0.00717	0.00618	...	...	...
P-A-225	Atmospheric	200–225	392–437	0.0302	0.0241	0.0199	0.0169	0.0145	0.0125	0.0110	0.00899	0.00750	...	...	...
P-A-250	Atmospheric	225–250	437–482	0.0466	0.0348	0.0278	0.0227	0.0190	0.0162	0.0140	0.0112	0.00920	...	...	...
P-A-275	Atmospheric	250–275	482–527	0.0746	0.0534	0.0409	0.0324	0.0265	0.0220	0.0186	0.0143	0.0115	...	...	...
P-V-200	40-mm. vac.	175–200	347–392	0.131	0.0890	0.0642	0.0493	0.0385	0.0315	0.0258	0.0192	0.0148	0.0409	0.0290	0.0150
P-V-225	40-mm. vac.	200–225	392–437	...	0.139	0.0960	0.0700	0.0536	0.0424	0.0348	0.0242	0.0180	0.0572	0.0390	0.0183
P-V-250	40-mm. vac.	225–250	437–482	...	...	0.155	0.107	0.0786	0.0597	0.0472	0.0320	0.0231	0.0849	0.0542	0.0236
P-V-275	40-mm. vac.	250–275	482–527	...	...	...	0.173	0.121	0.0883	0.0678	0.0441	0.0303	0.133	0.0793	0.0311
P-V-300	40-mm. vac.	275–300	527–572	...	...	...	...	0.204	0.143	0.105	0.0633	0.0422	...	0.126	0.0433
P-R	Residuum			...	...	...	...	1.55	0.829	0.537	0.261	0.147	...	0.701	0.153
P-Mixt.	Mixture residuum and fraction P-V-225			...	...	...	...	0.173	0.125	0.0943	0.0579	0.0398	...	0.111	0.0407
B—California crude															
C-A-125	Atmospheric	100–125	212–257	0.0104	0.00913	0.00811	0.00735	0.00661	0.00603	0.00556	0.00475	...	...	...	...
C-A-150	Atmospheric	125–150	257–302	0.0125	0.0109	0.00959	0.00858	0.00768	0.00701	0.00649	0.00554	0.00485	...	...	...
C-A-175	Atmospheric	150–175	302–347	0.0165	0.0140	0.0120	0.0106	0.00936	0.00837	0.00760	0.00633	0.00547	...	...	...
C-A-200	Atmospheric	175–200	347–392	0.0227	0.0187	0.0158	0.0135	0.0118	0.0104	0.00928	0.00760	0.00648	...	...	...
C-A-225	Atmospheric	200–225	392–437	0.0339	0.0268	0.0217	0.0181	0.0154	0.0134	0.0118	0.00941	0.00785	...	...	...
C-A-250	Atmospheric	225–250	437–482	0.0532	0.0401	0.0313	0.0252	0.0209	0.0177	0.0152	0.0118	0.00950	...	...	...
C-A-275	Atmospheric	250–275	482–527	0.0956	0.0667	0.0491	0.0377	0.0302	0.0247	0.0207	0.0154	0.0120	...	...	...
C-V-200	40-mm. vac.	175–200	347–392	0.220	0.136	0.0916	0.0652	0.0487	0.0383	0.0306	0.0213	0.0161	0.0524	0.0349	0.0164
C-V-225	40-mm. vac.	200–225	392–437	...	0.289	0.174	0.115	0.0807	0.0596	0.0456	0.0298	0.0213	0.0882	0.0535	0.0217
C-V-250	40-mm. vac.	225–250	437–482	...	0.845	0.436	0.254	0.161	0.110	0.0790	0.0467	0.0309	0.181	0.0966	0.0317
C-V-275	40-mm. vac.	250–275	482–527	...	...	...	0.688	0.383	0.233	0.154	0.0798	0.0480	0.450	0.198	0.0498
C-V-300	40-mm. vac.	275–300	527–572	...	...	...	...	0.825	0.457	0.280	0.127	0.0710	...	0.379	0.0741
P-C-Mixt.	Mixture of Pennsylvania residue and C-V-250			...	...	...	...	0.332	0.216	0.149	0.0817	0.0515	...	0.187	0.0532
C—Wyoming crude															
W-A-125	Atmospheric	100–125	212–257	0.00942	0.00838	0.00745	0.00674	0.00605	0.00561	0.00524	...	...	...	...	...
W-A-150	Atmospheric	125–150	257–302	0.0116	0.0101	0.00891	0.00801	0.00724	0.00660	0.00610	0.00531	0.00469	...	...	...
W-A-175	Atmospheric	150–175	302–347	0.0153	0.0131	0.0114	0.0100	0.00890	0.00798	0.00739	0.00611	0.00526	...	...	...
W-A-200	Atmospheric	175–200	347–392	0.0210	0.0174	0.0148	0.0128	0.0113	0.00995	0.00891	0.00738	0.00621	...	...	...
W-A-225	Atmospheric	200–225	392–437	0.0304	0.0244	0.0201	0.0169	0.0145	0.0126	0.0112	0.00895	0.00744	...	...	...
W-A-250	Atmospheric	225–250	437–482	0.0462	0.0354	0.0283	0.0232	0.0193	0.0164	0.0142	0.0112	0.00905	...	...	...
W-A-275	Atmospheric	250–275	482-527	0.0753	0.0552	0.0418	0.0329	0.0268	0.0223	0.0189	0.0143	0.0113	...	...	...
W-V-200	40-mm. vac.	175–200	347–392	0.147	0.0997	0.0709	0.0531	0.0413	0.0330	0.0272	0.0196	0.0151	0.0439	0.0305	0.0153
W-V-225	40-mm. vac.	200–225	392–437	...	0.152	0.104	0.0751	0.0565	0.0442	0.0354	0.0247	0.0183	0.0606	0.0403	0.0186
W-V-250	40-mm. vac.	225–250	437–482	...	...	0.179	0.122	0.0879	0.0659	0,0516	0.0344	0.0246	0.0953	0.0596	0.0251
W-V-275	40-mm. vac.	250–275	482–527	...	...	...	0.210	0.143	0.104	0.0774	0.0478	0.0327	0.158	0.0922	0.0335
W-V-300	40-mm. vac.	275–300	527–572	...	...	...	...	0.255	0.173	0.124	0.0722	0.0464	...	0.151	0.0478
D—Oklahoma crude															
O-A-100	Atmospheric	75–100	167–212	0.00770	0.00692	0.00627	0.00567	0.00523	0.00484	...	...	...	...	...	...
O-A-125	Atmospheric	100–125	212–257	0.00929	0.00824	0.00741	0.00663	0.00608	0.00558	0.00518	...	...	...	...	...
O-A-150	Atmospheric	125–150	257–302	0.0113	0.00991	0.00879	0.00786	0.00708	0.00645	0.00592	0.00510	0.00448	...	...	...
O-A-175	Atmospheric	150–175	302–347	0.0145	0.0125	0.0108	0.00957	0.00853	0.00766	0.00693	0.00587	0.00508	...	...	...
O-A-200	Atmospheric	175–200	347–392	0.0205	0.0170	0.0144	0.0124	0.0109	0.00966	0.00877	0.00719	0.00611	...	...	...
O-A-225	Atmospheric	200–225	392–437	0.0302	0.0242	0.0199	0.0168	0.0144	0.0125	0.0110	0.00888	0.00738	...	...	...
O-A-250	Atmospheric	225–250	437–482	0.0468	0.0359	0.0284	0.0231	0.0193	0.0165	0.0143	0.0111	0.00900	...	...	...
O-A-275	Atmospheric	250–275	482–527	0.0768	0.0555	0.0421	0.0330	0.0268	0.0222	0.0188	0.0142	0.0112	...	...	...
O-V-200	40-mm. vac.	175–200	347–392	0.153	0.102	0.0721	0.0536	0.0414	0.0330	0.0271	0.0194	0.0149	0.0441	0.0304	0.0151
O-V-225	40-mm. vac.	200–225	392–437	0.287	0.177	0.117	0.0834	0.0614	0.0472	0.0378	0.0258	0.0191	0.0662	0.0431	0.0195
O-V-250	40-mm. vac.	225–250	437–482	...	0.357	0.217	0.144	0.101	0.0742	0.0569	0.0365	0.0258	0.110	0.0666	0.0264
O-V-275	40-mm. vac.	250–275	482–527	...	...	...	0.262	0.173	0.121	0.0885	0.0529	0.0353	0.192	0.107	0.0362
O-V-300	40-mm. vac.	275–300	527–572	...	...	...	0.499	0.309	0.204	0.142	0.0792	0.0500	0.350	0.177	0.0516
O-R	Residuum			...	...	...	...	2.13	1.21	0.744	0.322	0.172	...	1.01	0.181
E—Texas crude															
T-A-200	Atmospheric	175–200	347–392	0.0255	0.0209	0.0175	0.0149	0.0128	0.0113	0.0100	0.00815	0.00680	...	...	...
T-A-225	Atmospheric	200–225	392–437	0.0410	0.0319	0.0257	0.0212	0.0178	0.0153	0.0135	0.0104	0.00855	...	...	...
T-A-250	Atmospheric	225–250	437–482	0.0696	0.0514	0.0388	0.0307	0.0249	0.0208	0.0176	0.0133	0.0105	...	...	...
T-A-275	Atmospheric	250–275	482–527	0.144	0.0948	0.0671	0.0495	0.0383	0.0307	0.0251	0.0180	0.0137	...	...	...
T-V-200	40-mm. vac.	175–200	347–392	0.406	0.226	0.141	0.0944	0.0673	0.0505	0.0393	0.0259	0.0187	0.0733	0.0456	0.0191
T-V-225	40-mm. vac.	200–225	392–437	...	0.648	0.339	0.201	0.130	0.0892	0.0656	0.0391	0.0262	0.145	0.0788	0.0270
T-V-250	40-mm. vac.	225–250	437–482	...	...	1.08	0.536	0.302	0.186	0.124	0.0658	0.0406	0.353	0.159	0.0419
T-V-275	40-mm. vac.	250–275	482–527	...	...	...	...	0.864	0.467	0.280	0.123	0.0668	...	0.385	0.0698
T-V-300	40-mm. vac.	275–300	527–572	...	...	...	...	2.69	1.25	0.666	0.245	0.116	...	0.993	0.123

similar. Curves for the Oklahoma and Wyoming oils have been intentionally omitted. In general, they possess characteristics intermediate between those of the California and Pennsylvania fractions, and resemble the latter more closely than they do the former.

This relationship is further illustrated in Fig. 2, in which are plotted the temperature-viscosity curves for the fraction (from each typical crude oil) distilled from 275° to 300° C. (527° to 572° F.) at an absolute pressure of 40 mm.—that is, P-V-300, W-V-300, O-V-300, C-V-300, T-V-300.

It should be pointed out, however, with reference to the lighter fractions derived from the typical Wyoming, Oklahoma, and Pennsylvania crudes, that the qualitative relationship shown in Fig. 2 does not hold invariably. In the case of the Oklahoma and Wyoming fractions distilled at atmospheric pressure up to 225° C. (437° F.), which may be roughly designated as representing the gasoline and naphtha portions of the crudes, the viscosity-temperature curves for the Wyoming products would lie for the most part slightly above the curves for the corresponding Oklahoma fractions. From the data of Table II the curves for the corresponding kerosene and gas oil fractions (W-A-250, O-A-250; W-A-275, O-A-275; W-V-200, O-V-200) are seen to cross, while, as indicated in Fig. 2, the curves for the lubricating fractions derived from the Oklahoma oil lie above those for the corresponding higher fractions from the Wyoming crude. A similar crossing of the temperature-viscosity curves may be noted for certain of the lighter Pennsylvania and Oklahoma fractions and also for a few of the Pennsylvania and Wyoming fractions. These facts corroborate the statement that the viscosity-temperature characteristics of oils derived from the different crudes show the greatest differences in the higher or less volatile fractions, while the lighter distillates are not unlike. The viscosity-temperature characteristics of mixtures were discussed in the first paper, and a limited amount of data on such mixtures will be found in Table II.

General Characteristics of Viscosity-Temperature Curves

The new data in the present paper only emphasize the points brought out.[3] In the first place, there is apparently no simple general rule for predicting the rate of change of viscosity of petroleum oils with temperature. Such variations depend upon the crude from which the oil is prepared, and upon the physical and chemical properties of the oil itself. This point was considered in detail in the first paper, Table VIII of which gives the comparative Saybolt viscosities at 37.8°, 54.4°, 98.9° C. (100°, 130°, 210° F.) for oils derived from the typical Pennsylvania and California crudes. This table illustrates the difficulties involved in attempting to estimate viscosity at any given temperature from experimental values determined at some other temperature. The difficulties would be still more impressive if data for the Texas oil fractions were included in the table.

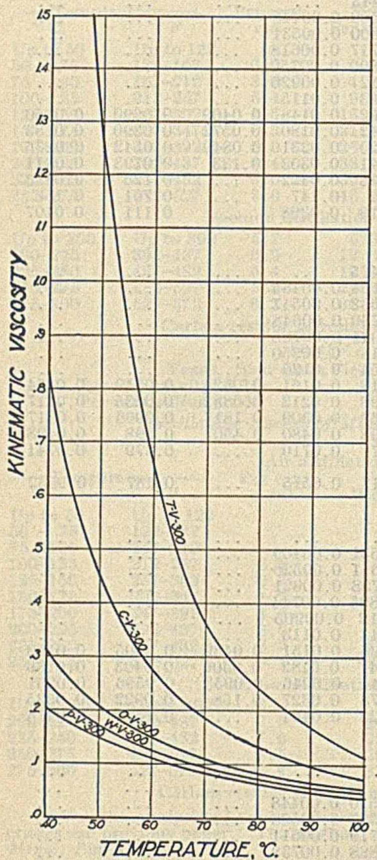

Fig. 2—Viscosity-Temperature Curves of the Fraction Distilled between 275° and 300° C. (527° and 572° F.) at 40 Mm. Absolute Pressure from Typical Pennsylvania, Wyoming, California, Mid-Continent, and Gulf Coast Crudes

Secondly, the temperature-viscosity data for all the oils examined may be represented by the equation

$$V_k = \frac{1}{K + At + Bt^2} \quad (1)$$

in which V_k is the kinematic viscosity, t is the temperature in degrees Centigrade, and K, A, and B are constants characteristic of each individual fraction from each crude. This does not differ essentially from the Slotte equation, which in the past has been employed chiefly in indicating the change of absolute viscosity with temperature. The authors have found it equally useful as applied to kinematic viscosity. When the values of the constants K, A, and B were determined by the method of least squares, and the kinematic viscosities calculated by means of the foregoing equation, the agreement between the figures so obtained and the experimental values was excellent. The values of these constants may, of course, be calculated by making use of the experimentally determined viscosity at three suitable temperatures and solving three simultaneous equations. While this method is sufficiently accurate for many purposes and is much less time-consuming than the method of least squares, the results obtained by it are naturally somewhat less satisfactory than those derived by the longer process. The significance of these constants has already been discussed.[3]

Other Graphical Methods of Presenting the Results

In the graphical presentation of results it is usually desirable, whenever possible, to adopt a method of plotting which permits the data to be represented by a straight line. If the reciprocals of the kinematic viscosities as ordinates are plotted against the Centigrade temperatures as abscissas, many of the curves obtained are nearly rectilinear, as is shown in Fig. 3, in which the data for the Oklahoma fractions are used. It will be observed that the viscosity-temperature relationship for the fractions comprising gasoline may be represented satisfactorily by a series of straight lines each of which is drawn through two suitable experimental points. With the heavier fractions, three or more experimental determinations are obviously necessary to locate the curve. This type of plot permits somewhat easier interpolation than that shown in Fig. 1, and if desired it can be so constructed that the ordinates can be read off directly in Saybolt seconds.

Herschel[7] has shown that when the fluidities (expressed in poises) as ordinates are plotted against the Centigrade temperatures as abscissas, the result, in the case of gasoline, is practically a straight line. Oelschlager[8] has recently maintained that within certain temperature limits a linear relationship may be obtained for certain lubricating oils, when a variable called the "viscosity factor" is plotted on logarithmic paper against the temperature in degrees Centigrade. More important still, it is claimed that these lines meet practically at a point, and the conclusion is drawn that the variation of viscosity with temperature in the case of many lubricating oils may be represented satisfactorily by drawing a line through one experimental point and the common meeting point. Herschel[9] has recently confirmed Oelschlager's results as far as the possibility of obtaining a straight-line relationship is concerned, but he adopts a different method of plotting and maintains that the lines converge to a common point only when the oils are derived from the same crude and lie within a certain viscosity range. As far as the writers are aware, the viscosity of the products ordinarily known as kerosene and gas oil has never been represented as a rectilinear function of the temperature.

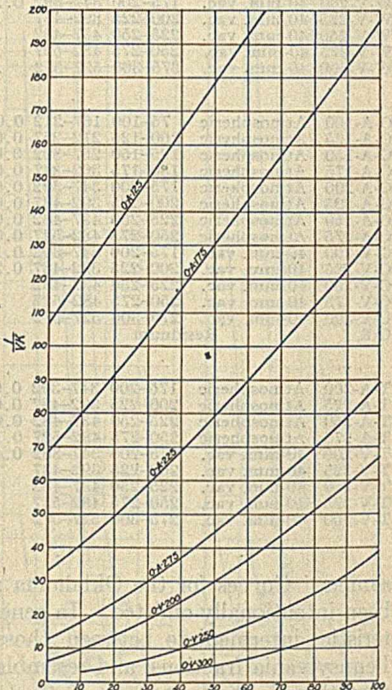

Fig. 3—Curves Obtained by Plotting Reciprocals of Kinematic Viscosities against Centigrade Temperatures for a Series of Products Derived from Mid-Continent Crude

The data of Table II can be represented very well by an equation of the form

$$V_k = c(t + \beta)^n \quad (2)$$

as well as by Equation 1. In Equation 2, V_k = the kinematic viscosity, t = the Centigrade temperature, and c, n, and β are constants for any given oil. The relationship between Equations 1 and 2 becomes more evident if $n = -2$ is placed in Equation 2, which then becomes

$$V_k = \frac{c}{\beta^2 + 2\beta t + t^2}$$

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[7] *Bur. Standards, Tech. Paper* **125**.

[8] *Z. Ver. deut. Ing.*, **62**, 422 (1918).

[9] This Journal, **14**, 715 (1922).

TABLE III—SAYBOLT UNIVERSAL VISCOSITIES OF A SERIES OF PRODUCTS DERIVED FROM CRUDE PETROLEUM

Designation of Product	Temperature Limits of Fractions ° C.	° F.	Saybolt Universal Viscosities 0° C. 32° F.	10° C. 50° F.	20° C. 68° F.	30° C. 86° F.	40° C. 104° F.	50° C. 122° F.	60° C. 140° F.	80° C. 176° F.	100° C. 212° F.	37.8° C. 100° F.	54.4° C. 130° F.	98.9° C 210° F.
							A—Pennsylvania crude							
P-V-200	175–200	347–392	72.2	56.1	47.3	42.5	39.1	37.1	35.4	33.7	32.5	39.9	36.4	32.6
P-V-225	200–225	392–437	...	75.4	58.7	49.3	43.8	40.3	38.0	35.0	33.4	45.0	39.3	33.4
P-V-250	225–250	437–482	...	...	82.0	62.8	52.3	45.8	41.8	37.2	34.7	54.6	44.0	34.8
P-V-275	250–275	482–527	...	...	...	89.4	68.2	55.8	48.6	40.8	36.7	73.0	52.6	37.0
P-V-300	275–300	527–572	...	...	...	...	103.	77.0	62.0	47.0	40.2	...	70.2	40.6
P-R	Residuum		...	...	...	...	718.	384.	252.	127.	78.7	...	525.	81.1
P-Mixt.	Mixture residuum and fraction P-V-225		...	...	...	...	89.4	69.8	58.0	45.2	39.5	...	64.4	39.8
							B—California crude							
C-V-200	175–200	347–392	110.	74.2	57.0	47.7	42.3	39.1	36.8	34.2	32.8	43.5	38.1	32.9
C-V-225	200–225	392–437	...	140.	89.8	65.9	53.1	45.8	41.3	36.6	34.2	55.8	43.8	34.3
C-V-250	225–250	437–482	...	391.	206.	124.	84.4	64.0	52.5	41.6	36.9	92.8	58.9	37.1
C-V-275	250–275	483–527	...	...	...	319.	182.	115.	81.5	52.8	42.1	212.	100.	42.6
C-V-300	275–300	527–572	...	...	...	...	382.	215.	136.	70.6	49.7	...	180.	50.7
P-C Mixt.	Mixture Pennsylvania residue and C-V-250		...	...	...	...	159.	108.	79.5	53.4	43.2	...	95.3	43.7
							C—Wyoming crude							
W-V-200	175–200	347–392	78.7	60.0	49.6	43.7	40.0	37.5	35.8	33.8	32.6	40.8	36.8	32.6
W-V-225	200–225	392–437	...	80.7	61.7	51.1	44.8	40.8	38.2	35.1	33.4	46.1	39.7	33.5
W-V-250	225–250	437–482	...	...	92.0	68.6	55.7	47.9	43.2	37.9	35.1	58.4	45.8	35.3
W-V-275	250–275	482–527	...	...	...	105.	77.0	61.7	51.9	42.0	37.4	83.2	57.3	37.7
W-V-300	275–300	527–572	...	...	...	...	125.	89.4	69.4	50.1	41.5	...	80.3	42.0
							D—Oklahoma crude							
O-V-200	175–200	347–392	81.1	60.9	50.0	43.8	40.0	37.5	35.8	33.7	32.5	40.8	36.8	32.6
O-V-225	200–225	392–437	139.	91.1	66.7	54.1	46.4	41.8	38.9	35.4	33.6	48.0	40.5	33.8
O-V-250	225–250	437–482	...	170.	108.	77.4	60.5	50.8	44.9	38.5	35.4	64.0	48.1	35.6
O-V-275	250–275	482–527	...	...	...	128.	89.4	68.2	55.9	43.6	38.2	97.5	62.8	38.5
O-V-300	275–300	527–572	...	...	...	235.	149.	103.	76.6	52.5	42.7	167.	91.1	43.2
O-R	Residuum		...	...	...	...	986.	560.	344.	155.	89.	...	468.	92.8
							E—Texas crude							
T-V-200	175–200	347–392	192.	112.	76.2	58.1	48.4	42.8	39.4	35.5	33.5	50.4	41.3	33.6
T-V-225	200–225	392–437	...	300.	162.	101.	71.8	56.1	47.8	39.3	35.6	77.8	52.4	35.8
T-V-250	225-250	437–482	...	...	500.	252.	146.	94.9	69.4	47.9	39.8	168.	83.6	40.2
T-V-275	250–275	482–527	...	...	...	...	400.	220.	136.	69.0	48.2	...	183.	49.3
T-V-300	275–300	527–572	...	...	...	...	1250.	579.	308.	120.	66.3	...	460.	69.0

The values of β were determined by the usual graphical method[10] and the values of V_k as ordinates were plotted on logarithmic paper against $(t + \beta)$ as abscissas. In this way it was possible to represent by straight lines, not only the viscosity-temperature relationship for the gasoline and lubricating fractions, but for the kerosene and gas oil fractions as well; in short, all the oils derived from the five typical crudes may be so represented provided Equation 2 is used in its logarithmic form and the value of β is suitably determined for each oil:

$$\log\ V_k = \log c + n \log (t + \beta) \qquad (3)$$

A series of these rectified curves for the oils derived from the typical California and Texas crudes is shown in Figs. 4 and 5, respectively. The approximate meeting point for the straight lines for the California lubricating fractions, as determined graphically on a plot of rather large dimensions, is ° C. + β = 302, V_k = 0.00362; that for the lubricating oils derived from the Texas crude is approximately ° C. + β = 261, V_k = 0.00433. The lines representing the gasoline and kerosene fractions do not in general pass through the common points. (Note the lines for the Fractions C-A-175, C-A-200, C-A-225, in Fig. 4.) Similarly, the rectified curves representing the lubricating oils from the typical Pennsylvania, Wyoming, and Oklahoma crudes converge to points characteristic of each crude, though the points appear to be somewhat less well defined than in the case of the Texas and California fractions.

TABLE IV—FILLING FACTORS

Temperature at which viscosity determination is made ° C.	° F.	Filling factor when viscometer is filled at 25° C. (77° F.)	100° C. (212° F.)
0	32	0.994	...
10	50	0.996	...
15	59	0.998	...
20	68	0.999	...
25	77	1.000	...
30	86	1.001	...
37.8	100	1.003	...
40	104	1.004	0.986
50	122	1.006	0.988
54.4	130	1.007	0.989
60	140	1.008	0.990
80	176	1.013	0.995
100	212	1.018	1.000

It is clear, however, that, in order to evaluate V_k in Equation 3 for any given temperature, it is necessary to know the values of c, n, and β for the oil in question. Three experimental points are therefore necessary before even the straight lines can be drawn, for the constant β must be known in order to plot $(t + \beta)$.

Thus the authors appear to have arrived, by an entirely independent method, at a conclusion comparable with that of Herschel.[9] It has been shown that when the logarithms of the kinematic viscosity as ordinates are plotted against the logarithms of the Centigrade temperature plus a constant as abscissas, the straight lines so obtained meet practically at the same point for the lubricating fractions derived from a given crude by the Bureau of Mines method. The common point is differently located for different crudes.

TABLE V—RELATION BETWEEN PREDICTED AND EXPERIMENTAL VISCOSITIES OVER A TEMPERATURE RANGE FROM 20° TO 100° C. (68° TO 212° F.)

The predicted values in each case were derived from the experimental value of the viscosity at 40° C. (104° F.) and the gravity at 60° F.

Temperature ° C.	° F.	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
		P-V-250		*P-V-300*		*W-V-275*	
20	68	82	82	..	..	..	..
30	86	63	63	..	..	105	105
40	104	52	52	103	103	77	77
50	122	46	46	77	77	62	61
60	140	42	42	62	61	52	52
80	176	37	37	47	46	42	41
100	212	35	34	40	38	37	37
		T-V-225		*T-V-250*		*C-V-225*	
20	68	162	163	500	509	90	88
30	86	101	101	252	249	66	65
40	104	72	72	146	146	53	53
50	122	56	57	95	96	46	46
60	140	48	48	69	70	41	42
80	176	39	40	48	49	37	37
100	212	36	36	40	40	34	34
		C-V-300		*O-V-250*		*P-R*	
20	68	..	..	108	107	..	..
30	86	..	..	77	78	..	..
40	104	382	382	61	61	718	718
50	122	215	226	51	51	384	407
60	140	136	145	45	45	252	255
80	176	71	75	39	38	127	114
100	212	50	51	35	36	79	64

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[10] Goodwin, "Precision of Measurements and Graphical Methods," 1920 ed.

When the source of the crude oil is known, the common point may be utilized, together with the value of β and one experimental point, to locate the straight-line relationship. It seems practically certain that the value of β for lubricants derived from a given crude oil may be regarded as a function of the gravity, as shown in Fig. 6. Hence, with lubricating oils prepared from a known crude, a single determination of viscosity at a suitable temperature together with the gravity at 15.6° C. (60° F.) is sufficient to define the viscosity-temperature relationship over a wide temperature range. Moreover, it will be evident that the kinematic viscosities and Centigrade temperatures used in the present work can be converted readily to Saybolt Universal seconds and Fahrenheit temperatures.

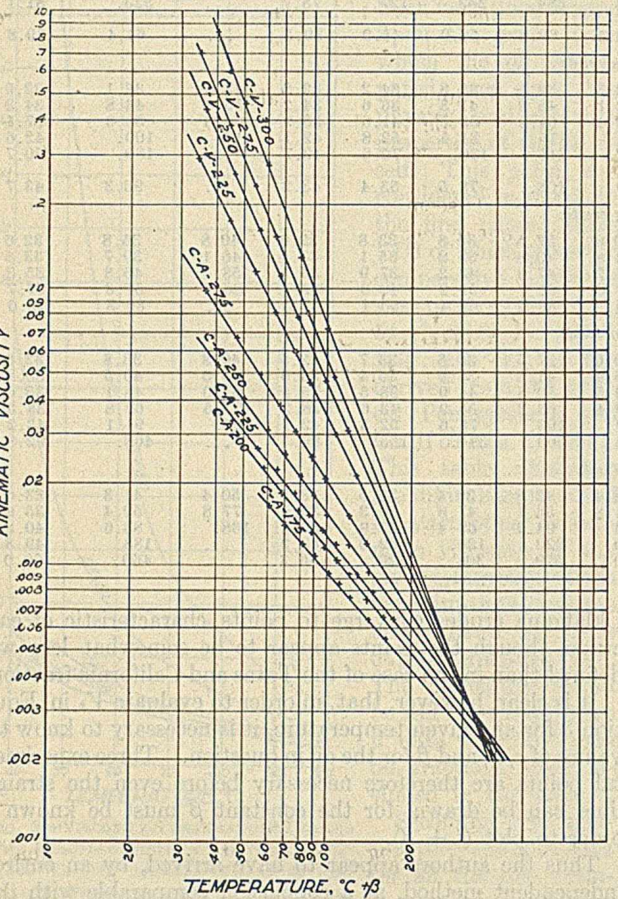

FIG. 4—ILLUSTRATING THE FACT THAT WHEN EQUATION 3 IS USED THE STRAIGHT LINES OBTAINED FOR THE LUBRICATING FRACTIONS DERIVED FROM CALIFORNIA CRUDE CONVERGE TO A POINT

The desirability of extending this method of determining the viscosity-temperature relationship from a single experimental point and the gravity at 15.6° C. (60° F.) to lubricants derived from different crude oils is evident. In this connection the authors have found it possible to apply the logarithmic Equation 3 to the lubricating distillates, as described in this paper, in such a way that, when the viscosity at 40° C. (104° F.) is known and the gravity at 15.6° C. (60° F.) is available, the change of viscosity from 20° to 100° C. (68° to 212° F.) can be predicted with considerable accuracy for any lubricating distillate produced by the Bureau of Mines method from any of the five typical crudes selected for this work. The method involved the assumption of an "average" common point through which pass the straight lines representing the change in V_k with $(t + \beta)$. An "average" curve similar to that shown in Fig. 6 was also constructed, from which the value of β for different specific gravities at 15.6° C. (60° F.) could be read. How closely the predicted values check those obtained experimentally may be judged from a few examples given in Table 5. The predicted values are derived from the experimental values of the viscosity at 40° C. (104° F.) and the gravity at 15.6° C. (60° F.). The temperature 40° C. (104° F.) was used because it is the experimental point nearest 100° F., which is one of the most common temperatures for the determination of viscosity in commercial practice.

It should not be concluded, however, that this method can be applied at once to commercial lubricants. In fact, certain preliminary trials seem to show that it may need considerable modification before it can be so used. For this reason only the more important steps in the application of the method have been given here. Furthermore, the excellent chart issued some time ago by the Texas Company[11] has been found very useful in practice, and there may be some doubt whether one of the type here suggested would be more valuable. The authors hope, however, to continue this work to the end of perfecting a method by means of which the change of viscosity of commercial lubricating oils with temperature may be determined with reasonable accuracy from a single experimental value of the viscosity and some other easily determined physical property, such as the specific gravity.

CONCLUSIONS

1—Viscosity-temperature data have been presented for a series of products obtained by the Bureau of Mines method

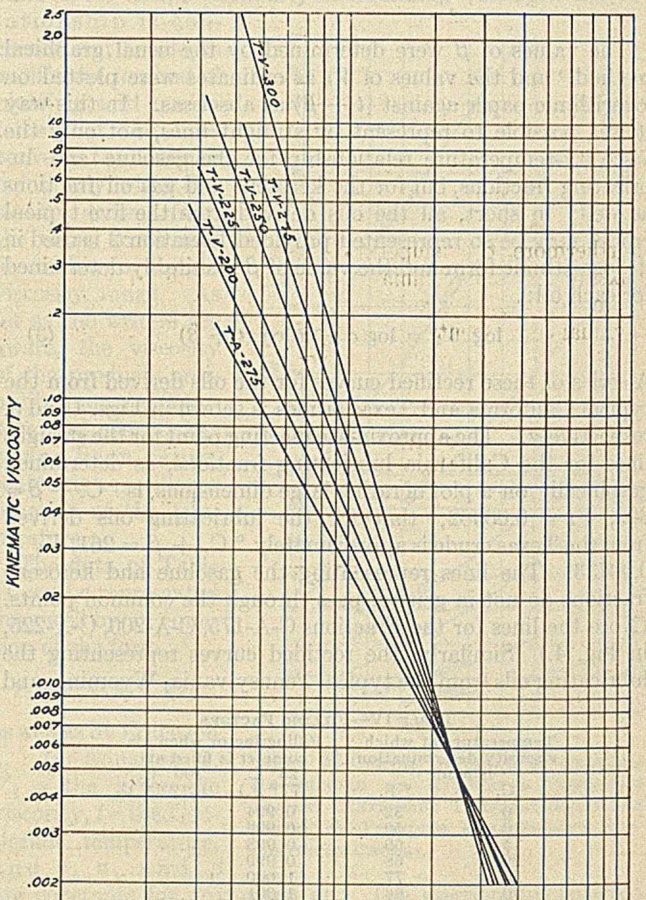

FIG. 5—ILLUSTRATING THE FACT THAT WHEN EQUATION 3 IS USED THE STRAIGHT LINES OBTAINED FOR THE LUBRICATING FRACTIONS DERIVED FROM TEXAS CRUDE CONVERGE TO A POINT

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[11] "Lubrication," June, 1921, p. 5.

from typical crude oils from Pennsylvania, Wyoming, Oklahoma, California, and Texas.

2—The Pennsylvania fractions show the least rapid change in viscosity for a given change in temperature; the California, Oklahoma, and Wyoming oils are intermediate in this respect; while the fractions from the Texas crude show the greatest change of viscosity for a given temperature increment. The temperature viscosity curves for the Oklahoma and Wyoming oils exhibit characteristics intermediate between those of the Pennsylvania and California fractions, but they resemble the former most closely.

3—The most impressive viscosity differences appear in the higher fractions; the curves representing the characteristics of the lighter oils are quite similar.

4—The data of Table II show that the viscosity-temperature relationship of the undistilled residuum from the Pennsylvania crude is of the same general type as the curves for the distilled fractions. The change of viscosity with temperature for a mixture of the Pennsylvania residuum and Pennsylvania distillate may be represented by a curve which is similar to those for the unblended Pennsylvania distillates. Furthermore, the temperature-viscosity characteristics for a mixture of Pennsylvania residuum and California distillate represents an average between the characteristics of the individual components. These points were fully discussed and illustrated in the previous paper.

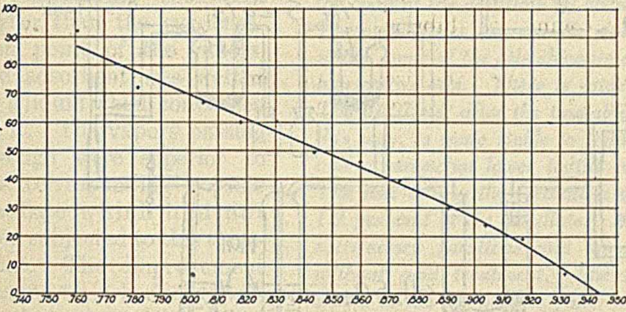

Fig. 6—Relationship between the Value of β and the Specific Gravity at 60° F. for Both the Heavier and Lighter Distillates from the Typical California Crude Oil

5—With certain exceptions already indicated, the temperature-viscosity curves for the kerosene fractions from the various crude oils studied show the same qualitative relationships as those for the lubricating fractions.

6—Viscosity-temperature data can be represented by equations of the general form:

$$V_k = \frac{1}{K + At + Bt^2}$$

or by

$$V_k = c(t + \beta)^n$$

The constants K, A, and B were discussed in the previous paper.

7—The logarithmic form of the second equation is

$$\log V_k = \log c + n \log (t + \beta)$$

When β is suitably chosen for each oil, the relationship between $\log V_k$ and $\log (t + \beta)$ for all fractions, including gasoline, kerosene, gas oil, and lubricants, may be represented by a series of straight lines. In the case of the lubricating fractions derived from any one of the typical crude oils, these straight lines converge practically to a single point. The location of the common point varies somewhat with the crude.

8—It follows from Conclusion 7 that, for lubricating oils derived from a known crude by the Bureau of Mines analytical method, the relation between temperature and viscosity may be determined when the viscosity at one suitable temperature and the value of β are available. It appears to be entirely feasible to plot β as a function of the gravity at 15.6° C. (60° F.). Hence, for lubricating fractions distilled from a given crude, a single determination of viscosity at a suitable temperature, together with the gravity at 15.6° C. (60° F.), is sufficient to define the viscosity-temperature relationship over a wide temperature range.

9—The possibility of extending the method described in Conclusion 8 to the determination of the viscosity-temperature relationship for lubricants produced from different crudes is discussed. It is pointed out that if the viscosity at 40° C. (104° F.) and the gravity at 15.6° C. (60° F.) are known for any of the lubricating distillates derived from any of the five typical crude oils by the Bureau of Mines analytical method, the change of viscosity from 20° to 100° C. (68° to 212° F.) can be predicted with considerable accuracy. Preliminary trials seem to indicate that this method cannot be used with entire success on commercial lubricants.

Combustion of Petroleum Hydrocarbons[1]

By C. F. Mabery

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Because of frequent inquiries for information concerning the details of hydrocarbon analysis, probably due to the increasing interest in the composition of petroleum, which must include analysis of its constituents, and having made some essential improvements that greatly facilitate the large amount of work now on hand, it seems worth while to present the method as it is now in use. In two papers presented many years ago[2] were set forth the errors in the analysis of organic compounds in general. It has recently appeared, however, that elimination of other sources of error, and a great reduction in the time required are made possible by certain changes in manipulation.

The details requiring particular attention in this analysis are as follows:

1—Instant and complete control of the initial rate of combustion.

2—An excess of hot oxygen in front of the oil.

3—Duplicate absorption bulbs filled with oxygen, and kept overnight or longer in large desiccators also filled with oxygen.

4—A second safety tube filled with soda lime and phosphorus pentoxide in front of the 50 per cent potassium hydroxide bulb.

5—Copper oxide heated to the full extent of a gas-heated furnace, a temperature that only the most infusible Bohemian glass or its equivalent can withstand.

6—The combustion train relieved from pressure or suction. Every one is familiar with the difficulty of obtaining tight joints with cork connections.

The apparatus shown in the figure, simple in construction and durable in operation, eliminates these sources of error. In hundreds of analyses the oxygen purifying train has been in use without change for more than two years. The oxygen supply is better regulated from an independent reservoir under slight water pressure than directly from a tank. It passes from a 6-liter bottle, regulated by an overflow, through two bottles containing a 50 per cent solution of potassium hydroxide on either side of which is a mercury safety seal, and then through a large U tube containing sulfuric acid. Two small U tubes containing sulfuric acid follow, one of which delivers oxygen just within the cork of the combustion tube, and the other in front of the boat

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[1] Received July 7, 1924.

[2] Mabery, *J. Am. Chem. Soc.*, **21**, 510 (1899); Mabery and Clymer, *Ibid.*, **22**, 213 (1900).

containing the oil and near the copper oxide, at a rate of a bubble in 2 or 3 seconds. This arrangement avoids the possibility of an accident from excess of pressure, or coming together of the acid and potassium hydroxide by a large depression in temperature in cold weather, or by careless operation. It is, in fact, "foolproof."

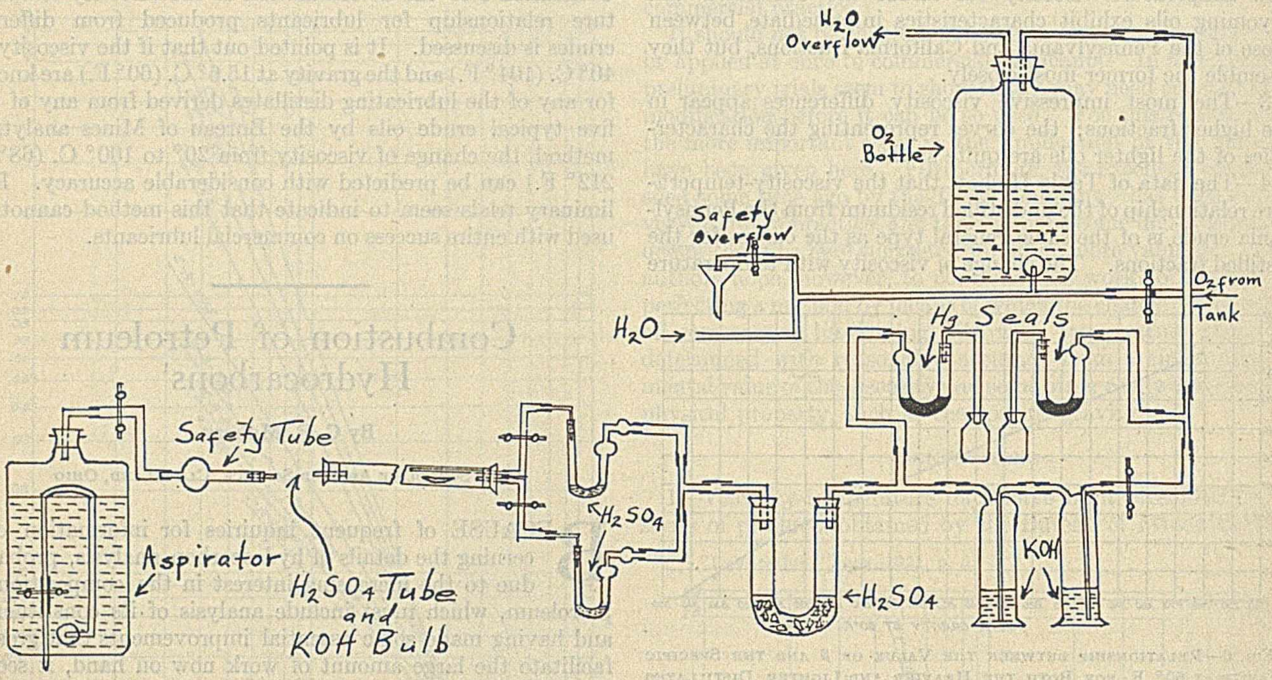

FIG. 1

The only combustion tube that will withstand the requisite high temperature, without vitrification, is the most infusible Bohemian glass. The oil is as clearly visible in the boat after fifty analyses as in the first analysis. Of course, at such temperatures copper oxide easily fuses into quartz. It is best to use a mixture of finely granulated and powdered copper oxide.

Since the absorption bulbs may be used in at least twenty analyses, the carbon dioxide held back in the acid, as shown in one of the earlier papers, does not affect the percentage of carbon. A 50 per cent solution of potassium hydroxide endures longer use without refilling. But even with the safety tube of the potash bulb filled with soda lime and phosphorus pentoxide, unless it is followed by another longer tube likewise filled, which invariably increases in weight of moisture 1 or 2 mg., there is a corresponding loss in carbon dioxide. This tube needs refilling only once in one hundred or more analyses.

Unless the combustion train is completely relieved from pressure or suction, there is danger of slight loss by leakage of carbon dioxide. This is of less consequence if other elements are present in the substances analyzed, but with only carbon and hydrogen such loss is prohibitive; it is easily avoided by the use of an aspirator with just sufficient length of siphon, as shown in the figure, to equalize the back pressure in the bulbs. With the bulbs filled as described much time is saved in replenishing, since aluminium oxide, calcium chloride, and soda lime are difficult to clean out, and none of these absorbents can be used more than two to five times. Besides their longer use, potassium hydroxide and sulfuric acid are much easier to manipulate.

By weighing duplicate bulbs filled with oxygen and keeping them in large desiccators also filled with oxygen, much time is saved by carrying the weights forward from one day to another, or, if longer time intervenes between analyses, the corrections are only a few tenths of a milligram. If kept in the open air they may be filled in a few minutes. By weighing the bulbs filled with oxygen a loss of time in replacing oxygen with air after sweeping out carbon dioxide is avoided. On account of the instability of petroleum hydrocarbons and the resistance of the escaping gases to oxidation, even at high temperatures, unless the progress of the oxidation is rigidly controlled in the beginning, there is danger of loss. Such control is only possible in the gas furnace. That the even heat of the electrically heated furnace cannot be varied to meet these requirements was shown by the failure in this laboratory to obtain concordant results in the analysis of hydrocarbons in an electric furnace, when closely agreeing results were obtained in the gas furnace. A solution of palladium chloride is not needed, since the oxidation is complete under the conditions herein described.

So much has been claimed for the aid of catalyzers in general organic analysis, it seemed advisable to test their efficiency in hydrocarbon analysis. A layer of pumice saturated with cerium oxide, which has been recommended as the best catalyzer, was placed in front of the oil, which was volatilized with ordinary rapidity. Several analyses showed loss of volatile hydrocarbons to the extent of 1.5 to 2 per cent. It appears, therefore, that, besides slow initial volatilization only hot oxygen delivered in front of the oil and an extremely high temperature of the copper oxide can prevent loss by incomplete oxidation of the volatile hydrocarbons.

By this method four or more analyses are possible in a day, instead of two, which formerly were considered a daily task. As an example of the time required, two perfect consecutive analyses were made in 1 hour and 50 minutes, which included 70 minutes in sweeping out the carbon dioxide.

In most of the lines of work with which the writer has been occupied during the last fifty years, he has had to study substances that involved combustions, and has always regretted the loss of time. Of all the different forms of apparatus he has used, the one herein described is the simplest and most efficient. When once started its oversight interferes very little with other continuous work.

Catalytic Treatment of Cracked Distillates in the Vapor Phase[1]

By T. T. Gray and M. R. Mandelbaum

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A preliminary description of a method of refining cracked distillates is given which is intended to obviate value losses due to the reaction of sulfuric acid with the olefins present. The process is based on the greater reactivity of the objectionable diolefins and similar unstable substances occurring in the cracked oils. When vapors containing these substances are passed through an adsorption catalyst, they are caused to polymerize into higher boiling products, which, although not retained by the catalyst, can be separated from the body of the distillate by virtue of the difference in boiling point. These polymers are usually dark-colored viscous oils or resinous solids, some of the oils showing excellent physical characteristics for lubricating oils. There is evidence that the reaction is exothermic. The distillate, after the unstable constituents have been removed in this way, is more stable to light, has a much lower gumming test, and a somewhat lower iodine number than the untreated product. The loss due to the formation of the polymers ranges from 0.1 to 1.0 per cent of the distillate. It is possible in this way to produce satisfactory gasolines and burning oils from pressure distillates without acid treatment. The most convenient catalyst of those suited to the purpose is fuller's earth, because of its wide refinery application.

In 1914 one of the authors[2] noticed that when a distillate from cracked hydrocarbon oils was passed through a tube containing fuller's earth, metallized fuller's earth, or similar materials, heated to a temperature somewhat higher than the condensation point of the vapors, the adsorbent was wetted by a liquid which condensed on it. The vapors passing through were superior to the corresponding cracked distillate which had not been subjected to this treatment. The improvement was most marked in respect to odor, color, and stability as manifested by the retention of good color, even on exposure to direct sunlight, and the absence of resinous deposits on standing. This was attributed to the polymerization of the more unstable constituents of the distillates under the influence of the adsorbent, resulting in the formation of higher boiling substances, which condensed out of the vapors. Taking advantage of this phenomenon, a process was devised for producing satisfactory gasolines and kerosenes from cracked distillates without recourse to acid treatment. The results obtained were so novel and interesting from the standpoint of petroleum technology, that a preliminary discussion of the method seemed justified, although the detailed investigation of the reactions involved is so far from completion that only the broadest lines it is taking can be given. Such adsorptive agents as silica gel, bauxite, and highly porous metals, used in the same way, have also been found to promote the reaction, but the use of fuller's earth has been emphasized in the work so far carried out.

Until recently fuller's earth treatment of petroleum oils was confined to their filtration through beds of that material for decolorization, the clay adsorbing the colored substances selectively. Gurwitsch[3] has shown, however, that with decolorization may be associated, as a secondary effect, the polymerization of the coloring matter removed by the earth into even more highly colored compounds. Further, we find records of suggestions[4] to combine the decolorization of petroleum fractions with the distillation necessary to separate them. However, these suggestions seem not to have been put to practical use. This is probably due to the difficulties involved in the distillation, through a bed of adsorbent material, of the heavier fractions, of which the improvement of color was usually necessary.

The introduction of cracking processes to increase the yield of more volatile distillates from petroleum rendered the refining problem more complicated. The light products obtained by these processes are differentiated from most of the corresponding straight-run fractions by their objectionable properties, such as instability of color, deposition of gums on standing, and the like, as well as by their high content of unsaturated hydrocarbons. However, the method of refining has been almost universally the same as that applied to straight-run products—i. e., treatment with sulfuric acid. That such treatment is unsatisfactory, wasteful, and unnecessary has been forcefully pointed out by Brooks[5] and others, and has been generally accepted by petroleum chemists. The chemical examination of cracked products has been hampered by the lack of quantitative methods for the determination of the various classes of compounds present, as well as by lack of uniformity of the products themselves. Nevertheless, certain general conclusions may be drawn. Unsaturated hydrocarbons are present in the volatile fractions in amounts ranging from 10 to 40 per cent, as measured by the sulfuric acid absorption method, which gives low results. They are almost entirely mono-olefins. Diolefins are thought to be present in small amounts—less than 1 per cent of the product—although processes for their production in larger amounts have been proposed,[6] based on conditions different from those obtaining where gasoline and kerosene are the desired products. Other hydrocarbons—benzene derivatives, naphthenes, and so on—may be found according to the crude used and the conditions of cracking. Sulfur and nitrogen compounds also occur, to an extent dependent on the amounts present in the original oil.

Brooks,[5] Leslie,[7] and others agree that the constituents to which cracked distillates owe their characteristic objectionable properties are the diolefins and similarly unstable substances —a view which the writers' work seems to bear out. The olefins cannot be held to be undesirable, either in motor fuels or burning oils, nor can the aromatic compounds. Yet, on treatment with strong sulfuric acid, substances of both types are attacked, along with the diolefins. That the loss, as far as the mono-olefins are concerned, is not only the volumetric one due to the adsorption of these compounds by the acid,

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[1] Presented under the title "Catalytic Treatment of Pressure Distillates in the Vapor Phase" before the Division of Petroleum Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] Gray, U. S. Patent 1,340,889 (1920). Application filed May 18, 1914.

[3] "Wissenschaftliche Grundlagen der Erdölarbeitung," p. 232.

[4] Thompson, British Patent 6786 (1884).

[5] *J. Am. Chem. Soc.*, **40**, 882 (1918).

[6] Mersereau, U. S. Patent 1,282,906 (1918).

[7] "Motor Fuels," pp. 295 and 332.

but in addition a value loss due to the polymerization of many of the olefins to higher boiling substances which remain in the oil layer, was brought out by Brooks, and is now accepted. Estimates as to the proportion of these losses differ widely, but it may safely be said that, combined, they are seldom less than 5 per cent (including losses due to the redistillation necessary) and are usually higher. This loss adds greatly to the cost of acid treatment of cracked distillates. Moreover, the products, particularly the burning oils, are usually unsatisfactory, and it is generally considered impossible to prepare practically a high-grade burning oil from cracked products by acid treatment.

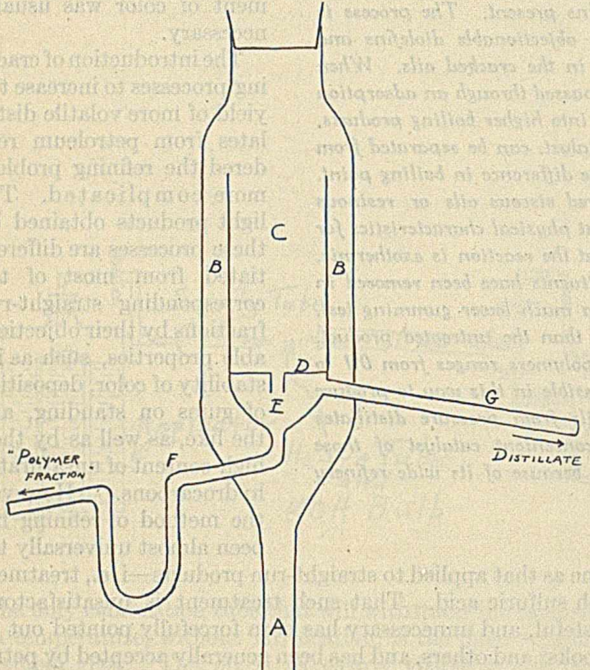

Fig. 1—Glass Tower

Theory of Process

The process described in this paper is based on the polymerizing action of adsorbent materials, which, while much weaker than that of sulfuric acid, is yet strong enough to cause the polymerization of the highly unstable substances which give cracked distillates their undesirable properties. It is carried out in the vapor phase.[8] This not only makes it possible to combine the operation with a fractionation, but has the added advantage of utilizing the heat of the vapors to maintain a temperature which allows the convenient separation of the polymerized substances by virtue of their increased boiling point. Finally, it has been found that the effect of the catalyst on the substances involved is markedly different in the vapor phase from that in the liquid phase. The latter was studied, in the case of amylene and pinene, by Gurwitsch,[9] and for pinene and terpenes by Venable,[10] who found that lively exothermic reactions occurred in each case, even at room temperature, resulting, for amylene, in the formation of as much as 85 per cent of a higher boiling substance; for the terpene, in rearrangement and some polymerization. The study of the vapor-phase reactions of these and other substances is not yet complete, but the indications are that, although the results are qualitatively the same, they are different in degree. Thus, in the case of amylene, it was found that by slowly distilling some of this substance through fuller's earth kept at 100° C. only 5 per cent of a higher boiling substance was obtained from the distillate, compared with the much higher amounts in the liquid phase reported by Gurwitsch. On the other hand, dimethylbutadiene reacts very vigorously with fuller's earth in the vapor phase. When a dilute solution of dimethylbutadiene in a mixture of chloroform, benzene, and toluene was distilled and the vapors were passed through fuller's earth, the distillate had an iodine number of 2.8, compared with that of 16.5 for the charge. From these observations the inference has been drawn that fuller's earth has only a mild polymerizing action on the vapors of olefins and a violent one on those of diolefins.

Apparatus

The apparatus at present used for the laboratory study of the action of these catalysts on the vapors of cracked distillates is a glass tower (Fig. 1) the inlet tube, *A*, of which is connected to a boiling flask by a stopper. The vapors pass up through an annular space, *B*, surrounding a tube, *C*, about 2.5 cm. (1 inch) in diameter and 3.8 cm. (1.5 inches) long, which holds when filled about 25 grams of 60 to 90-mesh fuller's earth. They then pass down through the catalyst, which is held in place in the tube by a wire screen or some steel wool supported by a glass shelf, *D*, and finally through an opening in the shelf into a separating chamber, *E*, from which a small tube, *F*, provided with a trap to prevent vapors from passing, removes any condensed liquids, while another tube, *G*, sealed into the side of the chamber, acts as a vapor outlet. The vapors are then connected to a condenser. The inlet tube acts also, in the laboratory device, as a reflux line for the outer shell.

Larger experimental towers are in use on a 10-gallon still, and one was used for a short time on a 6-barrel still. A tower with a capacity of 3 tons of fuller's earth has been built and will shortly be installed in a Midcontinent refinery. Another, with 8 tons capacity, is being built, also for a Midcontinent refinery. The principle of these larger units is the same as that of the laboratory device, and their structure similar. They differ only by the addition of a separate line for reflux and the necessary manholes for filling and emptying. The 8-ton tower will be 10 feet in diameter and 12 feet high over all. It is expected that it will treat over 2000 barrels of cracked gasoline or kerosene with each charge of clay.

Operation

When a cracked distillate is distilled through the apparatus, a thermometer in the catalyst shows, at the beginning of the operation, a considerably higher temperature than one in the entering vapors. Later the larger amount of vapor traversing the tube obscures this effect. The catalyst gradually darkens. A distillate greatly improved as regards color, odor, and stability is obtained at *G*. Twenty-three grams of fuller's earth will treat from 500 to 1500 cc., according to the nature of the cracked distillate. This is from 125 to 375 barrels per ton. The liquid condensed in *F* is dark in color, ranging from yellow to ruby-red or dark green, depending on the source of the cracked oil and the conditions of cracking. It usually amounts to about 15 per cent of the distillate. This liquid is largely the result of partial condensation of the vapors in the clay, and on being re-run it yields 90 to 95 per cent of colorless distillate, which can be added to the main distillate. The residue (about 0.3 to 1.0 per cent of the distillate) is a heavy, viscous, dark-colored oil, formed by polymerization of the unstable constituents of the vapors. It is expected that in refinery operation this liquid will not necessarily be col-

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[8] An interesting example of the simultaneity of inventions was furnished by Hall's application for a patent on a process of vapor-phase treatment with fuller's earth while Gray's was pending.

[9] *Kolloid-Z.*, **11**, 17 (1912).

[10] *J. Am. Chem. Soc.*, **45**, 728 (1923).

lected from the separating chamber, but may be run back into the still, either by direct refluxing or by pumping. The partial condensation in the catalyst is apparently due to the fact that the heat furnished by the reaction and the surrounding vapor is insufficient to raise the temperature of the clay to that of the end point of the distillation. That the reaction is exothermic is shown by the temperature effect noted above, and also by the fact that under the same running conditions a distillate gives much less condensate in an active catalyst than in the same weight of inactive substance of about the same specific heat. This condensation not only serves to wash out the polymerized substances, but gives an additional fractionating effect. In fact, the combination of refluxing in the outer shell and condensation in the catalytic body is so efficient a fractionating device that it becomes possible, by connecting the tower to the cracking apparatus, to combine the refining and cutting in one step, and run finished gasoline directly from the cracking still. Operating in this manner with a catalytic tower containing fuller's earth connected to a pressure still, higher yields of gasoline were obtained than under similar conditions without the fuller's earth. This is attributed to the effect of the tremendous pressures exerted by the adsorbent on vapors passing through, and is analogous to the action of charcoal in the recovery of gasoline from natural gas. This increased yield has been noticed in some cases when straight-run gasoline has been cut from the crude using, as a fractionating device, a tower containing fuller's earth.

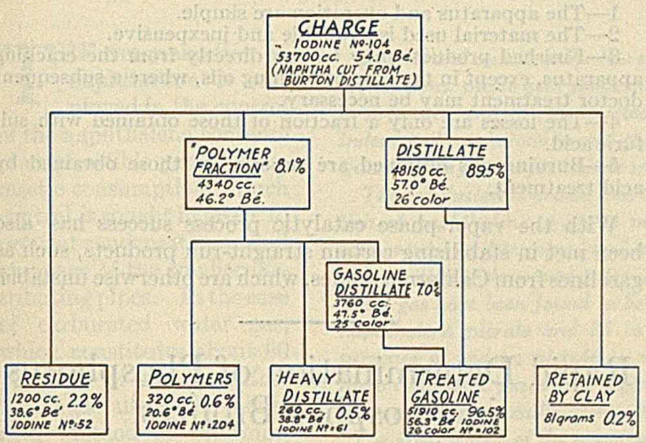

Fig. 2—Flow Sheet, Fuller's Earth Treatment, Vapor Phase

The material used as catalyst in the majority of the runs has been Florida fuller's earth, 60 to 90 mesh, prepared in a manner similar to that used for filtering lubricating oils. Texas and other earths have also been successfully applied. At the conclusion of the operation the earth is dry and flows as freely as when fresh, whether it is removed from the tower immediately or allowed to remain in it until cool. The easy flowing of the clay simplifies the design of large-scale units, as they need but be provided with a manhole in the bottom for discharging the catalyst.

Experimental Run

A description of one of the experimental runs, the data of which are given in Fig. 2, will best serve to illustrate the method and results. In this case, in order better to be able to trace the changes taking place in the portion actually treated, it was separated from the remainder of the crude pressure distillate, which had been prepared from Midcontinent crudes by the Burton process, by a preliminary fractionation using a short column filled with steel wool. The fraction taken was that boiling below 425° F. Its Engler distillation is shown in Fig. 3. The apparatus used for this run consisted of a 10-gallon still, to which was attached a steel catalytic tower with an inner shell 5 inches in diameter and 6 inches high. This was charged with 1000 grams of the 60 to 90 Florida clay.

At the end of the run the clay was removed from the tower and weighed. It was found to have gained 81 grams, or approximately 0.2 per cent of the vapor passing through it. This, added to the 0.5 per cent polymerization loss, gives a total of 0.7 per cent of the material treated, which may be considered the losses inherent in the process for this distillate. It will be noted that the actual polymerization loss is only 5 per cent of what is called the "polymer fraction," the rest of it being due to condensation in the catalyst. That portion of the polymer fraction called "heavy distillate" was ascribed to incomplete fractionation of the original charge, rather than polymerization, because of its low iodine number, which clearly classified it with the residue, rather than with the much more unsaturated polymers. Working with other cracked products, the sum of these losses has varied between 0.3 and 1.5 per cent.

Nature of Products Formed

The distillate obtained in this run represented a yield of 291 barrels per ton of fuller's earth, and exhibited satisfactory properties. Its color was stable, it remained clear on standing, with no deposition of solid, and seemed in every respect to be the equal of straight-run products. In comparison it should be noted that on acid-treating the same charge with 3 pounds of 66 acid per barrel, not only was there a volumetric loss of 1.6 per cent observed, but the end point of the product was raised 15° F. as shown in Fig. 3. In addition, the color of the acid-treated product rapidly deteriorated, being +20 on the Saybolt colorimeter immediately after treatment and falling to 7 after exposure for a few days.

The nature of the polymers formed in the process remains to be discussed. Unfortunately, the amount so far available has been too small to make attempts to isolate pure substances from them profitable. It is expected that this difficulty will be overcome in the near future with the installation of the commercial units already mentioned.

The polymerized material in each case so far studied seems to be composed of at least two types of components. One of these, a viscous, colored liquid, is distillable at pressures of the order of 0.1 mm. The other is a semisolid, sometimes tacky mass, which does not flow at ordinary temperatures. Both have high iodine numbers, which clearly differentiate them from the still residues. In the one case in which sufficient of the polymer was obtained to make possible the examination of its physical properties, the distillable component (0.4 per cent of the distillate treated) boiled between 300° and 400° F. at 0.2 mm. Its iodine number (Hanus) was above 200. It had a gravity of 28.6° Bé. at 60° F. and a Saybolt viscosity of 407 at 100° F.

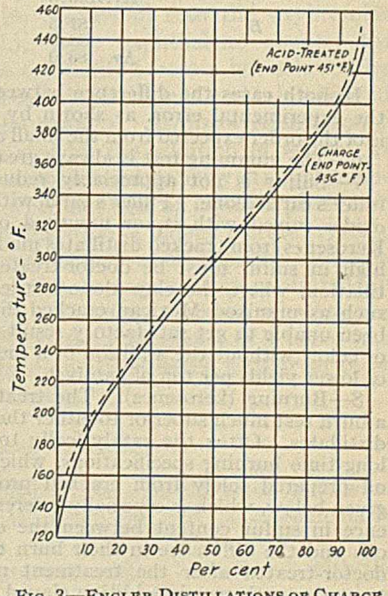

Fig. 3—Engler Distillations of Charge and Acid-Treated Product (3 Pounds Acid per Barrel)

Its cold test was +5° F., at which point it was perfectly clear. As according to the physical characteristics already determined this oil seems to correspond with high-grade lubricating oils, the possibilities of vapor-phase polymerization as a source of lubricants should be considered. It is possible so to regulate the conditions of cracking that the substances which polymerize to form them would be present in greater proportions. This point can be discussed in greater detail when the chemical nature of the polymers is more definitely known.

Comparison of Treated and Untreated Products

In order to obtain a basis of comparison between products treated by this process and the corresponding untreated products, the following procedure was adopted. Equal portions of the same cracked distillate were run at the same time and under the same conditions through similar glass towers, one containing the catalyst and the other the same weight of Ottawa sand. To assure equal fractionation, both distillations were carried to the same point, above the desired end point; after which each polymer fraction was added to the corresponding distillate and the mixture re-run, with a LeBel Henninger column, to the same end point in each case. A comparison of the products shows:

1—There is no difference in the Engler distillations.

2—The specific gravity of the treated product is slightly higher than that of the untreated; representative figures are 0.7592 as against 0.7572; another case gave 0.7499 against 0.7467.

3—The color of the treated distillate is usually better when freshly prepared; it is always much more stable than the untreated.

4—The unsaturation, as measured by the sulfuric acid absorption method, is not appreciably different. This does not vitiate the conclusion that the more unstable unsaturated compounds are removed by polymerization, since the amount of polymer formed indicates that there would be a difference amounting to about 0.5 per cent, which is unmeasurable by this method.

5—The iodine number of the treated distillate is slightly lower than that of the untreated:

	Treated	Untreated
A	99.8	101.7
	100.1	101.8
	100.0	102.1
	100.2	102.0
	Av. 100.0	Av. 101.9
B	87.5	94.5
	88.5	93.7
	Av. 88.0	Av. 94.1

In both cases the difference between the two is well outside the experimental error, as shown by the checks obtained, and is of the order expected from the small amount of polymer formed.

6—The gumming test is always greatly reduced by treatment.

7—Sulfur is not appreciably reduced when the catalyst is fuller's earth alone. Fuller's earth with porous metals or metallic oxides mixed with it, or mounted on it, is more satisfactory. Kerosenes from cracked distillates made from gas oils moderately high in sulfur must be doctor-treated after the catalytic distillation, where the clay alone is used. With high-sulfur oils, such as unmixed Mexican cracked distillates, the writers have been unable to get satisfactory results, even as regards stability of color, without the addition of a metal, except at the expense of lower yields per ton of catalyst.

8—Burning (kerosenes). The treated distillate always gives a burn test much superior to either the untreated or acid-treated distillates. Often the catalytically treated distillate passes the long-time burning specifications, which is unusual for a refined oil prepared solely from cracked products. One such case is given below, which is especially interesting because of the difference in sulfur content between the acid-treated and catalytic oils and the difference in their burn tests. Both samples were doctor-treated after the treatment mentioned, and the acid-treated sample was in addition clayed.

	Catalytic	Acid-treated
Gravity	42.0° Bé.	42.7° Bé.
Viscosity/60° (Saybolt)	485 sec.	467 sec.
Corrosion	Slight	None
Doctor	Sweet	Sweet
Color (Saybolt)	+25	18
Unsaturated (per cent)	12.1	12.4
Sulfur (per cent)	0.070	0.045
Long time burn	Yes	No

The yield in this catalytic run was 286 barrels per ton of fuller's earth.

Conclusion

It is possible by vapor-phase treatment with an adsorbent catalyst, such as fuller's earth, to produce satisfactory gasoline and burning oils from pressure distillates. The advantages of the process over current practice are:

1—The apparatus and operation are simple.

2—The material used is available and inexpensive.

3—Finished products may be run directly from the cracking apparatus, except in the case of burning oils, where a subsequent doctor treatment may be necessary.

4—The losses are only a fraction of those obtained with sulfuric acid.

5—Burning oils obtained are superior to those obtained by acid treatment.

With the vapor-phase catalytic process success has also been met in stabilizing certain straight-run products, such as gasolines from California crudes, which are otherwise unstable.

Rapid Determination of Phosphorus in Phosphor Bronzes[1]

By Leif Lindemann

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Complete oxidation of the phosphorus cannot be accomplished by means of nitric acid alone, although many of the published methods are based on the quantitative separation of phosphorus along with the metastannic acid. This new determination is dependent upon the complete oxidation of the phosphides, preventing the hydrolysis of the tin and the precipitation of ammonium phosphomolybdate.

Place 0.5 gram of the malleable bronzes or 0.2 gram of the cast phosphor bronzes in a small beaker. Add 25 cc. of hydrochloric acid (specific gravity 1.12) (approximately 5 parts water to 7 parts concentrated HCl) and 5 cc. of nitric acid (specific gravity 1.2), cover with a small watch glass and warm gently until action commences; then remove from the heat until action slackens. (The reaction must not be allowed to proceed too violently.) When solution is complete, heat nearly to the boiling point and evaporate the solution for 10 minutes to remove chlorine, dilute with 50 cc. of cold water, neutralize a little with 10 cc. of dilute ammonia (1:1), and at once add 50 cc. of a regular molybdate solution made by adding to 100 grams of molybdic oxide 400 cc. of water and 100 cc. of concentrated ammonia and pouring the cold solution slowly, with constant stirring, into 1 liter of nitric acid (specific gravity 1.2). In case there is any arsenic in the sample, the precipitation should not take place at a temperature higher than 40° C.

Combined with the alkalimetric determination the method described is very rapid. For a gravimetric determination the precipitate should be dissolved in dilute ammonia on the filter and precipitated again with a little nitric acid and molybdate solution.

By oxidizing the escaping gases in a nitric acid–potassium permanganate solution by dissolving fine borings as described, the writer has never found any phosphorus escaping as hydrogen phosphide.

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[1] Received April 30, 1924.

New Tariff Effective in Poland—The new Polish tariff became effective at the end of June, and provides for a reduction in the duty on textiles, sole and upper leathers, fertilizers, scrap iron, and paper.

Effects of Indene on Naphthalene Determinations by Picric Acid[1,2]

By R. L. Brown and H. G. Berger

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Indene and coumarone, when entrained in a gas and passed through an aqueous picric acid solution, form insoluble picrates. Evidence is presented and literature cited showing definitely the presence of indene and coumarone in coal gas and indene in carbureted water gas. Quantitative figures for indene in coal gas are given.

The conclusion is drawn that the picrate method for the determination of naphthalene in gas is much in error unless the indene picrate present be determined and a correction applied.

In sixteen instances picrates obtained from coal gas and carbureted water gas have been found to be mixtures of from 50 to 75 per cent naphthalene picrate and 25 to 50 per cent indene picrate. The presence of indene picrate in naphthalene picrates obtained from these industrial gases is a logical explanation of many determinations which give results higher than theory permits.

The significance of the true character of the precipitate obtained in naphthalene determinations in the gas industry is pointed out, both in the sale and distribution of manufactured gas, and as a guide to operation of the carbureting units in water-gas plants.

THE determination of naphthalene is employed in the control of the naphthalene contents of combustible gases for domestic consumption. Such control is sought in order to prevent condensation in and stoppage of the smaller distributing pipes. In the case of carbureted water gas, which constitutes about 60 per cent of the manufactured gas used, the picric acid method of determining naphthalene is also employed at producing plants to a greater or lesser degree as a guide in the operation of the carbureting units.

The prevailing methods[1,*] of determining naphthalene in gas and in by-product oils, either from carbureted water-gas plants or from coal-gas or coke-oven plants, are based on the formation of an insoluble picrate of naphthalene in aqueous picric acid solution. The details of the methods are too well known and generally accessible to require description, except to say that they depend upon the determination of the amount of picric acid that combines with naphthalene to form naphthalene picrate. This is determined in one of two ways—namely, (1) from the amount of the naphthalene picrate formed, or (2) from the change in concentration of picric acid in the solution in which the naphthalene picrate has formed and from which it has been removed. This change is determined from the difference in titrations against a standard alkaline solution, or by the change in the electrical conductivity of the solution.

As the method is at present employed, it is evident that the presence of appreciable amounts of any hydrocarbons or other compounds which give an insoluble precipitate with picric acid in its aqueous solution would destroy the accuracy of the method. Little regard has been given to this possibility, although Kuster[1] warns against the presence of acenaphthene, chrysene, and both naphthols, but says that phenanthrene does not interfere. Höfsass, Hermann, and Mezger[1] state that chrysene, acenaphthene, and phenanthrene all form picrates and, if present, interfere with accurate naphthalene determinations. In 1916 an investigation of the literature on solvent naphtha resins revealed to the writers the strong probability of the presence of other interfering compounds in most gases. Experience in investigating the gummy meter problem[2] convinced the writers early in 1922 that the method must be at fault. Kramer and Spilker[3] in 1890 reported that indene and coumarone formed picrates when the solvent naphtha fraction containing the two hydrocarbons was treated hot with solid picric acid and the solution then allowed to cool.

Indene brought into contact with an aqueous solution of picric acid gives an insoluble picrate. The properties are such as to permit this picrate, when it is present, to be carried along with naphthalene picrate, and to be reported as naphthalene in a determination of the latter by the prevailing methods. The evidence for these statements follows.

Indene Picrate

The indene used boiled at 179° to 180° C. at 760 mm. pressure, and showed a specific gravity of 0.9893 at 20° and an index of refraction n_D^{20} 1.5600. It yielded the characteristic dibromide (2,3-dibromoindan) and oxybromide (2-bromo-3-hydroxyindan), the latter melting at 129° to 130° C. When a stream of nitrogen was led through a sample of the indene at room temperature and then through a saturated or nearly saturated aqueous solution of picric acid, an immediate precipitation in that solution occurred. This precipitate was indene picrate melting at 98° C., which, on being decomposed with alkali, yielded indene, which was again characterized by its conversion into the oxybromide (melting point 130° C.). Like naphthalene picrate, the picrate of indene may be crystallized from a hot solution by allowing it to cool. It is soluble in benzene and is left behind by the evaporation of the benzene. It dissolves in alcohol, from which it is precipitated by the addition of water. It shows approximately the same thermal stability as naphthalene picrate. Liquid indene in contact with an aqueous picric acid solution gives a ready precipitation of indene picrate crystals.

Coumarone also forms a picrate when brought into contact with an aqueous solution (approximately saturated) of picric acid. Precipitation of a picrate results whether the coumarone is in the liquid state or entrained as a vapor in a gas stream. The picrate showed properties similar to those enumerated for indene picrate.

Indene in Coal Gas

With these facts established, the question arose as to what extent indene was present in coal gas, and more particularly in carbureted water gas.

In a search of the literature the writers have found, with the exception of benzene, toluene, and xylenes, and the assertions in patent claims for solvent naphtha resins, little information as to the actual molecular composition of the light oils in coal gases produced in the United States and in modern installations. The presence of indene in coal gas and its light oil was shown by Kramer and Spilker[3] about thirty years ago,

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[1] Received April 7, 1924. Presented before the Section of Gas and Fuel Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[*] Numbers in text refer to bibliography at end of article.

and by other workers in Germany, mostly during the ten years that followed.

Several samples of coke-oven light oil were examined, with the results given in Table I. (Coke-oven data have been used in considering the case of coal gas, because the writers are more familiar with data from that source.)

TABLE I—LIGHT OIL ANALYSES

		Distillation			Fraction 175° to 190° C.			
					Volume	Unsaturation		
Sample	Material	First drop ° C.	At 100° C. Per cent	At 200° C. Per cent	Per cent total light oil	Per cent	Per cent total light oil	Melting point oxybromide ° C.
1	Crude benzene	72	55	80	3	60	1.8	130.5 to 131
2	Primary light oil	75	78	94	2.5	70	1.75	130 to 131
3	Secondary light oil	90	2.5	25	7[a]	60	18.0	129 to 130
4	Commercial secondary solvent naphtha	100	5 (140° C.) 10 (150° C.) 92 (190° C.)	..	30	90	..	130 to 131

[a] 30 per cent of light oil up to 200° C.

It can therefore be definitely asserted that indene is a proved constituent of present-day coke-oven gas. On the basis of Sample 1, in which indene constitutes at least 2.25 per cent of that portion boiling below 210° C. (1.8 per cent being in the fraction boiling between 175° and 190° C. and 0.45 per cent in the fractions collected below 175° and above 190° C.), calculation shows the possible error due to the presence of indene in a naphthalene determination by the picric acid method to be 34 grains per 100 cubic feet.

One ton of coking coal yields 10,000 cubic feet of gas, which contains on the average 3 gallons of light oil[4] and its content may be taken at 0.3 gallon per 1000 cubic feet. Taking its approximate specific gravity at 0.880, the light oil content is therefore (8.33 pounds × 0.88 × 7000 × 0.3) 15,390 grains per 1000 cubic feet, or 1540 grains per 100 cubic feet. Since the indene content alone is 2.25 per cent of the total light oil, it follows that there are 34+ grains of indene per 100 cubic feet, which may give picrates when the gas is passed through a picric acid solution.

Since gas at 20° C. and saturated with naphthalene[5] carries approximately 15 grains per 100 cubic feet, the potential error due to indene is enormous. In those light-oil fractions boiling from 160° to 174° C., a large part of this bromine-absorbing material was found to be indene. The chemical literature lists coumarone as the only other unsaturated compound to be expected in appreciable quantities in solvent naphtha boiling between 160° and 190° C. As previously stated, coumarone gives a picrate under favorable conditions. In fact, the picrate-forming content of the total light oil, exclusive of naphthalene, totals 3.0 per cent. This is equivalent to about 45 grains per 100 cubic feet of possible picrate-forming material.

The correctness of this figure is attested by the fact that the sum of the indene and coumarone present in solvent naphthas, as determined by complete polymerization by the acid method, averages 35 to 40 per cent. A typical example from dozens of such determinations is as follows:

First drop, 149° C.; 5 per cent up to 165° C.; 40 per cent at 175° C.; 90 per cent at 187° C.; 97.5 per cent at 200° C. Resin content, 39 per cent.

The composition of light oil has been variously reported in the literature.[6] An average and approximate composition of coke-oven light oil, exclusive of naphthalene and wash oil, may be considered as benzene, 65 per cent; toluene, 14 per cent; xylenes and other hydrocarbons boiling up to 150°, 8 per cent; secondary solvent naphtha boiling between 150° and 200° C., 8 per cent; forerunnings and residuals, 5 per cent. On the basis of 8 per cent for the secondary solvent and an approximate figure of 39.0 per cent for the picrate-forming constituents of that fraction, the total content of indene and coumarone in coke-oven light oil is thus seen to be approximately 3 per cent.

INDENE PICRATE FROM COAL GAS

The degree to which this potential source of error is real has been fixed. In the laboratory the average of many tests showed that from 45 to 50 per cent of the indene carried by nitrogen at 20° C. was removed as picrate by a saturated picric acid solution.

As a test on actual coke-oven gas, exactly 85 cubic feet of coke-oven gas, taken after the final cooler and before the light-oil scrubbers, were passed at an average rate of 1.2 cubic feet per hour through a train of three bottles containing saturated picric acid solution. The resulting picrates were decomposed with alkali, and the hydrocarbons thereby released were titrated for unsaturation. This unsaturation, calculated as indene, amounted to 0.82+ gram or 12.7 grains per 100 cubic feet of gas. From the material titrated, the oxybromide of indene was recovered and its identity established in the manner previously described.

Similar tests on the picrates obtained from the gas from several separate plants gave strictly analogous results. It was thus found that indene existed as a contaminating picrate in naphthalene-in-gas determinations, and apparently to a serious extent. The extent of the contamination was studied in a number of plants by the aid of methods described in the appendix to this paper. The results are given in Table II.

TABLE II—PICRATE ANALYSES—COAL GAS

				Indene		
Plant	Source of Oil	Sample	Total picrates $C_{10}H_8$ Grains	Grains	$C_{10}H_8$ equivalents Grains	Per cent of total picrates
A	Coke oven	1[a]	4.62	1.40	1.55	34
		2	1.64	0.58	0.64	39
		3	2.23	0.82	0.90	40
		4	1.91	0.75	0.83	43
B	Coke oven	1	30.00	12.7	14.0	47
C[b]	Vertical retort	1	7.18	2.33	2.57	36
		2	3.48	1.06	1.17	34
D	Horizontal	1	3.09	0.96	1.05	34
		2	3.69	1.26	1.39	38
E	Vertical	1	3.00	0.92	1.0	34
		2	6.31	1.85	2.0	32
F_1	Coke oven	1	5.96	1.37	1.51	25
		2	6.58	1.23	1.35	20
		3	3.12	0.68	0.75	24
F_2	Coke oven	1	5.89	1.27	1.4	24
		2	4.12	1.03	1.13	27+
G	Coke oven	1	5.53	1.57	1.73	31
		2	3.63	1.09	1.20	33
H	Lean coke oven	1	3.85	0.79−	0.87−	22.6
	Estimated average accuracy		0.01	±0.03	0.04	Within 2 to 5

[a] This sample was not dried as were the other three.

[b] Plants C and E are the same, samples were secured 1 month apart.

INDENE IN CARBURETED WATER GAS

In 1893 Dennstedt and Ahrens[7] reported the presence of traces of indene in condensate from the illuminating gas of Hamburg. The presence of indene in considerable quantities in the natural condensate of carbureted water gas in the United States was pointed out by Brown in 1922.[8] An examination of eight samples of natural condensate collected during that year from six different plants has given the results in Table III.

TABLE III—INDENE AND NAPHTHALENE IN CARBURETED WATER-GAS CONDENSATE

			Indene Isolated	
Sample	Size of sample Cc.	Naphthalene Per cent	As indene Per cent	As resin Per cent
86	2000	7.6	20.1	6.3
118	2000	1.5	15.9	8.0
121	2500	7.0	7.5	14.8
99	850	50.0	16.4	4.0
100	1500	30.0	25.4	2.3
102	1000	30.0	25.3	..
104	1500	13.0	11.2	6.5
105	1000	8.0	28.5	4.8

The presence of this amount of indene in the natural condensate indicates a relatively high partial pressure of indene. The vapor pressure of indene being about ten times that of naphthalene between 20° to 30° C., it follows that in the gas in the outer parts of the distributing systems the indene must be relatively much greater in amount than the naphthalene. Therefore the possibility of error in naphthalene determinations at holder or distributing stations is large. This is demonstrated by the fact that when natural gas containing drip-oil vapor was passed through a picric acid solution, picrates containing a considerable amount of indene picrate were obtained. This test was applied to three samples of drip oil, each of which was taken from a different system in various parts of the United States. All were strongly positive.

Indene is, of course, present in carbureted water gas at the plant,[9] and therefore constitutes a continued potential source of error there, where the majority of naphthalene tests, both qualitative and quantitative, are made. Qualitative tests in ten carbureted water-gas plants indicated this potential error to be an actual one, and quantitative measurements showed the error to be considerable. The extent of this error and the composition of the picrates obtained from carbureted water gas from six other plants are given in Table IV.

TABLE IV—PICRATE ANALYSES—CARBURETED WATER GAS

Plant	Sample	Total picrates Grains	INDENE		Per cent of total picrates	REMARKS
			Grains	As $C_{10}H_8$ grains		
A	1	5.74	1.30	1.43	25	
	2	5.44	1.27	1.40	26	
	3	5.58	1.22	1.47	26	
	4	4.18	0.96	1.06	25	
B	1	3.70	0.82	0.90	24	
C	1	9.56	4.24	4.66	49	
	2	10.63	4.34	4.78	45	
	3	6.46	2.60	2.86	44	
D	1	3.74	1.06	1.17	31	
	2	2.62	0.89	0.98	37	
E	1	3.04	1.47	1.62	54	Same plant as *C*
	2	8.12	3.9	4.3	53	Samples secured 1 month later
F	1	4.65	2.12	2.33	50	Same plant as *D*
	2	7.40	4.04	4.4	60	Samples secured separately; sample dirty; indene figures in 2 and 3 believed to be high
	3	5.83	3.18	3.50	60	
G	1	2.98	1.13	1.24	42−	
	2	5.34	2.12	2.33	44−	

After titration with bromine each of the samples mentioned in Tables II and IV was steam-distilled and the residue treated for the recovery of the bromohydroxyindan[10] produced from the indene originally present. It was present in every case. The combined crystals obtained from all coal-gas samples after being washed with alcohol melted at 129.8° C., and that from carbureted water gas melted at 129.4° C. These two materials, mixed with an equal part of 2-bromo-3-hydroxyindan, melting point 130.5° C., melted at 130.4° and 130.1° C., respectively.

It is therefore definite that the picric acid method for the determination of naphthalene in either coal or carbureted water gas is unreliable. It is equally apparent that many methods based on picrate formation for the determination of coal gas and carbureted water-gas by-products, such as oils, tars, etc., must be quite inaccurate.

SIGNIFICANCE OF ACCURACY IN THE DETERMINATION OF NAPHTHALENE

The determination of naphthalene in industrial gases is of considerable commercial significance. The deposition of solid naphthalene in pipes in distributing systems, which results in stoppages, entails economic loss and annoyance to both producer and consumer.

COAL GAS—The preceding statements hold whether the gas is distributed directly or is a by-product coke-oven gas sold to a distributing company. In the latter case, where the transfer may involve many million cubic feet daily, and where the naphthalene content must conform to limits specified by contract, its determination is essential. This is particularly true where penalties for overrunning the specified maximum are involved. It is therefore conceivable that indene picrate, being mistaken for naphthalene picrate, may cause the payment of indemnities or penalties, or the running of a naphthalene scrubbing system without sufficient grounds. In view of the evidence presented in this paper, reported tests on naphthalene scrubbing plants,[1,8] as well as all investigations involving measurements of naphthalene in coal gas and carbureted water gas in which the formation of picrates has been used as a basis of determination, must be subjected to re-interpretation, and certainly in proportion to the degree to which they are based on quantitative measurement.

CARBURETED WATER GAS—Carbureted water gas is composed by volume of about 80 per cent water gas and 20 per cent oil gas. To its heating value the water gas contributes about 230 B. t. u. of the normal 530 to 565 B. t. u. per cubic foot of finished gas, and the remaining 300 to 335 B. t. u. are supplied by the oil gas. It is the aim of the operator, therefore, to secure the maximum cracking efficiency—that is, to produce the maximum heating value per cubic foot of finished gas per gallon of oil used—in the carbureting units of carbureted water-gas plants. In the practical attainment of this aim, the chief factor considered is that of temperature, although contact and time are directly involved. It has been well established[11] and widely recognized that, other conditions being constant, cracking efficiency in a given installation increases with rise of operating temperature and reaches a maximum at a temperature 100° to 200° F. above the usual temperature (1350° to 1400° F.) employed today. The degree of cracking efficiency attainable in practice is limited by the necessity of keeping the production of naphthalene low enough to escape stoppages in the distributing system, and to escape carbon deposits in the machines such as would seriously interfere with the production of gas. Consequently in the control of the cracking process and its temperature, it has been considered desirable to follow the production of naphthalene.

In the past, the precipitation of picrates has been considered an indication of naphthalene in the gas, and the amount, a measurement. In view of the evidence in this paper the picrate method in that usage has been untruthful and misleading. In fact, instead of indicating excessive heats, as heretofore supposed, picrates, by reason of their high indene picrate content, are equally indicative of the presence of products of incomplete cracking in the gas. According to Egloff and Towmey,[12] when oils are cracked at 1300° F. or above, the condensable cracked oils are aromatic and contain no aliphatic hydrocarbons, and naphthalene production begins at 1380° F. The work just cited, as well as that of others,[13] has shown that under cracking conditions the order of thermal stability in the aromatic series is as follows: Higher homologs, xylene, toluene, benzene, naphthalene, anthracene, carbon plus hydrogen. Theoretical reasons previously developed and experimental evidence presented by the writer in an earlier paper[14] show that indene must be placed in this sequence as a higher homolog of benzene. Its presence in excessive quantities in the gas and in picrates therefrom is indicative, therefore, either of low cracking temperatures or of cracking that is incomplete or not uniform, which cannot be for *a priori* reasons, and is not the most efficient. It follows that, to the extent that the picrate test and its supposed determination of naphthalene have caused the lowering of cracking temperatures below that which (with the other factors involved) would give the maximum cracking results or efficiency, just to that extent has the picrate test been an expensive one to the industry. This is true for two reasons. First, the lessened cracking efficiency requires a proportionally greater oil input.

For 1 per cent loss in cracking efficiency an increase in oil input of 1 per cent must be made if the heating value of the gas is to be maintained. On the basis of 3 gallons of oil per 1000 cubic feet of gas produced, for each cent in price of the oil used, the cost is about 0.03 cent for each per cent decrease in cracking efficiency. Differences of 10 units in cracking efficiencies in quite similar plants are often encountered, while 5-point differences are everyday affairs. With gas oil at 4 cents a gallon, a 5-point drop in cracking efficiency entails a cost increase of about 0.6 cent per 1000 cubic feet. For a plant with a daily output of only 5,000,000 cubic feet, this means $10,940 a year.

Second, poor cracking ultimately gives rise to gummy deposits in meters, unless offset through compression and cooling, exceptional condensation, mixture with coal gas, or other means. The relationships between oil cracking, light-oil composition, and gummy deposits in meters have been presented in other papers.[14] The production of gummy deposits and the troubles they entail are decidedly costly.[15] The facts presented in this paper offer an entirely logical explanation for the fact that naphthalene determinations on gases often give values approximating or greater than the theoretical ones for naphthalene in a dry gas.[16] Such values are greater than can exist for a gas that is in contact and in approximate equilibrium with gas condensate (drip oil) in which naphthalene is so extremely soluble. It is unfortunate that, although the general picrate-forming properties of indene and its presence in coal gas have been known for thirty years, the picrate method for naphthalene has been adopted by the gas industry, and adapted by many experimenters up to the present time without sufficient question as to whether its basic reaction was specific.

ACKNOWLEDGMENTS

The writers are indebted for samples and valuable coöperation to the following officials of corporations of the gas and fuel industry:

J. A. GONDER, chief chemist, Chicago By-Product Coke Co., Chicago, Ill.
B. L. PEABLES, chemist, Haverhill Gas Light Co., Haverhill, Mass.
T. A. MIGHILL, research chemist, Stone & Webster, Inc., Pawtucket, R. I.
E. F. POHLMANN, chemist, People's Gas Light & Coke Co., Chicago, Ill.
E. H. EARNSHAW, assistant general manager, Public Service Gas Co., Newark, N. J.
J. F. WING, Boston Consolidated Gas Co., Boston, Mass.
A. A. KOHR, chief chemist, Seaboard By-Product Coke Corp., Jersey City, N. J.
R. W. CAMPBELL, chief chemist, coke plant, Jones & Laughlin Steel Corp., Pittsburgh, Pa.
W. A. WAGNER, chemist, coke plant, Jones & Laughlin Steel Corp., Pittsburgh, Pa.
H. M. WAXMAN, chief chemist, coke department, Wheeling Steel Corp., Wheeling, W. Va.
CALEB DAVIES, superintendent, Republic Iron & Steel Co., Youngstown, Ohio.
B. M. LIVEZEY, chief chemist, coke plant, Carnegie Steel Co., Clairton, Pa.

APPENDIX ON METHODS

BASIS OF THE METHOD

In the following description of the technic employed in the examination of mixtures of indene and naphthalene picrates, enough typical experimental data bearing on the basic steps of the method are given to indicate its accuracy and limitations. The method is not presented as a best or as a practical method, but rather as one which was considered sufficiently accurate to achieve the purpose of the writers. Since the object of the analyses was to determine the relative proportions of indene and naphthalene picrates constituting the mixture, efforts were directed towards obtaining a method for the quantitative estimation of small amounts of indene. With that and the easily and accurately obtainable value for the picric acid of the total picrate mixture the amount of naphthalene could be calculated. Following preliminary experiments on end points and other details in titrations of indene with a standard bromine solution, the accuracy and applicability of the method were tested through the various steps involved. The results are illustrated by the following representative data:

I—TITRATION OF INDENE

(A) *Sample*

Measured by volume and calculated Grams	Measured by volume and calculated Grains	Found Grains
0.10	1.54	1.50
0.20	3.08	3.15
0.40	6.16	5.95

(B) *Constancy of titration of samples of a standard solution*

	Cc. of bromine solution								Average
Solution I	0.86	0.86	0.85	0.85	0.86	0.85	0.86		0.856
Solution II[a]	0.86	0.87	0.88	0.89	0.88	0.87	0.88	0.87	0.875

[a] The last four titrations were made by a second operator.

II—RECOVERY AND TITRATION OF INDENE

(A) *From its picrate*

Indene introduced Grains	Volume picric acid solution used Cc.	Picrate formed Grains	Indene in picrate as determined Grains	Difference Grains
1.5	200	1.42	1.45	+0.03
3.0	200	2.86	2.55	−0.31
3.0	400	2.29	2.30	...
6.0	500	4.58	4.50	−0.08

(B) *From a mixture of indene and naphthalene picrates*

Indene introduced Grains	Volume picric acid solution used Cc.	Picrate formed Grains	Indene in filtrate as determined Grains	Total accounted for Grains
3.0	400	2.55	0.35	2.90
3.0	400	2.50	0.60	3.10
3.0	400	2.50	0.50	3.00

The picrates in the samples used under II were prepared by vigorously shaking the indicated volume of nearly saturated picric acid solution with the requisite amount of indene to give the weights indicated. Since the extremely small volumes of indene were measured as such, and in view of the agreement under I-*B*, the procedures were judged to be sufficiently accurate for the purpose of the paper.

PROCEDURE

The picrates, obtained at the various plants by the passage of the gas through bottles containing a saturated solution of picric acid,[18] were separated by filtration, pressed as dry as possible on filter paper, and divided into samples for analysis. Each sample was dissolved in 15 cc. of C. P. benzene in a glass-stoppered flask. About 5 cc. of water were added, and the picric acid in the solution was titrated with 0.1 *N* sodium hydroxide, sodium alizarin sulfonate being used as the indicator. The end point was approached slowly, much shaking being necessary near the close to complete the titration.

The benzene, which contained the indene and naphthalene set free, was carefully separated and poured into a 1-ounce "French square," glass-stoppered bottle. A second extraction with 10 cc. of benzene was made and the solution added to the first portion, the whole being dried with a few granules of calcium chloride. The benzene used for this purpose showed a sulfuric acid color test of less than 1 and no immediate absorption of bromine. The determination of the indene was based on the fact that 1 molecule of indene adds 1 molecule of bromine at room temperatures, and the titrations were made with a solution containing bromine (0.3 gram per cc.) dissolved in carbon tetrachloride. Since very small volumes were involved, a buret constructed from a Haldane gas pipet and graduated to 0.01 cc. was used. It yielded drops 0.01 cc. in volume. The bromine solution was added a few drops at a time until a definite bromine color began to persist. In fixing the end point use was made of certain of the color standards used in the sulfuric acid color test for benzene.[18] The end point was considered reached when first the solution being titrated, having been brought to a color equivalent of No. 8 of the standards, had not faded in color below that of standard No. 6 at the close of 3 minutes. Additions of 0.02 and 0.03 cc. were involved at the end. A determined blank of 0.03 cc. was subtracted from the observed volume of solution used, this representing the solution necessary to produce a color equal to standard No. 6 in the 25 cc., used in the extraction and titration. From the bromine added in the titration the indene present was calculated in grams, then in grains, and converted into naphthalene equivalents in grains, as expressed in the tables. For good results, samples of picrates free from tarry matter, C. P. reagents, and thoroughly experienced technic were found essential.

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Effect of Ammonium Chloride upon the Growth of Yeast and the Hydration of Gluten in Beer Wort[1]

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IT HAS been shown[2] that in a synthetic medium the concentration of ammonium chloride optimum for the growth of yeast is identical with the concentration of the salt in which a protein, wheat gluten, is least swollen. The experiments here described were undertaken to determine whether this relationship applies to a complex medium containing various sources of nitrogen.

TABLE I

Normality of NH_4Cl	30° C. synthetic medium "count" (48 hrs.)	Wort		42° C. synthetic medium "count" (20 hrs.)	Wort	
		Count (22 hrs.)	Gluten (3.5 hrs.)		Count	Gluten (3.5 hrs.)
0.00	53	230	58	18	29	65
0.0118	194	270	62	35	63	..
0.0236	256	352[a]	76[a]	47	94	89
0.0294	295	232	71	..	157[a]	93[a]
0.0341	356	..	..	..	..	..
0.0353	389[a]	242	60	63	83	74
0.0365	270	..	..	..	..	..
0.0382	220	..	..	77	..	..
0.0412	213	..	..	99	86	..
0.0418	..	..	..	139	..	..
0.0424	..	..	..	156[a]	..	..
0.0430	..	..	..	145	..	..
0.0435	..	..	..	139	..	..
0.0470	190	245	74	123	83	..
0.0588	173	244	88	98	84	64
0.0700	..	..	..	..	77	..
0.0820	..	246	100	..	72	78
0.0940	..	251	..	..	81	..
0.106	..	281[a]	102[a]	..	..	..
0.118	..	235	..	..	..	91
0.129	..	233	82	..	142[a]	108[a]
0.140	..	..	..	..	111	..
0.153	..	..	..	..	84	95

[a] Indicates maximum effect.
"Count" refers to yeast crop.
"Gluten" expresses grams loss in weight per 1000 grams of gluten.

Beer wort was prepared by mashing at 55° C. 360 grams of malt with 1150 cc. of distilled water. The mash was filtered through toweling, then through filter paper, and heated for 30 minutes under 15 pounds pressure in an autoclave. After standing for 3 days to permit coagulated matters to settle, the liquid was filtered and was ready for use after sterilization in live steam.

The yeast used (*Saccharomycea cerevisiae*) had been growing continuously in a synthetic medium for 4 years. The methods of estimation of yeast crop and of the hydration of gluten as affected by varying concentrations of ammonium chloride are as described in the previous communication.[2] Typical results are given in Table I.

CONCLUSIONS

1—Less ammonium chloride is required for the maximum growth of yeast and minimum hydration of gluten in wort than in a synthetic medium, showing that there is present in wort something which plays a similar role to that of ammonium ion. This conclusion is strengthened by the fact that there is greater relative effect at higher temperatures.

2—Extracts containing bios or ammonium chloride are mutually beneficial in a medium. The main role of bios in yeast growth cannot be the same as that of ammonium chloride—i. e., the maintenance of the proper state of hydration of protein.

3—Systems of wort and ammonium chloride producing greatest yeast growth are identical with those in which wheat gluten is the least swollen. This is true of both maxima at the temperatures tested. The generalization seems to be indicated that if the addition of ammonium salt to a medium increases its ability to dehydrate gluten, the addition will likewise improve the medium for the growth of yeast, the effect being maximum in any combination in which the gluten is least swollen.

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[1] Received December 22, 1923.

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Influence of Accelerators on Plasticity of Uncured Rubber Stocks[1]

By Stanley Krall

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The tendency of raw rubber stocks to set-up or scorch during processing has been determined in the laboratory by means of plasticity measurements. Data are given for some well-known organic accelerators.

At a temperature of 90° C., thiocarbanilide and aldehyde ammonia are the only ones of those tested that produce appreciable set-up, when the amounts used are within the range generally employed; quick curing stocks containing a high concentration of accelerator are not included.

The influence of the concentration of accelerator varies with the accelerator. The concentration of diphenylguanidine has appreciable influence, while that of thiocarbanilide or the condensation product of aniline with acetaldehyde and formaldehyde has only a slight effect.

The effect of the concentration of sulfur is small indicating that the concentration of sulfur is much less important in connection with the factory workability of stocks than either the kind or concentration of accelerator.

Zinc oxide decreases the influence of aldehyde ammonia in producing premature vulcanization; it increases that of diphenylguanidine slightly and of thiocarbanilide tremendously.

Lime and calcined magnesia in the presence of zinc oxide increase the setting-up tendency of stocks containing aldehyde ammonia and diphenylguanidine. In some cases the actions appear to be simply additive, in others, more than additive.

This method is not adapted to the study of most superaccelerators, because when they begin to set-up, the action is too rapid to permit determining the rate of change.

Sulfur, even up to 12 per cent on the rubber, does not act as a softener of raw rubber, at least so far as can be determined by this method.

In the commercial application of organic accelerators, the workability of the raw rubber stocks containing them is of major importance. The stocks must be plastic, but not too soft and sticky or they will adhere to the liners and books in which they are stored. On the other hand, if they are not soft enough, they will require a higher temperature to make them run with smooth surfaces during processing, and at the same time, as a result of their stiffness, the temperatures developed may be sufficiently high to set-up or scorch them owing to premature vulcanization.

The majority of organic accelerators have a softening action on raw rubber, but in the presence of sulfur this softening action may be entirely masked by the tendency of the accelerator to bring about premature vulcanization during milling, calendering, etc., when temperatures of 80° to 100° C. are attained. If the temperature is kept low enough during mixing, the softening action of the accelerator will predominate, even in the presence of sulfur. For example, when the compound (rubber 100, zinc oxide 3, sulfur 4) containing 0.75 per cent of diphenylguanidine, or even 1.25 per cent of aldehyde ammonia, was mixed at a sufficiently low temperature (55° C.), plasticity values, K,[2] of 2.02 and 1.92, respectively, were obtained while the same stock in the absence of any accelerator had a value of 2.27.

To be able to predict, in the laboratory, the behavior of an accelerated stock in the factory is of considerable importance and in the past has been a thing of considerable difficulty. An instance of this is the situation which arose at the time thiocarbanilide was introduced in the rubber industry, when enormous quantities of "thio" stocks were ruined by scorching.

Premature vulcanization, scorching or setting-up produces changes in raw stocks that are thought of in physical rather than chemical terms. Without doubt, premature vulcanization is accompanied by a chemical combination of rubber and sulfur, but the extent of the reaction is so small that the determination of combined sulfur is impractical. The change in the physical properties of the raw stocks, however, is sufficiently marked to be measurable.

Several investigators have published methods for measuring this physical change in raw stocks. Cadwell and Smith[3] heated films of the raw stocks in an atmosphere of carbon dioxide at a fixed temperature and then determined the stiffness of the films, at stated intervals of time, by a hand examination. The method suffices for qualitative comparisons only. Marzetti[4] devised a plastometer for this purpose. Essentially the method consists in placing the sample in a cylinder, with a conical bottom provided with an outlet at its apex, and forcing the sample through the orifice, at a stated temperature, by means of a compressed gas. The stock extruded after successive periods of time is measured, and the decrease in amount extruded during the successive intervals is taken as a measure of the rate of premature vulcanization at that temperature. Owing to the time required to bring the relatively large volume of rubber to the temperature of the bath, Marzetti recommends that the portion extruded during the first half hour be ignored. Of these two methods the latter appears the more promising, but the type of plastometer used is such that the method is long and laborious.

The plastometer designed by Williams[2] permits of a much simpler procedure. The sample used is small, the time required for a single determination is only 25 to 30 minutes, and the manipulation is very simple. In the work recorded herein this plastometer has been employed in studying the influence of both organic accelerators and compounding ingredients on the premature vulcanization of raw stocks.

Procedure

A pellet of 2-cc. volume is placed in the press at a fixed temperature, and readings are taken at stated intervals, preferably 5-minute intervals, up to 30 minutes. These readings follow the true plasticity curve ($K = YX^{0.196}$) until setting-up begins. When this occurs, the curve deviates from the normal and quickly approaches a parallel to the time axis. The true plasticity value, K, from the first portion of the curve, being known, the deviation or increase in K may be expressed as percentage increase at any time interval. The percentage increase in K is plotted against the time of heating to obtain a setting-up curve for the stock. The true

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[1] Presented under the title "The Influence of Organic Accelerators on the Plasticity of Uncured Rubber Stocks" before the Division of Rubber Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

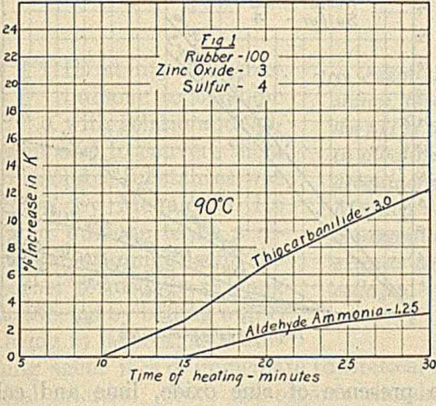
[2] This Journal, 16, 362 (1924).

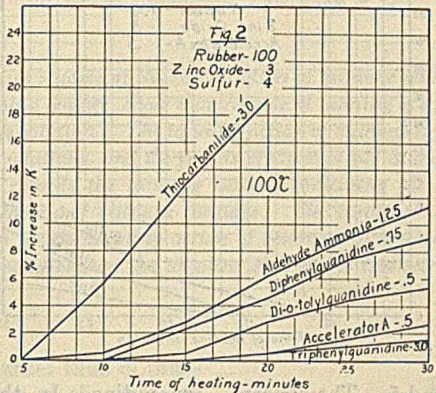
[3] *India Rubber World*, 68, 782 (1923).

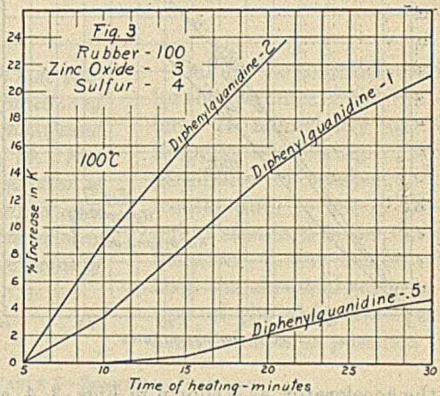
[4] *Ibid.*, 68, 776 (1923).

plasticity value is attained after 5 to 10 minutes of heating, but in instances where the stock starts to set-up almost immediately upon placing in the press, the 5-minute plasticity value is taken as the normal value, although in such cases it may be slightly high.

other hand, when information concerning the tendency for premature vulcanization only is desired, it is necessary to maintain only approximately the same conditions, as in this case small variations in the absolute plasticity have no apparent effect.

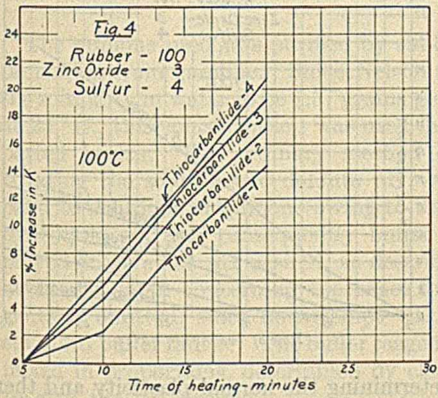


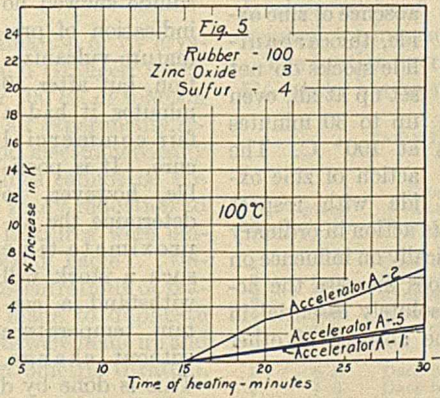


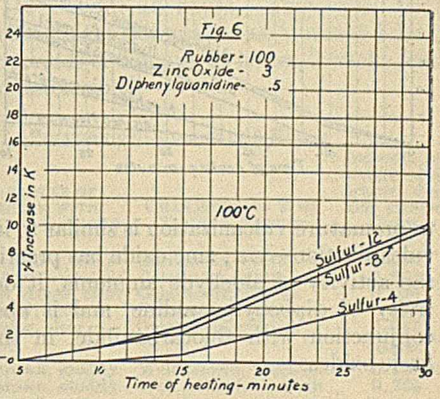


This method measures change in plasticity, and therefore cannot be employed after the plasticity curve becomes flat or parallel to the time axis. The test should be completed within 30 minutes, as the actual decrease in thickness after that time is generally so small that the experimental error becomes too large for satisfactory results. This is especially true when the stock shows appreciable tendency to set-up, but is also the case when the sample does not begin to set-up within 30 minutes. It is not advisable to rely on a single reading after the stock begins to set-up, as the experimental error is sufficiently large to give erroneous conclusions. The curves approach straight lines, but they are invariably somewhat irregular, as is apparent from the curves in this paper.

Aside from information on the premature vulcanization occurring at the temperatures developed during factory processing, a knowledge of the plasticity changes which take place at ordinary or slightly elevated temperatures is also quite essential. For such work, the original plasticity value, K, is determined and then a portion of the stock is heated, in the absence of air and preferably in a mold, at the desired temperature for any suitable period of time. The plasticity of the treated sample is determined and the increase in K is expressed in percentage.







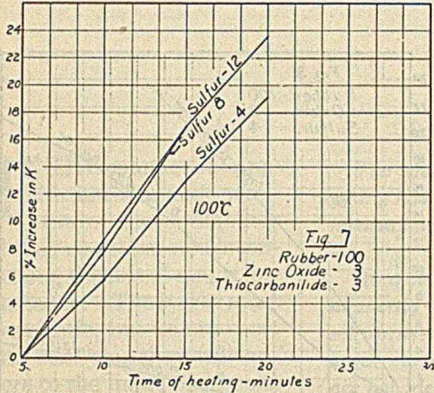
When a comparison of the absolute plasticity of stocks is required, it is essential that all mixes compared be given uniform treatment during the milling operation. The conditions to be maintained identical are size of batch, distance between rolls, temperature of rolls, and time of milling. Obviously, the stocks compared must be run on the same mill or on mills of the same size, speed, and gear ratio. On the

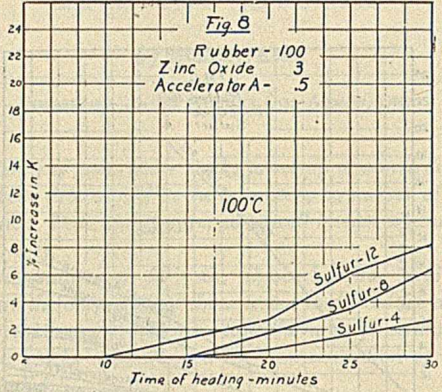
The concentration of accelerator is an important factor; hence equivalent quantities should be used in all comparisons. Almost without exception, the quantity of accelerator employed in the present work was the amount necessary to produce the maximum modulus or stiffness when the stock was cured for 60 to 75 minutes at 143.3° C. (290° F.). The base formula used was as follows:

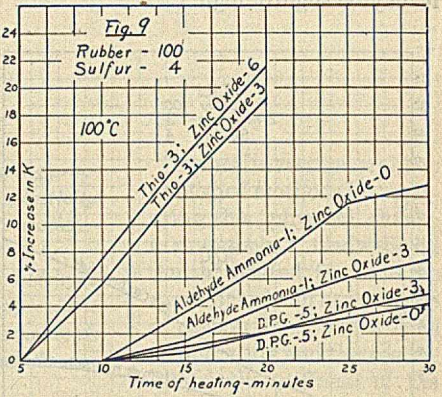
Smoked sheets	100
Zinc oxide	3
Sulfur	4

DATA

The setting-up curves for some well-known accelerators are shown in Figs. 1 and 2. Over a period of 30 minutes at 80° C., there is no setting-up of this type of stock with any of these accelerators. Some of these accelerators, however, will cause premature vulcanization at this temperature if heated for a longer period of time, but the rate of setting-up is insufficient to be serious from a factory handling standpoint, provided time is allowed for the proper cooling of the stocks prior to storage. At 90° C. the thiocarbanilide stock sets up appreciably, the aldehyde ammonia stock only slightly, and the remaining stocks not at all. At 100° C. the influence of the accelerators is in the following order, the one with the greatest effect heading the list, and the last three showing no effect: thiocarbanilide, aldehyde-ammonia, diphenylguanidine, di-*o*-tolylguanidine, accelerator A (condensation product of aniline with acetaldehyde and formaldehyde, melting point 73° C.), triphenylguanidine, hexamethylenetetramine, ethylidine aniline (condensation product of aniline with acetaldehyde, melting point 78° C.), and *p*-nitrosodimethylaniline.







The effect of the concentration of accelerator varies with the accelerator, as is shown in Figs. 3, 4, and 5. The concentration of diphenylguanidine has an appreciable influence, while that of thiocarbanilide and accelerator A has only a slight effect.

The influence of the concentration of sulfur on premature vulcanization is shown by the curves in Figs. 6, 7, and 8. The mass action effect is noted when the concentration of sulfur is increased. The increase in rate of setting-up, however, is nominal, indicating that the concentration of sulfur is much less important, in connection with the factory workability of stocks, then either the kind or concentration of accelerator.

The influence of zinc oxide on the action of several accelerators is demonstrated by the curves in Fig. 9. The addition of zinc oxide *decreases* the influence of aldehyde ammonia in producing premature vulcanization, *increases slightly* the influence of diphenylguanidine, and *increases tremendously* the influence of thiocarbanilide. In the absence of zinc oxide, thiocarbanilide stocks do not set up at all, even up to 30 minutes at 100° C. The action of zinc oxide with respect to premature vulcanization is similar to its action in ordinary vulcanization—viz., zinc oxide has practically on influence on the activity of aldehyde ammonia, it does increase the activity of diphenylguanidine, and is absolutely essential in conjunction with thiocarbanilide, in the absence of other basic oxides.

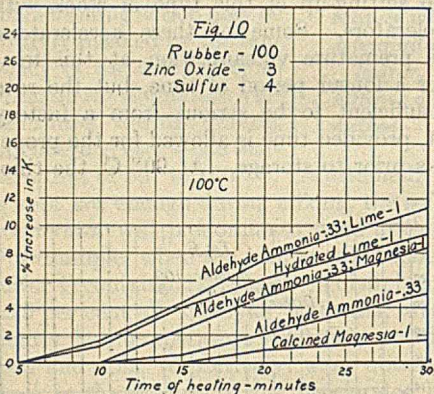


TABLE I—INFLUENCE OF THIURAM DISULFIDE ACCELERATORS ON SCORCHING AT 100° C.

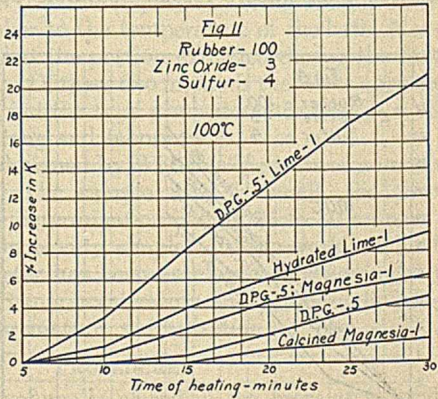
	NORMAL		AFTER 16 HOURS AT 60° C.	
Minutes in press	Thickness Mm.	*K*	Thickness Mm.	*K*
5	1.28	1.75	..	..
10	1.07	1.67	1.06	1.66
15	0.97	..	..	..
20	0.915	1.65	..	..
25	0.87	1.64	..	..
30	0.845	1.64	..	..
35	0.82	1.64	..	..
40	0.80	1.65	..	..
50	0.80	..	..	..

In Figs. 10 and 11 are plotted data showing the effect of hydrated lime and calcined magnesia on the setting-up properties of stocks containing aldehyde ammonia and diphenylguanidine. In the presence of zinc oxide, lime and calcined magnesia increase the setting-up tendency of stocks containing the above-mentioned accelerators. Lime alone causes premature vulcanization to an appreciable extent, while the effect of calcined magnesia is only slight. In some cases the actions appear to be additive, in others more than additive.

TABLE II—EFFECT OF SULFUR ON THE PLASTICITY OF RAW RUBBER FORMULAS

Rubber	100	100	100	100
Sulfur	..	4	8	12
Minutes in press	Thickness readings (mm.) at 80° C.			
10	1.48	1.47	1.50	1.46
15	1.34	1.35	1.37	1.34
	Plasticity value, *K*, at 80° C.			
10	2.32	2.31	2.33	2.30
15	2.28	2.29	2.33	2.28
Average	2.30	2.30	2.33	2.29

When a stock containing the thiuram disulfide class of super accelerators starts to scorch, the action is so rapid that this method cannot be employed for following the rate of change. This is clearly demonstrated by the data obtained at 100° C. (Table I); at the end of 40 minutes the base stock containing 0.1 per cent tetramethylthiuram disulfide showed no indication of premature vulcanization, but after 50 minutes it had a fair commercial cure. It is possible, however, to determine the approximate time such a stock will withstand a certain temperature without change. This is done by determining the normal plasticity and then heating a portion of the sample at the desired temperature and again determining the plasticity at stated intervals of time. The data presented indicate that this type of stock can be heated without change for approximately 40 minutes at 100° C. and for more than 16 hours at 60° C.



Many rubber technologists are of the opinion that sulfur has a softening action on raw rubber. Data are given in Table II indicating that sulfur, even up to 12 per cent on the rubber, does not act as a softener for raw rubber, at least so far as can be determined by this method.

Quinone Tannage[1,2]

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Quantitative studies of the combination of quinone with hide substance, forming leather, show that the rate of tanning is a function of the pH of the solution. The tanning action of quinone is manifested in alkaline solutions, and the rate is greatest at pH 8 and 10. Hydroquinone retards the tanning action, indicating the validity of Meunier's theory of quinone tannage. The results obtained offer a suggestion for the tanning action of commercial vegetable tanning extracts in solutions on the alkaline side of the isoelectric point of collagen.

The ability of benzoquinone to combine with gelatin and collagen and to convert them to insoluble substances was shown by Meunier.[3] He found quinone to be a remarkable tanning agent, the leather formed by it being unaffected by boiling water. Owing to its cost, as a tanning agent it is of immediate theoretical rather than of practical interest. Since the organic chemistry of the complex commercial vegetable tannins is only in its initial stages, it seems that the study of any simple organic substance having tanning properties should help elucidate the chemistry of the action of the very complex natural tannins.

Meunier's experiments were qualitative only. No quantitative studies have been previously undertaken, possibly because a satisfactory method was unavailable. Quinone tannage is not amenable to the "by difference" technic as ordinarily used to estimate the amount of tannin combined with skin substance. The reason is that quinone is about as volatile as water. Moreover, titration of quinone in the residual liquors fails, owing to the dark-colored products formed in alkaline solutions. The new Wilson and Kern method[4] of determining tannin fixed has solved this problem. The writers have found that the fixation of quinone by collagen can be followed by this method.

Since it has been demonstrated that the rate of fixation of vegetable tannins by collagen varies enormously with the hydrogen-ion concentration of the solution,[5] the fixation of quinone as a function of the pH value of its solution was investigated first.

Effect of pH

The quinone used was purified by sublimation or by crystallization from gasoline. Since Nelson and Granger[6] found the solubility in water to be 1.37 grams per 100 cc. of solution at 25° C., this concentration was used in all experiments reported herein. The ordinary method of electrometrically titrating the solutions to definite pH values cannot be applied to solutions of quinone owing to its ready reduction to hydroquinone, and consequently buffer mixtures were employed to give the pH desired, as described in Table I. Unnecessary detail concerning the exact concentrations of reagents is omitted, since no attempt was made to duplicate standard buffer tables. The buffer reagents were made up and mixed in proportions, determined by electrometric titration, to give the pH desired.

Calling the solutions used for the extremes of pH "buffers" is admittedly questionable, but, owing to the possibility of confusion in results due to use of different standard buffer combinations, it was decided to keep the chemical composition of the solutions as nearly similar as possible.

Table I—Solutions Employed

pH	
1.0	Approximately $M/2$ H_3PO_4
2.0	Approximately $M/50$ H_3PO_4
3.0	Approximately $M/1000$ H_3PO_4
4.0	$M/15$ KH_2PO_4 and $M/10$ H_3PO_4
5.0	Mixture of $M/15$ KH_2PO_4 and $M/15$ Na_2HPO_4
6.0	Mixtures of $M/15$ KH_2PO_4 and $M/15$ Na_2HPO_4
7.0	
8.0	
8.5	
9.0	$M/15$ Na_2HPO_4
9.5	Mixtures of $M/15$ Na_2HPO_4 and $M/10$ NaOH
10.0	
11.0	
12.0	

Technic

Portions of 2.74 grams of quinone were placed in wide-mouthed pint bottles. Two hundred-cubic centimeter portions of the buffer solutions were added. When the quinone had dissolved, portions of defatted hide powder equal to 2 grams of absolutely dry substance were added. The bottles were then stoppered and rotated at room temperature. At the end of the time selected, the contents of the bottles were transferred to Wilson and Kern extractors and washed therein with distilled water until no reaction for quinone was obtained by means of the starch-iodide test. This test, as employed, was delicate to 1 part of quinone in 50,000 of water. The tanned samples were then air-dried, after which they were dried *in vacuo* at 110° C. for 16 hours. They were then weighed, the increase in weight being taken as "quinone fixed."

The fixation over periods of 6 hours, 24 hours, 2 weeks, and 5¹/₇ weeks has been determined.

Table II—Fixation of Quinone in 6 Hours

No.	pH of solution	Character of Solution with Dissolved Quinone	Character of Wet Tanned Powder	Increase in weight of 2 grams dry hide powder Gram
				Loss
1	1.0	Orange-yellow, clear	Gelatinous, white	0.103
2	2.0	Reddish yellow, clear	Gelatinous, white	0.083
3	3.0	Reddish yellow, clear	Gelatinous, reddish	0.030
4	4.0	Wine color, clear	Gelatinous, reddish	0.029
5	5.0	Wine color, clear	Gelatinous, reddish	0.012
				Gain
6	6.0	Dark brown, muddy	Well tanned, blackish	0.107
7	7.0	Dark brown, muddy	Well tanned, blackish	0.236
8	8.0	Dark brown, some precipitate	Well tanned, blackish	0.402
9	9.0	Dark brown, some precipitate	Well tanned, blackish	0.399
10	10.0	Dark brown, some precipitate	Well tanned, blackish	0.420
11	11.0	Dark brown, slight precipitate	Well tanned, blackish	0.408
12	12.1	Greenish black, no precipitate	Well tanned, blackish	0.314

Tests on the filtrates showed quinone present in all cases.

When the samples were dried, all were dark in color: Nos. 1 and 2 showed pronounced evidence of hydrolysis; 3,

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[1] Presented by Miss Kelly before the Division of Leather Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

[2] Contribution No. 451 from the Chemical Laboratories, Columbia University.

[3] *Compt. rend.*, **146**, 987 (1908); *Collegium*, **1908**, 195; **1909**, 58, 319; **1914**, 523; *Cuir*, **3**, 465 (1914).

[4] This Journal, **13**, 772 (1921).

[5] Thomas and Kelly, *Ibid.*, **15**, 1148 (1923).

[6] Granger Dissertation, Columbia University, **1920**.

4, and 5 were dark brown, while 6 to 12 were blackish and of good texture. Although 3, 4, and 5 showed loss in weight, the color indicated some fixation of quinone.

Determination of nitrogen in the filtrates showed the following percentages of hydrolysis of the hide powder:

No.	pH	Per cent hydrolyzed	No.	pH	Per cent hydrolyzed
1	1.0	5.8	7	7.0	2.2
3	3.0	2.6	9	9.0	1.6
5	5.0	2.4	11	11.0	1.9
			12	12.1	2.5

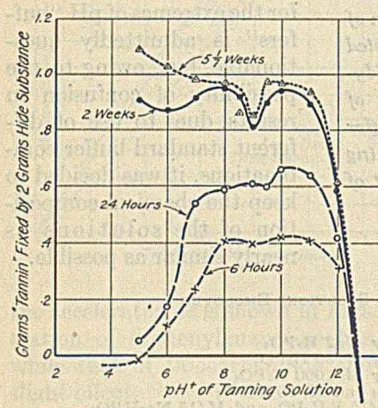

FIG. 1

The results shown in Table II are plotted in Fig. 1 along with those for the longer time intervals. In the longer time interval experiments, acidities greater than pH = 5 were omitted, but since fixation was evident at pH = 12, pH = 13 was included, as shown in Table III.

TABLE III—FIXATION OF QUINONE IN 24 HOURS, 2 WEEKS, AND 5¹/₇ WEEKS

		INCREASE IN WEIGHT OF 2 GRAMS DRY HIDE POWDER		
No.	pH	24 Hours	2 Weeks	5¹/₇ Weeks
1	5.0	0.056	0.908	1.089
2	6.0	0.170	0.868	1.028
3	7.0	0.540	0.915	0.980
4	8.0	0.587	0.947	0.964
5	8.5	...	0.919	0.860
6	9.0	0.607	0.811	0.851
7	9.5	0.596	0.897	0.973
8	10.0	0.658	0.938	0.966
9	11.0	0.636	0.893	0.937
10	12.0	0.416	0.587	0.617
11	13.0	Loss of 0.303	Discarded	Discarded

All filtrates showed positive tests for quinone. Some of the filtrates in the 24-hour series were subjected to the Kjeldahl determination. The degree of hydrolysis of the hide substance so found is shown below.

No.	pH	Per cent hydrolysis	No.	pH	Per cent hydrolysis
1	5.0	2.9	9	11.0	2.1
3	7.0	2.5	10	12.0	2.2
6	9.0	1.8	11	13.0	20.0

The high degree of hydrolysis in the solution of pH = 13 shows the futility of studying the fixation beyond pH = 12.

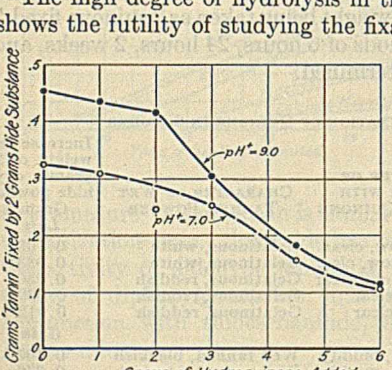

FIG. 2

The data are plotted in Fig. 1. In the 6-hour period a slight fixation is noted at pH = 5, which rapidly rises to pH = 8 and remains fairly constant until pH = 11, except for a slight depression at 9 followed by a slight rise at 10. The result obtained in 2 weeks is striking with its marked depression at pH = 9. In solutions more alkaline than pH = 9, it is quite possible that the nature of the substance acting as a tannin is different from that in the less alkaline solutions, owing to polymerization and other changes in quinone in alkaline solutions.

Meunier believes that, in tanning by quinone, quinone first oxidizes the collagen as it does aromatic amines. As a result of this oxidation of the collagen, hydroquinone is formed. The oxidized collagen combines with part of the remaining quinone. All the filtrates in the experiments described above reduced Fehling's solution, indicating the presence of hydroquinone. More specific tests for hydroquinone failed owing to the dark color of the filtrates.

Since indication of the validity of Meunier's theory was found, it was considered possible to subject it to a more conclusive test. If hydroquinone is formed during the tanning, then the addition of hydroquinone should repress the tanning action of quinone. The addition of hydroquinone to quinone solutions results in the formation of the addition compound, quinhydrone, but since this compound dissociates partially into its constituents in aqueous solution, the formation of quinhydrone should not produce any complications.

Hide powder was drummed as before with quinone solutions of the same concentrations but with different amounts of hydroquinone present. The experiment was carried out in two series, one in a buffer at pH = 7 and another at pH = 9, and the time was 6 hours.

TABLE IV—EFFECT OF HYDROQUINONE ON QUINONE TANNAGE

Hydroquinone present Grams	INCREASE IN WEIGHT OF 2 GRAMS DRY HIDE POWDER At pH = 7 Gram	At pH = 9 Gram
None	0.323	0.454
1.0	0.309	0.433
2.0	0.247	0.416
3.0	0.251	0.302
4.5	0.156	0.181
6.0	0.106	0.115

These data are shown graphically in Fig. 2. The presence of hydroquinone reduces the tanning action of quinone. It is more marked at pH = 9, and also when the amount of hydroquinone equals and exceeds the amount of quinone present, where the latter is in the form of quinhydrone.

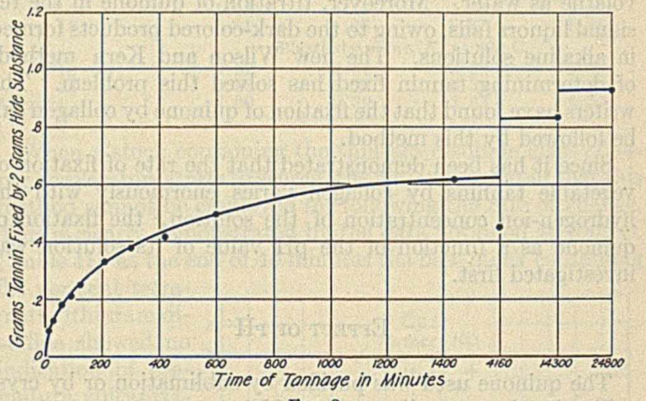

FIG. 3

SPEED OF FIXATION

The speed of fixation of quinone in solutions at pH = 8, using 200 cc. of solution containing 2.74 grams quinone and portions of hide powder equal to 2.000 grams dry substance, was determined at 25° C. The rotating machine containing the bottles was immersed in a water thermostat at this temperature. The data in Table V and Fig. 3 show a smooth curve of parabolic shape, which, however, when submitted to calculation by the monomolecular and dimolecular laws, showed that the reaction was of higher order.

TABLE V—RATE OF QUINONE TANNAGE AT PH = 8 AND AT 25° C.

Time Minutes	Increase in weight of 2 grams hide powder Gram	Time Minutes	Increase in weight of 2 grams hide powder Gram
18	0.094	300	0.378
32	0.126	420	0.418
60	0.180	600	0.496
91	0.211	1440	0.615
121	0.254	14296	0.835
210	0.333	24800	0.947

The authors are pleased to acknowledge the generous support of A. F. Gallun & Sons Company in this investigation.

Consistency of Rubber-Benzene Solutions[1,2]

By Winslow H. Herschel

Bureau of Standards, Washington, D. C.

THE rubber experimental stations in the Dutch East Indies have found that, although the behavior of rubber during and after vulcanization cannot be predicted from determinations of the so-called relative viscosity, this test, combined with vulcanization tests, gives valuable indications, and in certain investigations viscosity determinations alone may be of use.

In the method adopted by the rubber experimental stations, using the Ostwald viscometer, ratio of time of flow of the rubber solution to time of flow of benzene at the same temperature of 30° C. (86° F.) is called the "relative viscosity," although, strictly speaking, it is only at very low velocities of flow that the ratio of time of flow is equal to the relative viscosity. Since it is practically impossible to have the solution, as run, of exactly the desired concentration, a diagram is furnished to correct results to the standard concentration of 1 per cent.

An examination of this method shows the following possible objections:

1—Inasmuch as the time of flow is greatly reduced if the crepe rubber is milled before being dissolved, the question naturally arises whether the rolling received by the crepe at the plantation would not have the same effect, so that tests on benzene solutions should take account of the method of preparing the crepe.

2—There seems to be no adequate reason for comparing the time of flow of the solution with that for benzene. Water has the advantage of being a definite chemical compound of known viscosity, easily procurable, and of high purity. C. P. benzene is less readily procurable. The difference in time of flow of commercial and C. P. thiophene-free benzene was found to be hardly greater than the experimental error with an Ostwald viscometer at 30° C., being 17.4 seconds with the former and 17.3 seconds with the latter. With water at 30° C. and a time of flow of 21.0 seconds, the percentage error in timing would not be so great.

3—Since the equation connecting absolute viscosity with time of flow contains two instrumental constants,[3] it is necessary to determine two times of flow with water, at two temperatures, to calibrate the viscometer so that its readings may be readily convertible into viscosity in c. g. s. units, provided that the benzene solutions of rubber are not plastic but viscous. The distinction between viscosity and plasticity is very important and will be considered later.

4—As Ostwald viscometers are of glass, it is impracticable to make them all of exactly the same dimensions. A correction must therefore be applied to reduce all results to those of a standard instrument. This correction is made most easily by calibrating each instrument with water and expressing all results as viscosity in poises, the poise being the c. g. s. unit of viscosity. If, however, the solution is not viscous but plastic, the magnitude of the correction depends upon the nature of the solution, as well as upon the dimensions of the instrument, and a single time of flow is inadequate to determine the consistency of the solution.

Distinction between Viscous and Plastic Materials

Viscosity is the constant ratio of shearing stress to rate of shear. A material is considered plastic if the apparent viscosity (ratio of shearing stress to rate of shear) varies with the rate of shear. Viscosity can be expressed by a single numerical value, but the consistency of a plastic material must be expressed by an equation or other means which completely defines the variable relation between rate of flow and the force that produces it.[4]

It is to be expected that true solutions and mixtures of miscible liquids will be viscous, but that mixtures of a liquid with a powder or finely divided material will be plastic, if of sufficiently high concentration. In cases of doubt tests are necessary, the essential requirement being that successive trials be made at different rates of shear. The standardization of the rate of shear, as has been proposed,[5] may enable different laboratories to obtain the same numerical results but the complete relation between the rate of flow and the force which produces it cannot be obtained by a single test. Two different plastic materials which show the same apparent viscosity on a single test would not necessarily have the same consistency.

The Ostwald viscometer is not suitable for the measurement of plasticity as ordinarily used, because the pressure head, and consequently the rate of flow for a given material, is fixed. By tests with the Bingham viscometer,[6] in which the rate of flow can be varied, the ratio of rate of flow to pressure head was found to be a variable, thus showing that, at least in some concentrations, benzene solutions of rubber are plastic. The 1 and 2 per cent solutions of crepe rubber in commercial benzene, which were used in these tests, were prepared in accordance with the method of the Delft Institute.[7] It was found that if the crepe was milled before being dissolved, a 2 per cent solution would be viscous, and further milling resulted in a solution of lower viscosity. This is in agreement with the previous observation that the apparent viscosity decreases with the length of milling of the rubber before it is dissolved.

As the concentration is decreased a point must be reached where the solution is viscous. The exact concentration where this change takes place has not been determined, but solutions of between 0.03 and 0.47 per cent concentration have been reported as viscous.[8]

Conclusions

1—Tests of the consistency of benzene solutions of rubber should be made by a method which permits the distinction between a viscous and a plastic material to be observed and reported.

2—Results should be expressed in poises when the solution is found to be viscous.

3—At least two numerical values are required to express the consistency of plastic materials such as (at least in some cases) benzene solutions of unmilled rubber.

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[1] Presented under the title "Method of Determining Consistency of Benzene Solutions of Rubber" before the Division of Rubber Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] Published by permission of the Director, U. S. Bureau of Standards.

[3] Sheeley, THIS JOURNAL, **15**, 1109 (1923).

[4] Hall, *Bur. Standards, Tech. Paper* **234**, 351 (1923).

[5] Shulenberger, *Paint, Oil Chem. Rev.*, **72**, August 17, p. 10, and October 5, p. 10 (1921); see also THIS JOURNAL, **14**, 1164 (1922); **16**, 310 (1924).

[6] *Bur. Standards, Sci. Paper* **298**, 64 (1917).

[7] *Kolloidchem. Beihefte*, **10**, 83 (1918–19).

[8] *C. A.*, **18**, 1065 (1924).

New French Journal Specializes on Colloids—*La revue generale des colloides and de leurs applications industrielles* is the name of a new French periodical, which has been published monthly since November, 1923. This paper specializes in the study of colloids, the importance of which is becoming more and more recognized in industrial technology. Each issue of the new journal contains original articles and abstracts from foreign publications, classified into twenty-four different branches of the subject.

The subscription price to countries other than France is 55 francs. The office of publication is 92 rue Bonaparte, Paris, VIe.

Determination of Distribution of Particle Size[1]

By W. J. Kelly

The Goodyear Tire & Rubber Co., Akron, Ohio

A method is described by which the size of the particles of a suspension can be easily and accurately determined. The distribution of the particle size can also be obtained. The method presupposes the validity of Stokes' law for the rate of settling.

IN STUDYING the properties of pigments and fine powders it is often necessary to know, not only the average size of the individual particles, but also the percentage of particles of various sizes present in the powder. Several microscopic methods, such as the count method, have been devised, but these give only the average size and do not permit the determination of the distribution of sizes. It is usually more convenient to study the pigments and powders in liquid suspensions, and hence the most natural way of determining the size of particle would be to measure the rate of settling in a liquid and by the use of Stokes' law, so far as it is applicable, calculate the diameter.

Previous Methods

Oden[2] has worked out a very ingenious method for weighing the sediment forming at the bottom of a tube, and from the rate at which it formed he was able to calculate the diameter and also the distribution of the particles of different diameters. Svedberg and Rinde[3] improved this method to the extent of adding an automatic weight recorder which drew a practically continuous curve. Figures are given by Svedberg and Rinde showing the distribution of particle size for gold and mercury hydrosols. The great advantage of this method is that very small amounts of material can be used. However, if large amounts of material are available it is usually more convenient to operate with slightly more concentrated suspensions provided they are still dilute enough so that no flocculation takes place.

A rough method was devised by Wo. Ostwald and von Hahn[4] for determining the rate of settling, but in this method the use of very concentrated suspensions, as high as 20 per cent solids, is necessary. The method depends on the fact that a suspension is specifically heavier than the medium, and hence, if the suspension is placed in one arm of a U tube and the suspending medium in the other, the latter will stand at a higher level. As the solid settles out the suspension becomes specifically lighter and the level difference in the two arms of the tube decreases. From the rate at which the level difference decreases a rough idea of the rate of settling can be obtained. Von Hahn used a tube such as is shown in Fig. 1. The suspension is placed in the left-hand tube and the medium in the right. A scale is mounted at the back so that the menisci can be read. The side tube is about 130 cm. long and the whole apparatus about 150 to 160 cm. In order to get a readable level difference very concentrated suspensions were used. In these suspensions there was considerable flocculation and as a result the method measured more the rate of flocculation plus settling than that of settling alone.

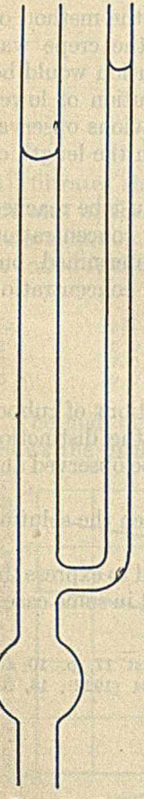

Fig. 1—Sedimentation Tube (von Hahn)

Present Method

The method described in this paper is a modification of von Hahn's, which permits the use of 0.5 to 1 per cent suspensions and by which the actual weight of the material settling past the entrance of the side tube can be calculated.

In a tube of the type shown in Fig. 2 the difference in level, a, in the two arms is given by the equation

$$a = \frac{D}{d}h - h \qquad (1)$$

where h is the height of the suspension, D its density, and d the density of the medium or the liquid in the side tube. In case of short tubes and dilute suspensions a is very small. If the side tube is bent over, the apparent value of a can be increased considerably and measured in terms of the length of the liquid column in the horizontal part of the side tube. If this length is l, then

$$a = l \sin b \qquad (2)$$

where b is the angle which the side tube makes with the horizontal.

In order to calculate the weight of material which settles past the side tube, the density of the suspension, D, has to be known in terms of the medium and the specific gravity of the suspended material. Thus

$$D = \frac{Vd - vd + w}{V} \qquad (3)$$

where V is the volume of suspension in the large tube above the side tube, v the volume of the pigment and hence also that of the medium displaced, and w is the weight of the solid phase.

If S is the specific gravity of the pigment, then

$$S = \frac{w}{v} \text{ or } v = \frac{w}{S} \qquad (4)$$

Substituting (4) in (3)

$$D = \frac{Vd - \frac{wd}{S} + w}{V} = \frac{SVd - wd + wS}{VS} \qquad (5)$$

Substituting (5) and (2) in (1)

$$l \sin b = \frac{h}{d}\,\frac{SVd - wd + wS}{VS} - h$$

which on simplification gives

$$w = \frac{dVSl \sin b}{h(S-d)} \qquad (6)$$

In this equation w and l are the only variables for any given experiment, and as soon as the values of the constants have been determined the equation may be written

$$w = K.l \qquad (7)$$

in which form it is easily used. The total weight of solid phase in the suspension being known, it is a simple matter to calculate the percentage which settles out in a given time.

In using this method the actual length of the side tube is immaterial, provided it is long enough to take care of the recession due to the settling. The zero point is taken at the upper end of the tube and the difference between this point and the position of the meniscus at any given time is taken as l. In this way the effect of capillarity is eliminated.

Precision Discussion

In Equation 6 all values with the exception of l and $\sin b$ can be determined so accurately that no error in w arises from them. For the values of b obtaining in the determination an error of

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[1] Presented at the Second National Colloid Symposium, Evanston, Ill., June 18 to 21, 1924.

[2] *Proc. Roy. Soc. Edinburgh*, **36**, 219 (1916).

[3] *J. Am. Chem. Soc.*, **45**, 943 (1923).

[4] *Kolloid-Z.*, **32**, 60 (1923).

1 per cent in measuring the angle which is about 1 degree 30 minutes will introduce an error of approximately the same magnitude in the percentage of material settling out. The position of the meniscus in the capillary can be read to ±0.01 cm., so that at the start a fairly large error can be introduced from this value. However, as the recession in the capillary proceeds this error grows less, and at 2 cm. has been reduced to 1 per cent. In the example given 18 per cent of the material has settled out when the recession attains 2 cm., so that at this point the weight of material is known within 1 per cent.

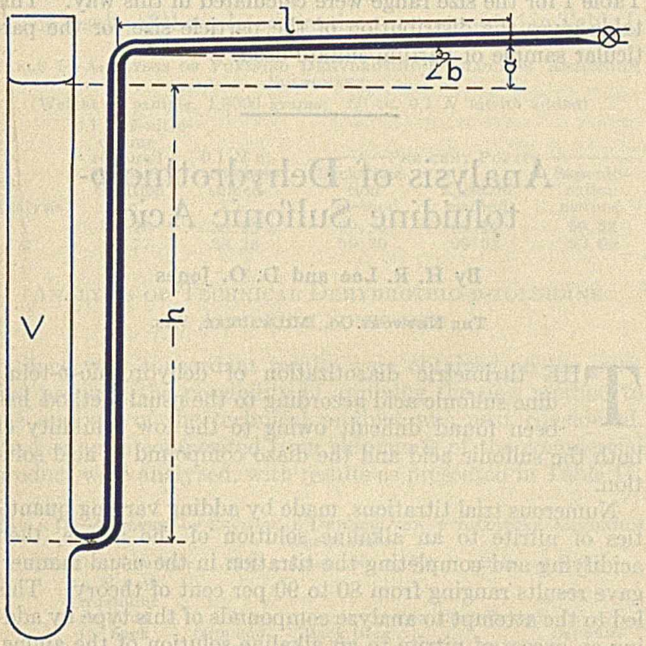


Fig. 2

For the calculation of the size of the particle it is assumed that Stokes' law is valid, and hence any error in the calculation will be only that inherent in the law itself.

Operation

The tube and capillary are first cleaned with potassium bichromate–sulfuric acid mixture and then rinsed thoroughly with distilled water. The whole tube is then filled with water to the proper level, which is such that the meniscus in the capillary is at the lower end of the horizontal portion. The height of the column in the settling tube is then measured from the entrance of the side tube and also the volume. The stopcock at the upper end of the side tube is closed and the settling tube emptied. The suspension is then poured in up to the same level where the water stood and the tube placed in the thermostat. The tube is held firmly so that the angle of inclination of the side tube is constant. The stopcock is then opened and readings begun. The first reading is taken 1 minute after setting the tube or at any other convenient interval. After about five readings have been made they are plotted and extrapolated to zero time in order to get the zero reading on the capillary tube. In the case of suspensions that settle slowly this is not necessary, as the reading at the end of 1 or even 2 minutes can be taken for the zero without introducing any appreciable error. In order to prevent the water from sticking in the capillary tube, it is recommended that a fairly large capillary (2 mm.) be used and also that some protective colloid, such as gum arabic, gelatin, saponin, etc., be added to the water in the capillary to reduce its surface tension and thus render it less liable to give false readings due to imperfections or specks of dirt in the capillary.

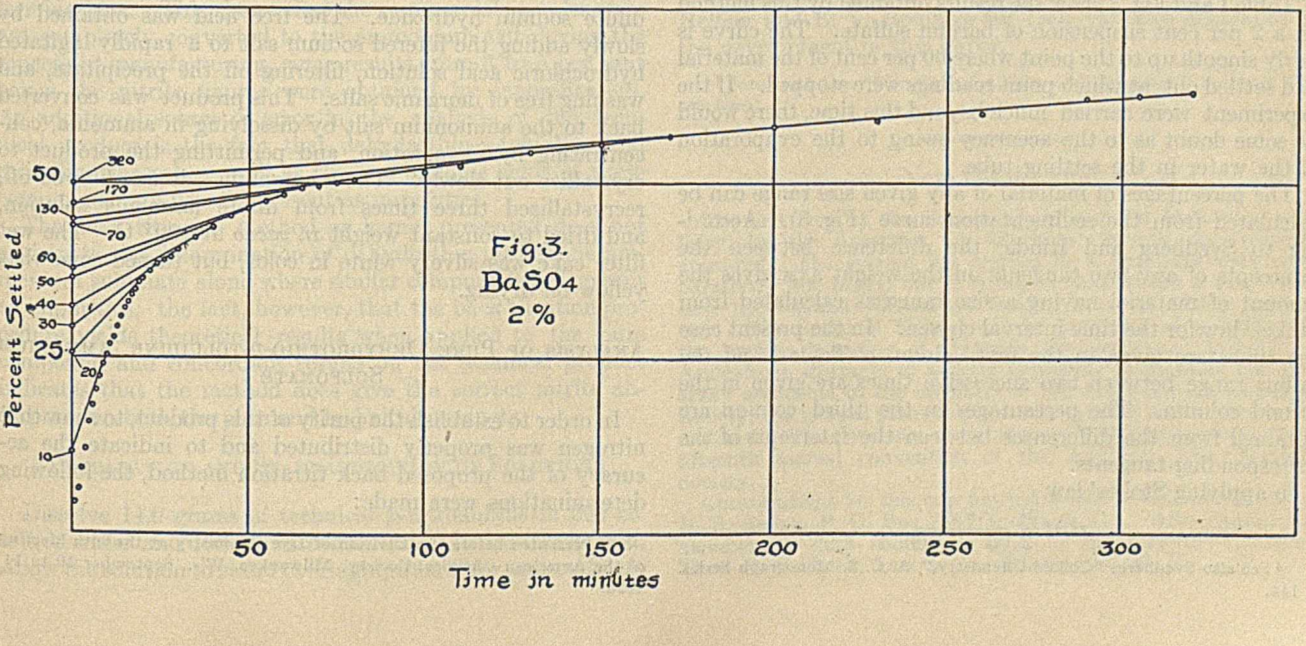
The tube as shown in Fig. 2 is not applicable in that form, because the water evaporates from both the large tube and the capillary, thus causing the recession to be more rapid than that due to the sedimentation alone. For that purpose a new tube (Fig. 4) has been designed (but not yet built).

The large tube, which should be about 2 cm. in diameter, has a ground, jointed cap, in the interior of which a small amount of water can be placed. This water is held at the same temperature as that in the tube proper, and hence by keeping the pressure of the water vapor constant below the cap any evaporation which takes place would naturally come from the water in the cap, as that is nearer the opening of the tube. The small bulb at the outer end of the capillary serves the same purpose.

The dimensions that should work best are given in Fig. 4, although the settling tube can be made any convenient length. Naturally, the longer the side tube the greater will be the initial level difference and hence the greater the accuracy, for a given suspension.

Preparation of the Sample

To get reliable results it is necessary that the sample be perfectly dispersed, or, in other words, all agglomerates must be broken up and only primary particles left. This may be



done by moistening a weighed amount, for instance, 1 gram, on a glass plate and rubbing it with a spatula. A few cubic centimeters of a protective colloid solution, such as 5 per cent gum arabic, and a small amount of an electrolyte, such as 1 cc. of a 5 per cent barium chloride solution for barium sulfate or zinc chloride or sodium hydroxide for zinc oxide, etc., is added as a peptizing agent and the whole mixture rubbed well with the spatula. The mixture is then diluted gradually until it is fairly thin, washed into a graduate and made up to 100 cc., or whatever volume is desired. In this way a very good dispersion can be made.

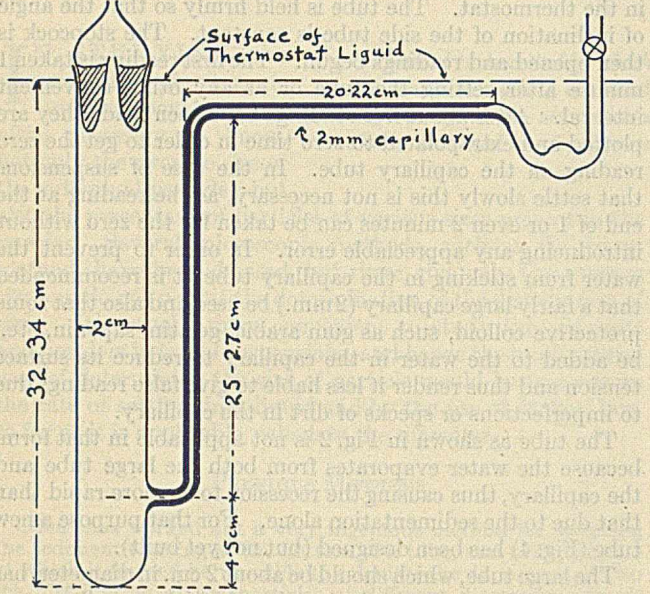


FIG. 4

TABLE I—DISTRIBUTION OF PARTICLE SIZE IN SUSPENSION OF BARIUM SULFATE

Time Minutes	Radius	Per cent
10	>7.1u	11.5
20	7.1 to 5.0	14.0
30	5.0 to 4.1	3.5
40	4.1 to 3.5	3.2
50	3.5 to 3.2	4.1
60	3.2 to 2.9	1.1
70	2.9 to 2.7	6.2
130	2.7 to 2.0	0.9
170	2.0 to 1.7	2.1
320	1.7 to 1.2	3.1
α	<1.2	50.3

RESULTS

Table I and Fig. 3 show the results obtained by this method on a 2 per cent suspension of barium sulfate. The curve is fairly smooth up to the point where 60 per cent of the material had settled out, at which point readings were stopped. If the experiment were carried much beyond this time, there would be some doubt as to the accuracy owing to the evaporation of the water in the settling tube.

The percentages of material of any given size range can be calculated from the sedimentation curve (Fig. 3). According to Svedberg and Rinde[5] the difference between the intercepts of any two tangents on the weight axis gives the amount of material having a size range as calculated from Stokes' law for the time interval chosen. In the present case the times are given in the first column of Table I and the radius range between two successive times are given in the second column. The percentages in the third column are obtained from the differences between the intercepts of the corresponding tangents.

In applying Stokes' law

$$r^2 = \frac{9}{2} \frac{\eta\ h}{(\Delta - \delta)gt}$$

h is measured from the surface of the liquid to the entrance of the side tube. Hence at any given time all particles of radius calculated from Stokes' law for this time will have reached the entrance of the side tube. By calculating the radii at successive time intervals the range of particle size settling between these time intervals is obtained. The figures given in Table I for the size range were calculated in this way. This table gives the distribution of the particle size for the particular sample of barium sulfate used.

Analysis of Dehydrothio-*p*-toluidine Sulfonic Acid[1]

By H. R. Lee and D. O. Jones

THE NEWPORT CO., MILWAUKEE, WIS.

THE titrimetric diazotization of dehydrothio-*p*-toluidine sulfonic acid according to the usual method has been found difficult owing to the low solubility of both the sulfonic acid and the diazo compound in acid solution.

Numerous trial titrations, made by adding varying quantities of nitrite to an alkaline solution of the amine, then acidifying and completing the titration in the usual manner, gave results ranging from 80 to 90 per cent of theory. This led to the attempt to analyze compounds of this type by adding an excess of nitrite to an alkaline solution of the amine, acidifying, and titrating back the excess of nitrite with a standard solution of a primary amine.

The first problem in the development of the back titration method was to find an amine, which would be stable in solution and which would diazotize rapidly and quantitatively at 0° C., to be used as a standard solution for the estimation of excess nitrous acid. *p*-Nitroaniline and nitrocresidine were found to meet these requirements. The former, being a more common laboratory reagent and having greater solubility in acid solution, was considered more suitable.

PREPARATION OF PURE DEHYDROTHIO-*p*-TOLUIDINE AMMONIUM SULFONATE

A sample of technical dehydrothio-*p*-toluidine ammonium sulfonate was converted into the sodium salt by boiling with dilute sodium hydroxide. The free acid was obtained by slowly adding the filtered sodium salt to a rapidly agitated hydrochloric acid solution, filtering off the precipitate, and washing free of inorganic salts. This product was converted back to the ammonium salt by dissolving in ammonia, concentrating by evaporation, and permitting the product to crystallize out slowly. The ammonium salt was filtered off, recrystallized three times from dilute ammonia solution, and dried to constant weight *in vacuo* at 100° C. The wet filter cake was silvery white in color, but turned somewhat yellow on drying.

ANALYSIS OF PURE DEHYDROTHIO-*p*-TOLUIDINE AMMONIUM SULFONATE

In order to establish the purity of this product, to show that nitrogen was properly distributed and to indicate the accuracy of the proposed back titration method, the following determinations were made:

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[5] See also Svedberg, "Colloid Chemistry," A. C. S. Monograph Series, p. 144.

[1] Presented before the Division of Dye Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

(1) Amino nitrogen, by the nitrite back titration method herein described.

(2) Total nitrogen, by the Kjeldahl method.

(3) Ammonium salt nitrogen, by saponification with caustic soda solution, distillation, and titration of the liberated ammonia, as in the usual Kjeldahl method. (Paraffin was used to prevent foaming. The use of zinc for this purpose resulted in the reduction of the product to *p*-toluidine.)

The results of these determinations are presented in Table I.

Table I—Analyses of Purified Dehydrothio-*p*-toluidine Ammonium Sulfonate

(Weight of sample, 1.3000 grams; 50 cc. 0.1 *N* nitrite added)

Analysis	0.1 *N* *p*-nitroaniline required for back titration Cc.	0.1 *N* nitrite consumed Cc.	Per cent Purity: Back titration method	Per cent Purity: Kjeldahl method	Per cent Purity: Saponification method
1	11.75	38.25	99.26	99.12	99.23
2	11.77	38.23	99.20	99.02	99.09

Analysis of Technical Dehydrothio-*p*-toluidine Ammonium Sulfonate

Since very concordant results were obtained on the purified product, the possibility of applying the new method to the analysis of the technical product was next considered. Five samples composited from shipments of the commercial product were analyzed, with results as presented in Table II.

Table II—Analyses of Technical Dehydrothio-*p*-toluidine Ammonium Sulfonate

(Weight of sample, 1.3000 grams; 50 cc. 0.1 *N* nitrite added)

Sample	0.1 *N* *p*-nitroaniline required for back titration Cc.	0.1 *N* nitrite consumed Cc.	Per cent Purity: Back titration method	Per cent Purity: Kjeldahl method	Per cent Purity: Saponification method
1	14.66	35.34	91.70	91.51	88.34
	15.69	35.31	91.62	91.51	88.13
2	13.24	36.76	95.39	95.14	92.32
	13.24	36.76	95.39	95.23	92.32
3	23.34	36.66	95.13	95.35	90.19
	13.30	36.70	95.23	95.44	90.13
4	13.24	36.76	95.39	95.40	91.83
	13.27	36.73	95.31	95.36	91.83
	13.27	36.73	95.31	95.34	92.16
	13.32	36.68	95.18	95.19	92.16

Discussion of Results

Dehydrothio-*p*-toluidine is used principally as the first component in azo dyes. For this reason the nitrite absorption is considered the most desirable criterion of purity. In the case of the technical samples the results by the back titration method are in excellent agreement with the Kjeldahl analyses, but do not check the ammonium salt nitrogen determinations. This shows that the commercial samples were not completely converted to the ammonium salt during the process of manufacturing, since results from 3 to 5 per cent below the nitrite figures were obtained by saponification. An additional source of error in the analysis of the technical product is the fact that dehydrothio-*p*-toluidine and primuline (bases), as well as the free sulfonic acids of these compounds, are usually present as impurities.

The back titration method as herein presented does not anticipate the determination of dehydrothio-*p*-toluidine ammonium sulfonate alone where similar compounds are present as impurities; the fact, however, that the back titration procedure yields theoretical results when applied to the pure compound and concordant results on the technical product indicates that the method does give the correct nitrite absorption on both the pure and technical products.

Preparation and Standardization of Solutions

Dissolve 14.0 grams of technical *p*-nitroaniline in 200 cc. of hot water and 150 cc. of concentrated hydrochloric acid. Allow the solution to stand overnight, then filter and make up to volume in a 1-liter volumetric flask. Standardize the nitrite solution against sulfanilic acid of known purity. Determine the relative strength of the nitrite to the *p*-nitroaniline by titrating a 10-cc. sample of the nitrite with *p*-nitroaniline in the same volume and under the conditions as described in the back titration method.

Diazo-*p*-nitrobenzene has a rather strong oxidizing effect on starch iodide which accounts for the use of a 10-cc. sample of nitrite in this standardization.

Method of Analysis

Weigh 1.3 grams of dehydrothio-*p*-toluidine ammonium sulfonate, transfer into a 600-cc. beaker, add 200 cc. of water and 5 cc. of 10 per cent caustic soda solution to dissolve. Cool to 0° to 5° C., and add chipped ice. Add from a buret 50 cc. of 0.1 *N* sodium nitrite solution, or a sufficient quantity to allow for an excess of approximately 10 cc. of 0.1 *N* nitrite after diazotization. While stirring, acidify with 25 cc. of concentrated hydrochloric acid and 10 cc. of concentrated nitric acid (N_2O_3 free).[2] Cover the beaker with a watch glass and allow to stand for 10 minutes. Titrate back the excess of nitrous acid with approximately 0.1 *N* *p*-nitroaniline solution. The end point is reached when, upon spotting a small drop of the solution from a stirring rod onto a drop of starch iodide solution on the level surface of a spot plate, no immediate formation of blue color results. On spotting with starch iodide a gradual development of blue color takes place, which has no relation to the end point. At the end point this development of color is comparatively slow (about 2 seconds), but upon the further addition of one or two drops of *p*-nitroaniline solution the blue color develops more rapidly. An analysis by this method can be completed in 20 to 30 minutes.

1 cc. of 0.1 *N* nitrite ≈ 0.033733 gram of dehydrothio-*p*-toluidine ammonium sulfonate

Application of Method

The method can be applied to dehydrothio-*p*-toluidine, primuline, and dehydrothio-*m*-xylidine sulfonic acids, or to the free bases of these compounds if preceded by sulfonation of the sample with 20 to 25 per cent oleum. It is also applicable to the analysis of color bases and numerous other compounds which diazotize with difficulty because of their insolubility in acid solution.

Acknowledgment

The authors desire to express their appreciation to Bertram Helfaer and E. V. Romaine for their valuable assistance in the development of this paper.

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[2] Jones and Lee, "Titration of Aniline and Homologs." See page 948, this issue.

New Oil Journal

The first issue of the *Journal of Oil and Fat Industries*, published by the American Oil Chemists' Society, has recently appeared. The journal has started as a quarterly with comparatively few pages, but it is hoped that within a very short time the demand will warrant issuing it as a monthly publication. The Board of Editors will be composed of specialists in the various branches of glyceride chemistry and technology. Aside from abstracts of articles appearing in journals not generally accessible to the members of the American Oil Chemists' Society, the journal plans to print only original and authoritative material. The first issue contains most of the proceedings of the fifteenth annual convention of the American Oil Chemists' Society.

Contributions for this new journal should be sent to the editor, H. S. Bailey, P. O. Box 756, Savannah, Ga. Subscription and membership dues should be paid to the secretary-treasurer, Thos. B. Caldwell, Law & Co., Wilmington, N. C.

Vapor Pressure Curves for Systems Containing Alcohol, Ether, and Water[1,2]

By E. A. Louder, T. R. Briggs, and A. W. Browne

Cornell University, Ithaca, N. Y.

A convenient apparatus for determining vapor pressure has been described. The vapor pressures of certain mixtures in the following systems have been determined between 0° and 50° C.: diethyl ether, ethyl alcohol; diethyl ether, ethyl alcohol, water; diethyl ether, ethyl alcohol, water, diphenylamine.

The vapor pressures of purified diethyl ether, ethyl alcohol, and water have been redetermined between 0° and 50° C. From the data pressure-temperature curves have been constructed.

In connection with the problem of recovering the solvents used in the manufacture of certain explosives, a study of the pressure-temperature diagram in various two, three, and four-component systems has been undertaken in this laboratory. The investigation has comprised determinations of the pressure-temperature curves over a range from 0° to 50° C. for the systems (1) diethyl ether, ethyl alcohol; (2) diethyl ether, ethyl alcohol, water; (3) diethyl ether, ethyl alcohol, water, diphenylamine.

Materials

Diethyl Ether—Diethyl ether was shaken with concentrated sodium hydroxide, and after being dried, first over anhydrous calcium chloride and then over sodium, it was at length distilled for use from a flask containing sodium. The normal boiling point was found to be 34.60° C.

Ethyl Alcohol—Technical absolute alcohol was boiled for 10 hours with anhydrous calcium oxide, distilled, and again boiled with anhydrous calcium oxide for an additional period of 48 hours. After being distilled, the alcohol was freed from aldehyde by treatment with dry silver oxide. It was then boiled for 48 hours with anhydrous barium oxide and was finally distilled for use from a flask containing sodium. The normal boiling point was found to be 78.36° C.

Water—Water of special purity was prepared by distillation from a potassium dichromate solution. The steam was passed through a calcium hydroxide solution to remove carbon dioxide, and the condensate was stored in a closed container.

Apparatus

The vapor pressure apparatus is shown in Fig. 1. The pressure bulb, B, containing the system under investigation, the manometer, M, the leveling tube, L, and the water bath, A, comprise the essential features. The liquid to be studied was stored in the reservoir, K, which in turn was protected by the glass-stoppered U tubes, T and T', containing, in order, phosphorus pentoxide and anhydrous calcium chloride. To prevent distillation of the volatile liquid from the reservoir into the desiccants, care was taken ordinarily to close the connection between the two by turning the stopper in T. The pressure bulb could be placed into communication with the storage reservoir via the ground-glass joint at J, or it could be connected with the external atmosphere through a soda-lime tower, T''. The leveling bulb was fitted with a glass plunger for the delicate adjustment of the mercury level in the pressure bulb, and the manometer was mounted beside a boxwood meter scale. Two complete pieces of apparatus were employed in the investigation.

The temperature was controlled by immersing the pressure bulb in a water bath to a point above the stopcock, S, the bath being stirred thoroughly during each determination. The temperature of the bath was maintained at the desired point without the use of an automatic thermoregulating device, one of the operators either making small additions of ice or heating the water with a nichrome coil, according to the temperature desired. It was found that this method sufficed to keep the temperature constant to within 0.02° C. over the period of time required for a pressure determination. During this period the pressure bulb, connected with the manometer through the flexible glass spiral, C, was steadily shaken, for the purpose of bringing about, as rapidly as possible, the necessary condition of equilibrium between liquid and vapor.

All thermometers used in this investigation were compared with a standard thermometer recently calibrated by the Bureau of Standards. The readings were corrected for stem immersion when necessary. All readings of barometer and manometers have been reduced to 0° C. and are expressed in millimeters of mercury.

Procedure

After the apparatus had been supplied with a sufficient quantity of redistilled mercury, the pressure bulb was placed in communication with the external atmosphere through the soda-lime tower, T'', and the mercury level was brought to a fixed point in the narrow connecting tube below B, as shown in the sketch. This adjustment was made by bringing the

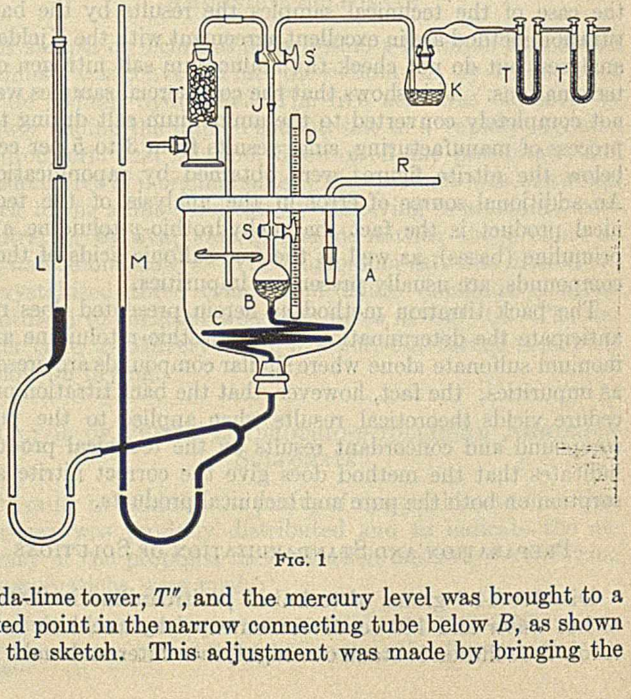

Fig. 1

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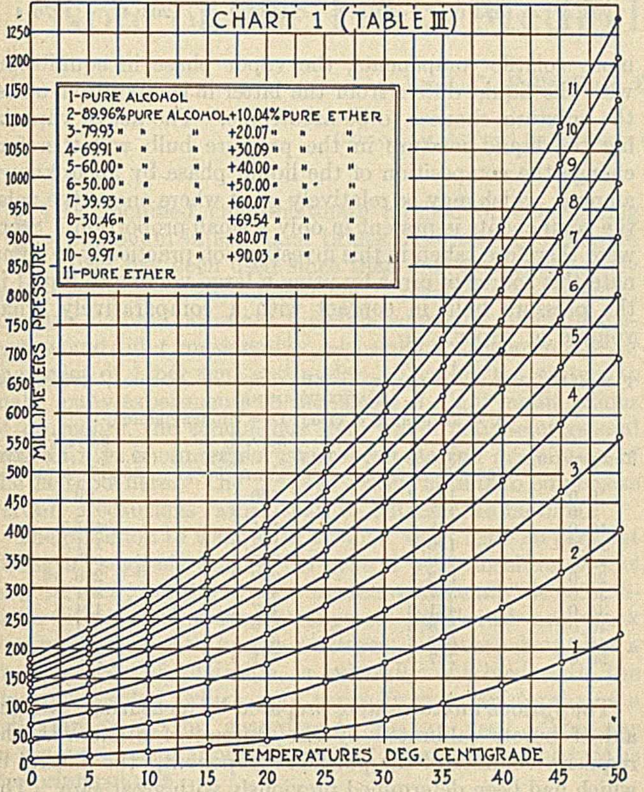
[1] Received April 25, 1924.

[2] This article is based upon the thesis presented to the faculty of the Graduate School of Cornell University by E. A. Louder in partial fulfilment of the requirements for the degree of doctor of philosophy. The work was undertaken at the suggestion of Major J. H. Hunter, Ordnance Department, U. S. A., and has been supported by a grant from that department. It is now published with permission of the Chief of Ordnance. Acknowledgment is here made of the assistance rendered by A. B. Hoel in certain parts of the experimental work.

level of the mercury exactly opposite a definite line on the scale *D*, which consisted of an inverted buret held firmly in position in the supporting framework of the apparatus and bearing calibration marks which passed entirely around the stem. By ascertaining the position of the mercury level in the manometer, a reading of the latter was obtained when the vapor phase in the pressure bulb consisted simply of the dry air under barometric pressure.



The pressure bulb was then filled completely with mercury, the stopcock was closed, and mercury was withdrawn until its level was again brought opposite the fixed point on the buret scale. The difference between the manometer reading now obtained and the previous reading should, of course, be equal to the height of the barometer, and since this was found to be true within 0.2 mm., the apparatus was considered to be in satisfactory working condition. The actual measurement of vapor pressure was thereupon begun.

A definite quantity of liquid was drawn into the pressure bulb from the storage reservoir, and the bulb was placed in communication with the atmosphere as before. After adjusting the temperature of the water bath to 0° C., the mercury level was brought opposite the fixed point on the buret scale and the manometer reading was obtained, this time with the bulb containing air and volatile liquid under barometric pressure. For the sake of convenience, this will be called an open-bulb reading.

TABLE I—VAPOR PRESSURE OF ETHER

Temperature ° C.	New data	Data by Ramsay and Young	Data by Regnault
0.0	185.3	184.9	184.4
5.0	233.2	232.5 (curve)	230.9
10.0	291.7	291.78	286.2
15.0	360.7	361.0 (curve)	353.6
20.0	442.2	442.36	432.8
25.0	537.0	537.5 (curve)	525.9
30.0	647.3	647.92	634.8
35.0	775.5	776.0 (curve)	761.2
40.0	921.3	921.18	907.0
45.0	1089.8	1091.5	1074.5
50.0	1276.4	1276.11	1264.8

The air above the liquid was next expelled by raising the level of the mercury, the stopcock was closed, and steps were taken to eliminate the dissolved air carried by the liquid. This was done conveniently by lowering the mercury level until a fairly large volume of vapor was formed above the liquid in the pressure bulb, when, on causing this vapor to be condensed by a sudden increase in pressure, a portion of the air carried into the vapor remained uncondensed and was trapped in the form of a bubble below the stopcock *S*, through which it was expelled. This process was repeated several times until no visible trace of uncondensable gas remained.

The mercury level in the pressure bulb was finally brought opposite the fixed point on the buret scale and the manometer reading was obtained, after due care had been taken to bring liquid and vapor into complete equilibrium. The difference between this closed-bulb reading and the open-bulb reading previously obtained was subtracted from the barometric pressure. The result was the vapor pressure of the liquid.

TABLE II—VAPOR PRESSURE OF ALCOHOL

Temperature ° C.	New data	Data by Ramsay and Young	Data by Regnault
0.0	12.41	12.24	12.70
5.0	17.31	17.30	17.60
10.0	24.34	23.77	24.20
15.0	33.22	32.50	33.00
20.0	44.40	44.00	44.50
25.0	59.7	58.8 (curve)	59.40
30.0	79.3	78.06	78.50
35.0	103.1	102.0 (curve)	102.90
40.0	134.6	133.42	133.70
45.0	173.3	172.0 (curve)	172.20
50.0	221.1	219.82	219.9

Certain special precautions should be mentioned. Owing to the fact that the mercury in the spiral below the pressure bulb was at the temperature of the water bath while the rest of the mercury in the apparatus was at the temperature of the room, the open-bulb readings varied slightly as the temperature of the water bath was changed. Since the temperature of the room remained practically constant, it was found to be sufficient, however, to determine once for all the open-bulb readings for each apparatus over the whole temperature range (0° to 50° C.), and to use the data thus obtained to correct the open-bulb readings determined once only at 0° C. for each single liquid or liquid mixture investigated. It was found, for example, that the open-bulb reading for apparatus No. I changed 0.4 mm. for a rise of 10° C. In any given series

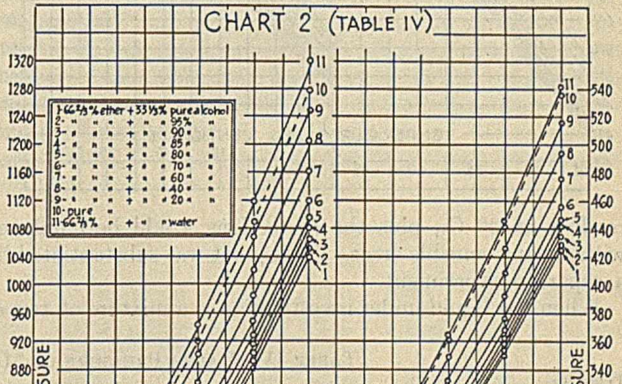
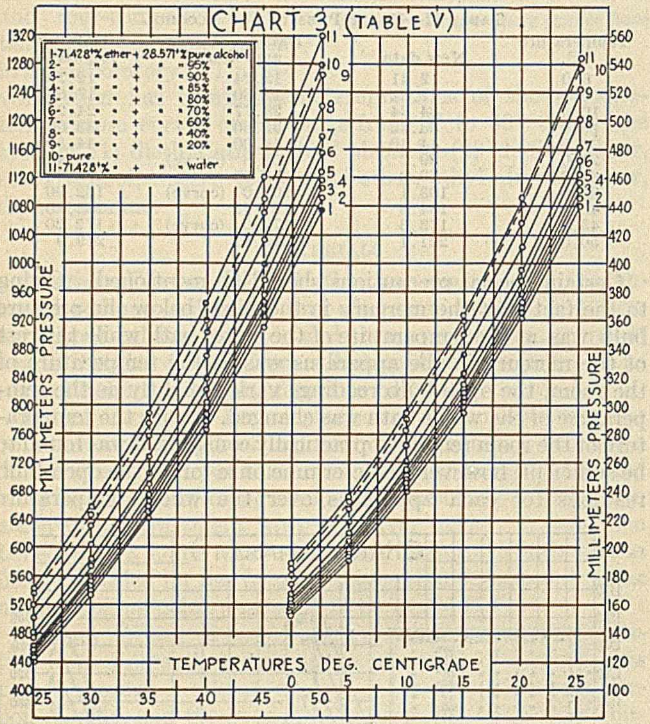


TABLE III—VAPOR PRESSURES OF MIXTURES OF ALCOHOL AND ETHER

(A = alcohol; E = ether)

Temperature ° C.	Pure alcohol	89.96% A 10.04% E	79.23% A 20.07% E	69.91% A 30.09% E	60% A 40% E	50% A 50% E	39.93% A 60.07% E	30.46% A. 68.54% E	19.93% A 80.07% E	9.97% A. 90.03% E	Pure ether
0.0	12.41	43.3	70.9	93.7	111.8	126.7	141.1	151.7	160.8	172.0	185.3
5.0	17.31	54.6	90.2	118.1	139.5	158.5	178.1	190.5	203.6	217.0	233.2
10.0	24.34	70.1	114.4	147.2	175.0	197.9	221.7	236.8	253.9	271.7	291.7
15.0	33.22	89.2	144.5	182.1	215.5	247.9	271.2	293.6	314.4	335.7	360.7
20.0	44.40	112.4	174.0	224.8	268.1	302.7	332.9	359.2	384.4	410.8	442.2
25.0	59.7	140.7	214.2	274.0	324.5	367.8	405.2	436.1	467.5	499.3	537.0
30.0	79.3	174.8	262.9	333.9	395.3	446.2	491.7	529.2	566.9	604.4	647.3
35.0	103.1	217.3	318.5	403.7	476.7	536.4	590.6	632.1	681.7	726.2	775.5
40.0	134.6	266.3	386.6	486.2	571.0	641.5	708.6	758.0	812.2	865.8	921.3
45.0	173.3	327.4	467.1	582.0	679.2	762.1	842.8	901.0	965.2	1025.8	1089.8
50.0	221.1	400.3	558.1	693.2	804.6	903.5	995.0	1062.7	1136.0	1208.4	1276.4

of determinations, of course, the open-bulb reading depends upon the height of liquid contained above the mercury in the pressure bulb; but since the latter remained very nearly unchanged during each series of pressure determinations for a given liquid over the temperature range, the open-bulb reading at 0° C., plus the corrections, could be employed without any sensible error. This point was substantiated by a separate experiment.



When the liquid under investigation is a mixture of two or more volatile components, the vapor phase in equilibrium with the liquid differs from the latter in composition, unless the mixture chances to be azeotropic. The act of vaporizing the liquid mixture in the pressure bulb will therefore change the composition of the liquid phase by an unknown amount, which may be relatively great where one of the volatile components is present in only a small proportion. Steps were therefore taken in this investigation practically to eliminate this source of error by using a large volume of liquid in the pressure bulb in contact with a comparatively small volume of vapor.

TABLE VI—VAPOR PRESSURE OF MIXTURES OF ALCOHOL, ETHER, AND DIPHENYLAMINE

(A = alcohol, E = ether, D = diphenylamine)

Temperature ° C.	33¹/₃% E 66²/₃% A (95%)	33¹/₃% (99.7% E; 0.3% D) 66²/₃% A (95%)	33¹/₃% (99.4% E; 0.6% D) 66²/₃% A (95%)
0.0	102.2	100.1	99.3
5.0	127.4	124.5	...
10.0	158.8	155.7	155.5
15.0	196.1	193.9	191.8
20.0	240.9	237.5	236.3
25.0	293.1	290.0	288.3
30.0	357.6	353.3	351.8
35.0	431.2	427.2	424.9
40.0	518.5	516.6	514.4
45.0	620.6	614.1	612.0
50.0	737.5	731.0	728.7

The various mixtures were prepared by measuring, with the aid of burets calibrated by the Bureau of Standards, the requisite volumes of the purified components, the density of which had been determined previously with great care. The mixtures were produced directly in the reservoir *K* in such wise as to prevent any appreciable loss through volatilization.

EXPERIMENTAL DATA

The effectiveness of the apparatus and of the experimental method was first tested by determining separately the vapor pressures of two of the individual components, diethyl ether and alcohol. The data so obtained are submitted in

TABLE IV—VAPOR PRESSURE OF MIXTURES OF ALCOHOL, ETHER, AND WATER

Temperature ° C.	Water 100%	66²/₃% ETHER; 33¹/₃% ALCOHOL								66²/₃% E 33¹/₃% W	Pure ether	Pure alcohol
		Pure A	95% A	90% A	85% A	80% A	70% A	60% A	40% A	20% A			
0.0	5.10	147.3	148.6	149.8	152.0	154.5	157.9	165.4	173.6	181.0	187.4	185.3	12.4
5.0	6.90	185.6	186.8	189.2	192.8	193.7	198.9	207.0	217.3	227.0	236.4	233.2	17.3
10.0	9.36	231.7	233.8	236.1	239.3	242.5	248.3	259.4	269.2	282.5	294.3	291.7	24.3
15.0	13.16	285.4	288.3	292.0	295.0	300.3	307.7	319.9	332.2	348.6	363.5	360.7	33.2
20.0	17.37	350.5	353.1	358.8	362.8	368.0	376.0	392.3	407.6	426.0	445.2	442.2	44.4
25.0	23.66	425.7	429.7	435.4	442.6	447.3	457.2	476.0	494.5	517.0	542.5	537.0	59.7
30.0	32.18	516.6	521.7	529.7	536.6	542.5	555.4	577.0	600.4	628.0	658.2	647.3	79.3
35.0	42.38	623.1	628.3	635.7	645.4	654.0	667.8	695.2	721.8	754.0	790.4	775.5	103.1
40.0	55.37	742.6	749.9	759.7	771.4	780.0	798.4	829.0	861.0	902.0	943.9	921.3	134.6
45.0	71.87	882.1	891.8	903.0	916.1	928.5	948.6	984.0	1021.7	1069.0	1120.6	1089.8	173.3
50.0	92.71	1041.3	1052.5	1066.0	1082.4	1095.0	1120.0	1161.7	1206.4	1262.0	1321.2	1276.4	221.1

TABLE V—VAPOR PRESSURES OF MIXTURES OF ALCOHOL, ETHER, AND WATER

Temperature ° C.	71.43% ETHER; 28.57% ALCOHOL									71.43% E 28.57% W	Ether
	Pure A	95% A	90% A	85% A	80% A	70% A	60% A	40% A	20% A		
0.0	152.8	154.7	157.4	160.0	161.2	164.2	167.1	174.5	181.8	189.3	185.3
5.0	191.6	194.7	197.3	199.8	200.6	204.8	210.7	218.2	227.2	236.1	233.2
10.0	240.5	243.4	246.5	248.8	251.2	255.3	261.6	272.2	283.3	295.6	291.7
15.0	294.9	299.7	303.5	305.7	308.5	315.5	323.0	336.3	350.2	364.4	360.7
20.0	361.7	366.1	370.2	374.2	378.7	387.1	395.6	412.0	428.7	446.7	442.2
25.0	440.6	446.3	452.8	457.3	462.2	473.2	481.9	501.1	521.0	543.2	537.0
30.0	534.7	541.3	547.1	553.6	560.2	573.6	585.6	606.7	631.5	658.7	647.3
35.0	643.2	651.4	659.4	665.7	673.2	690.3	704.9	729.6	757.4	791.8	775.5
40.0	767.6	777.1	789.0	796.3	804.4	823.4	838.5	870.0	903.4	944.6	921.3
45.0	911.4	924.1	935.9	945.8	955.8	977.0	998.0	1033.6	1071.6	1122.0	1089.8
50.0	1075.1	1092.0	1105.7	1116.1	1128.8	1155.2	1178.5	1220.5	1264.3	1322.3	1276.4

Tables I and II, in which they have been compared with the values of Ramsay and Young. All determinations were carried out in duplicate and agreed within 1 mm.

The vapor pressures of the various special systems were then measured. The data appear in Tables III and VI, and have also been plotted in the form of pressure-temperature curves in the accompanying charts. All determinations were carried out in duplicate.

Note on the Hicks Method of Determining Potassium[1,2]

By R. C. Wells, R. K. Bailey, and J. G. Fairchild

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The modified chloroplatinate method of determining potassium in salts and brines described by Hicks[3] in 1913 has been used since that time for rapid survey work with generally satisfactory results. Occasionally, however, determinations on the same sample by different analysts would differ considerably, especially with percentages of the order of 1 per cent and under. This led the writers to make many experiments on the effects of slight modifications of procedure, the conclusions from which may be of general interest. It is unnecessary to repeat the full description of the method here. The purpose of this note is to emphasize certain precautions rather than to criticize the method.

The direction to wash with alcohol "of at least 80 per cent strength" suggests that 95 per cent or even absolute alcohol may be used, and the writers made a good many determinations with alcohol of these strengths. Blank tests and check determinations with known mixtures, however, show that a small excess of platinum is generally obtained with the stronger alcohol, which may range from a few tenths of a milligram to 4.0 mg. according to the care used. This was in the presence of about 0.5 gram of pure sodium chloride as the principal salt.

In most of the tests the filter papers were not drained by suction, but in other respects the Hicks procedure was carefully followed. The results led to the conclusion that each analyst should without fail make blank tests with salts similar to his unknown mixtures rather than rely too much on his ability to follow an outlined procedure. Working as uniformly as possible, corrections based on blank tests have been made occasionally when the results seemed of sufficient importance. Many tests, however, led to the belief that it is unwise to count very strongly on the significance of the tenths of a milligram of platinum and the corresponding quantities of potassium. Geologists should also understand this and not attempt to make fine distinctions between reported percentages of potassium in salt beds, brines, etc., when the method of analysis does not warrant it. This applies especially to very small percentages. The relative magnification of errors that fall entirely on a minor constituent, as in this case, suggests that for strictly accurate results with small percentages of potassium the great excess of other salts should be removed before an estimation of potassium is attempted.

The persistent positive error referred to above seems to be caused in part by the enclosure of some platinum compound in the sodium chloride. Dittmar and McArthur[4] found a similar behavior with sodium sulfate.

The results are also affected, however, by the strength of the wash alcohol. Sufficient washing with alcohol of 80 per cent by weight will dissolve out several tenths of a gram of sodium chloride, and of course with it any enclosed excess of reagent. Further, although potassium chloroplatinate is almost insoluble in absolute alcohol, it becomes increasingly soluble in weaker alcohol. Thus, with weaker alcohol any positive error is both reduced and compensated by a negative error. The extent of compensation, however, will depend on the proportions of the different salts, the volume of wash alcohol, and to an even greater extent on the "personal equation" of the analyst. According to the writers' experience 90 or 95 per cent alcohol should give better results with small percentages of potassium than either 80 per cent or absolute alcohol, but they feel that, in general, blank tests are a much better insurance against errors than reliance on definite specifications.

The improvement resulting from a double evaporation with intervening decantation of the excess of reagent does not warrant the extra expenditure of time. Adding at least 5 cc. of hydrochloric acid before beginning the evaporation is recommended, however. Also, it cannot be too strongly emphasized that the mixture of salts must be very thoroughly ground during the leaching with alcohol, and in washing chlorides out of the platinum a silver nitrate test should be required, as the platinum moss appears to retain a little chloride tenaciously.

In Table I are given some representative results that illustrate these tests.

TABLE I

(Figures are in grams)

Expt.	Conditions of Experiment	NaCl taken	KCl taken	Pt found	Theoretical Pt	Error in Pt
13W	Absolute alcohol	0.5000	None	0.0009	None	+0.0009
58W	5 cc. HCl, absolute alcohol, suction	0.5000	None	0.0004	None	+0.0004
33W	Absolute alcohol	0.5000	0.0025	0.0038	0.0033	+0.0005
16W	Absolute alcohol	0.2000	0.0500	0.0676	0.0655	+0.0021
31W	5 cc. HCl, absolute alcohol	0.5000	0.0025	0.0037	0.0033	+0.0004
50F	5 cc. HCl, absolute alcohol	0.5000	0.0060	0.0080	0.0079	+0.0001
56W	5 cc. HCl, absolute alcohol, suction	0.5000	0.0100	0.0131	0.0131	None
27B	95 per cent alcohol	0.5000	0.0160	0.0221	0.0209	+0.0012
42F	95 per cent alcohol	0.2000	0.0450	0.0609	0.0589	+0.0020
33B	95 per cent alcohol	1.5000	0.0112	0.0166	0.0147	+0.0019
55W	5 cc. HCl, 80 per cent alcohol, suction	0.5000	None	0.0002	None	+0.0002
57W	Same as preceding	0.5000	0.0100	0.0108	0.0131	−0.0023
39aF	74 per cent alcohol (80 per cent by volume)	0.5000	0.0140	0.0171	0.0183	−0.0012
41F	74 per cent alcohol (80 per cent by volume)	0.5000	0.0350	0.0442	0.0458	−0.0016
17W	74 per cent alcohol (80 per cent by volume)	0.2000	0.0500	0.0662	0.0655	+0.0007
36aF	67 per cent alcohol	0.5000	0.0020	0.0010	0.0026	−0.0016
24W	Two evaporations, absolute alcohol	0.5000	0.0037	0.0057	0.0049	+0.0008
36W	Two evaporations, absolute alcohol	0.5000	0.0250	0.0324	0.0328	−0.0004

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[1] Received May 10, 1924.

[2] Published by permission of the Director, U. S. Geological Survey.

[3] This Journal, 5, 650 (1913).

[4] *Trans. Roy. Soc. Edinburgh*, 33, 595 (1888).

A New Correction Tube for Gas Burets[1]

By F. C. Vilbrandt

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THE usual variations in temperature and pressure that take place during the course of an analysis of a gas entail an excessive amount of calculation in order to prevent errors. To obviate these numerous calculations many of the commercial sets of standard laboratory design are fitted with compensating tubes of the Peterssen[2] type attached to the measuring burets. All readings of volumes are thus rendered to a comparable basis, either to volumes under standard conditions of temperature and pressure (760 mm. pressure and 0° C.) or to readings that are compensated for any changes in temperature and pressure taking place during the course of the analysis.

The original correction tube of Hempel[3] consisted of a candelabra-shaped arrangement of three arms, too bulky to enclose any part of it in the water jacket with the buret used for measuring the gas. Peterssen's tube[2] is constructed so that the gas enclosed in the correction tube is at the same temperature as the gas being measured, but the construction of the manometer in this apparatus is such as to make it extend outside of the water jacket. It is under strain and easily broken. To build it so the manometer will be in the jacket would require a very large, unwieldy apparatus.

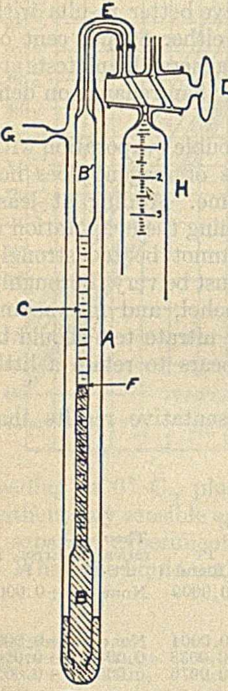

Fig. 1

The author has used the Peterssen tube for a number of years and, aside from the foregoing objections, has found it a very useful and reliable adjunct to the measuring buret in gas analysis. Attempts to instruct students and assistants in the use of this apparatus have amplified its weaknesses—that is, ease in breaking off the manometer, which is under strain, and the frequent recalibration due to breakage. This difficulty can be overcome by modifying the correction tube and manometer in such a manner that the entire apparatus can be enclosed in the water jacket holding the gas buret, with all strains in the apparatus eliminated.

Apparatus

The compensating tube, *A* (Fig. 1), has sealed into it, opening below, a tube, *C*, which serves as the manometer in place of the reverse U-shaped arrangement of Peterssen. Mercury in the well at the bottom of the compensator *A* seals off the gas enclosed in it from the gas in communication with the buret. Changes in temperature and pressure cause the mercury in *C* to rise or fall when in communication with the gas in the measuring buret. Since this apparatus is submerged in the same water in the jacket as the measuring buret, *H*, no difference in temperature exists between the gas to be measured and the gas enclosed in the compensator *A*. Compensations are made for the difference in pressure by forcing more or less gas into the part of the compensator in communication with the gas in the measuring buret by raising or lowering the level bulb on the measuring buret so that the level of the mercury meniscus reaches some point, *F*.

In the same way as the Peterssen apparatus provides for excessive pressure or vacuum in the compensator, by carelessly bringing the gas in the measuring buret in communication with the compensator, two reservoirs, *B* and *B'*, are provided at the top and bottom of the capillary, *C*. If these reservoirs are not provided, the adjustment of the mercury column might be thrown out by carelessness.

When the apparatus is to be used only for compensating changes in temperature and pressure which occur during the course of an analysis, the side arm, *G*, is unnecessary. To adjust under these conditions, an amount of air is forced into the space in tube *A* through the mercury in the wall at the bottom of *C*, sufficient to raise the level of the mercury in *C* to some etched mark on this capillary. The tube *C* should be made from tubing with marks etched upon it. It is usually rather difficult to set a mercury meniscus accurately to some predetermined etched mark, so by using a previously graduated tube, as suggested above, a mark to be selected and used for the compensating mark can be readily obtained without laboriously striving to bring it to a desired mark.

When readings are desired to read to volumes under standard conditions, a small side arm is sealed onto the compensating tube *A* to permit ready forcing of air into this chamber to bring the mercury level to the proper point, after the usual calculations for differences in temperature and pressures have been made according to the procedure used in adjusting and calibrating the Peterssen tube.[4]

After the proper precautions and calculations have been made the side arm, *G*, is sealed off. It may be advisable to seal a stopcock onto the side arm to permit the tube to be cleaned with greater ease, but the necessity of cleaning is never great if clean mercury is used and if care is exercised in manipulation to prevent any corrosive gases from entering the compensator. A stopcock on the side arm, however, detracts from the adaptability of the compensator in that it prevents its insertion in its entirety into the water jacket along with the measuring buret.

The volumes of *B* and *B'* depend largely upon the volume of the measuring buret to which it is to be attached. They must be of sufficient size to take care of the difference in expansion or contraction that gases undergo during the use of the equipment, together with a small additional volume as a factor of safety so that readjustments and recalculations due to careless manipulation of the compensator need not be so frequent. This is no different from the precautions called for in the use of the Peterssen apparatus.

This compensating device can be made in lengths suitable to the water jacket and measuring buret to be used with it. It simplicity, ease of manipulation and construction, compactness, flexibility, comparative ruggedness, and inexpensiveness suggest its use, not only for laboratory gas analysis sets, but also for the portable field sets with but a minor change at the top of the measuring buret with which the present sets are provided—i. e., sealing on a 2-way stopcock and attaching

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[1] Received January 28, 1924.

[2] *Z. anal. Chem.*, **25**, 467 (1886).

[3] Hempel-Dennis, "Methods of Gas Analysis," **1902**, p. 94. The Macmillan Co., New York.

[4] Dennis, "Gas Analysis," **1913**, p. 94. The Macmillan Co., New York.

the compensating device at this point, using a slightly larger water jacket to enable inserting the compensator alongside the measuring tube.

The accuracy of the single column mercury meniscus used in this apparatus is as great as that of the 2-level adjustment used on the Peterssen tube, and much more delicate and accurate than the wide 2-bulb Tutwiler modification of the Peterssen compensator.

Solubility of the Petroleum Hydrocarbons[1]

By C. F. Mabery

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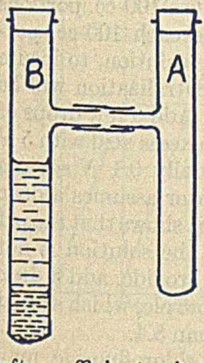
BESIDES the solubility of the petroleum hydrocarbons in one another, they are generally characterized by insolubility under different conditions in single solvents. It is only with variable mixtures of ether, in which, except the last residues of the asphaltic crudes, these hydrocarbons are all extremely soluble, and alcohol, in which they are at most only slightly soluble, that efficient solvents may be made capable of a good separation of the homologs and isologs. A method of separation based on these differences in solubility was employed as described in an earlier paper on this subject.[2] While the results then presented were sufficient to indicate wide variations in solubility, no attempts were made in that work to show precisely these differences in the hydrocarbons separated.

In taking up the study of the Midcontinental oils—using this term in a broad sense to include Oklahoma, Wyoming, Illinois, and Ohio crudes—and other southern oils, it seemed desirable to ascertain with greater precision the extent to which this method may be relied on for the separation of the individual hydrocarbons. By reference to the paper cited it appears that, starting with a given quantity of oil, the solvent dissolves out first in successive portions all the series, graduated in solubility, and after a sufficient number of repetitions the fractions show a similar graduation in physical properties. Then from this mixture of homologs and isologs, with the use of a properly graded solvent, the isologs, the lighter D-hydrocarbons, may be fractionated from the less soluble homologs, the H-hydrocarbons.

METHODS



The solvent was tried in two forms—ether 50, alcohol 50; and ether 100, alcohol 50, by volume; the former on fractions in the most soluble end, and the latter on the fractions of the least soluble end. For the manipulation of the solution two common test tubes with side tubes were used, as shown in the figure.

In the tube *B*, closed by a cork and rubber cap, a quantity of the oil with the solvent was allowed to stand at 20° C. for 2 hours, or until it settled clear after sufficient agitation. The tube *A*, also closed with a stopper and cap, was weighed, cooled to the same temperature, attached to the tube *B* as shown, and after a portion of the solution in tube *B* was decanted into it, again closed with its cap and weighed. The cork and cap were then removed and this tube was heated in an air bath to 110° C. for the removal of the solvent and moisture (from the solvent), and the tube and oil weighed. By this means it was possible to prepare and weigh a saturated solution of the solvent without loss.

In making the saturated solutions care is necessary in limiting the amount of the oil, especially in the 100–50 solvent, for a large excess of the oil is liable to dissolve the ether away from the alcohol. On this account the solubility of the Cabin Creek Fraction D-7 in the 100–50 solvent could not be determined. This often happens in extractions with too rich a solvent. The addition of more alcohol attracts the ether from the oil so quickly that the stopper may be blown out of the bottle.

RESULTS

The results obtained by this method are recorded in the table, which includes fractions of the oils described in the former paper together with those from an Oklahoma oil and from a Gulf Coast, Texas, oil. From the last two oils, a description of which has not been published, fractions were separated from distillates, −300° C. 30 mm., and from residues of these distillates. As in the earlier paper, the numbers of the fractions are taken from the H and D series, No. 1, the most soluble end, to No. 10 or 13, the least soluble end.

SOLUBILITY OF THE PETROLEUM HYDROCARBONS

	Fraction	Composition of solvent, ether-alcohol	Solubilty Per cent
Cabin Creek (+300° C., 30 mm.)	H-2	50–50	4.33
	D-2		15.86
	H-7		2.19
	D-7		4.86
	H-7	100-50	42.53
	D-7		9.60 (Ether dissolved by oil)
Rosenbury (+300° C., 30 mm.)	H-1	50–50	6.10
	D-1		19.45
	H-5		4.64
	D-5		11.26
Mecca (+300° C., 30 mm.)	H-2		7.25
	D-2		9.66
	H-7	100–50	7.58
	D-7		13.53
Sour Lake, Texas (+300° C., 30 mm.)	H-2	50–50	7.26
	D-2		16.66
	H-5	50–50	7.27
	D-5		22.04
	H-5	100–50	10.52
	D-5		25.62
Russian (+300° C., 30 mm.)	H-1	50–50	12.55
	D-1		17.60
	H-5	100–50	3.25
	D-5		6.94
Oklahoma (−300° C., 30 mm.)	H-2	50–50	28.27
	D-2		35.30
	H-9		12.22
	D-9		30.39
Oklahoma (+300° C., 30 mm.)	H-2		8.40
	D-2		16.54
	H-13		4.72
	D-13		6.82
	H-13	100–50	11.00
	D-13		15.82
Gulf Coast, Texas (−300° C., 30 mm.)	H-2	50–50	20.24
	D-2		29.28
	H-8	50–50	9.83
	D-8		15.54
Gulf Coast (+300° C., 30 mm.)	H-2		9.16
	D-2		18.84
	H-10		6.52
	D-10		12.20
	H-13	100–50	4.73
	D-13		9.57

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[1] Received July 7, 1924.

[2] Mabery, THIS JOURNAL, 15, 1233 (1923).

Fluorine Determination in Nickel-Depositing Solutions[1,2]

By L. D. Hammond

BUREAU OF STANDARDS, WASHINGTON, D. C.

INASMUCH as fluorides have recently been employed in nickel-depositing solutions,[3] a method for the analysis of such solutions is desirable. In this paper a method is described by which fluorine can be determined in the presence of nickel sulfate, boric acid, and other usual constituents of nickel baths.

If the nickel is removed by electrolysis of the ammoniacal solution, and any precipitate of ferric hydroxide is filtered out, the filtrate will contain, chiefly as ammonium salts, fluoride, borate, sulfate, and possibly chloride. The problem therefore involves the determination of the fluorine in such a solution.

The precipitation and filtration of calcium fluoride, either directly,[4] or together with calcium carbonate,[5] or with calcium oxalate,[6] proved so slow as to be unsuitable for control analysis.

Attempts were made to apply a volumetric method[7] in which, after the addition of sodium chloride, the fluoride is titrated with ferric chloride, forming a precipitate of sodium ferric fluoride (Na_3FeF_6). This method was inapplicable, because it was not found possible to regulate the pH of the solutions containing ammonium borate so that the solution was neither acid enough to dissolve the double fluoride nor alkaline enough to precipitate basic ferric compounds.

Methods based upon the evolution of volatile compounds of fluorine were not attempted, as they would probably not be adaptable for laboratory control work.

The method found most satisfactory is an adaptation of that proposed by Stark,[8] and subsequently confirmed by Adolph,[9] for the determination of fluorides in neutral solutions. This method depends upon the precipitation of lead chlorofluoride (PbFCl) by the addition of lead chloride solution. As this precipitate is appreciably soluble in pure water, it is washed with lead chloride solution, in which it is less soluble.

TABLE I—DETERMINATION OF FLUORINE

	Composition of Solution			Weight of PbFCl from 10 Cc.	
Expt.	NaF	H_3BO_3	$NiSO_4$	Calcd. Grams	Found Grams
1	0.2 *N*	..	..	0.5233	0.5295
2	0.2 *N*	..	..	0.5233	0.5297
3	0.2 *N*	..	..	0.5233	0.5290
4	0.2 *N*	..	..	0.5233	0.5291
5	0.2 *N*	0.5 *M*	..	0.5233	0.5300
6	0.2 *N*	0.5 *M*	..	0.5233	0.5301
7	0.2 *N*	0.5 *M*	2 *N*	0.5233	0.5253
8	0.2 *N*	0.5 *M*	2 *N*	0.5233	0.5213

The sodium fluoride used in the following experiments was prepared from a C. P. salt which was free from sulfates, chlorides, and carbonates, but contained a small amount of calcium fluoride. This was removed by filtration and the solution was evaporated to dryness in a platinum dish. The product was powdered and kept in a platinum crucible within a desiccator.

Determinations of fluorine were made in solutions of this salt, to which in some cases nickel sulfate and boric acid were added. Such portions of the procedure as were required by the constituents present were employed. The results are shown in Table I.

From Table I it is seen that the results are fairly reproducible, but are usually somewhat high. It does not appear feasible to obtain by this method with reasonable precautions an accuracy greater than about 1 per cent of the amount present. This accuracy is, however, usually adequate for works control of nickel-plating solutions.

PROCEDURE

Application of this method to a nickel solution is as follows: (The method may require modification if unusual constituents are present.)

To a 25-cc. sample add 50 cc. of water and 25 cc. of ammonium hydroxide (specific gravity, 0.90), and remove the nickel by electrolysis in the usual way. Filter the solution into a 250-cc. graduated flask and wash the precipitate (chiefly ferric hydroxide) with hot water. Add a few drops of a 0.4 per cent aqueous solution of bromophenol blue,[10] and neutralize the solution with nitric acid. Add enough nitric acid—e. g., 5 cc. of 5 *N* HNO_3—to make the solution approximately 0.1 *N* in nitric acid. In order to precipitate the sulfate as $PbSO_4$, add a slight excess of a lead nitrate solution (2 *N*), the volume of which may be calculated approximately from the nickel content if no other sulfates are present. The lead sulfate must be precipitated in an acid solution in order to avoid co-precipitation of lead fluoride or chlorofluoride. The solubility of lead sulfate in 100 cc. of 0.1 *N* nitric acid is about 11 mg. Some of this is probably precipitated subsequently with the chlorofluoride, which may account for the high results.

Dilute the solution to the 250-cc. mark, mix well, and pour at once into a Pyrex beaker, which is less attacked by the free hydrofluoric acid than is ordinary glassware. Filter the solution without washing the precipitate, and use 100-cc. portions of the filtrate for duplicate analyses. To each 100-cc. portion add about 2 cc. of *N* sodium chloride solution, to insure that any precipitate formed during the neutralization will be lead chlorofluoride and not lead fluoride. Add a few drops of bromophenol blue, neutralize most of the excess acid with 5 *N* sodium hydroxide, and finally add gradually 0.1 *N* sodium hydroxide until a fresh drop of the indicator assumes a deep blue color when it enters the solution. This shows that the pH is greater than 4.6. To make sure that the solution is not sufficiently alkaline to precipitate lead hydroxide, add a drop of a 0.4 per cent solution of bromocresol purple, which should turn yellow, showing that the pH is less than 5.4.

During the neutralization some lead chlorofluoride may separate. To precipitate it completely, add 300 cc. of a saturated solution (0.08 *N*) of lead chloride and allow to stand overnight. Filter through a weighed Gooch crucible, wash by decantation with a half-saturated (0.04 *N*) solution of lead chloride, and finally with about 20 cc. of cold water. Dry at 150° C. for 2 hours, cool, and weigh.

The factor for computing from PbFCl to NaF is 0.161. The weight of PbFCl from a 10-cc. sample—i. e., 100 cc. of the 250 cc. of solution prepared from a 25-cc. sample—multiplied

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[1] Received July 11, 1924.

[2] Published by permission of the Director, U. S. Bureau of Standards.

[3] Blum, *Trans. Am. Electrochem. Soc.*, **39**, 459 (1921).

[4] Berzelius, *Schw. J.*, **16**, 426 (1816).

[5] Rose, *Ann.*, **72**, 343 (1849).

[6] Stark and Thorin, *Z. anal. Chem.*, **51**, 14 (1912).

[7] Guijot, *Compt. rend.*, **71**, 274 (1870); Greeff, *Ber.*, **46**, 2511 (1913).

[8] *Z. anorg. Chem.*, **70**, 173 (1911).

[9] *J. Am. Chem. Soc.*, **37**, 2509 (1915).

[10] Clark, "The Determination of Hydrogen Ions," 2nd ed., 1922, p. 80.

by the factor 0.382 gives the fluoride normality in the original sample.

In those cases in which the volume of the lead sulfate precipitate in the 250-cc. flask is appreciable, an appropriate correction should be made. This may be roughly calculated, as the volume of the lead sulfate (specific gravity 6.2) is about 0.024 cc. for each cubic centimeter of normal sulfate solution originally present. In Expts. 7 and 8 (Table I), with 25 cc. of a 2 *N* nickel sulfate solution, this is equivalent to $2 \times 25 \times 0.024 = 1.2$ cc. of $PbSO_4$—i. e., 0.5 per cent of the 250 cc. The results given for these experiments include deductions of 0.5 per cent (0.0025 gram) based on this correction.

ACKNOWLEDGMENT

Acknowledgment is due to William Blum, under whose direction this work was conducted.

Variation of Stress-Strain Properties of Nitrocellulose-Camphor Mix with Its Composition[1,2]

By Paul Heymans and George Calingaert

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IT IS of interest for photoelastic work to be able to obtain celluloids of any specified elastic properties.[3] It is well known that the physical properties of celluloid vary with its composition. Nishida[4] has studied the comparative elastic properties of celluloids made with cellulose of different origins. As the various materials which he examined did not have as sole variable the origin of the cellulose, his results do not allow a reliable interpretation. Nishida states, as a general qualitative condition, that the physical properties of celluloid are much affected by the several operations during the manufacturing processes, and especially depend upon the nature and properties of the loading materials.

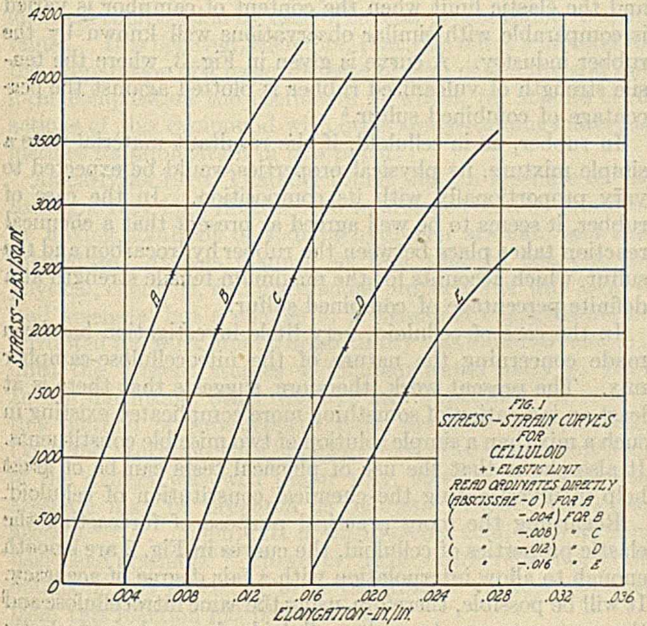

FIG. 1
STRESS-STRAIN CURVES FOR CELLULOID
+ = ELASTIC LIMIT
READ ORDINATES DIRECTLY
(ABSCISSAE -0) FOR A
(" -.004) FOR B
(" -.008) " C
(" -.012) " D
(" -.016 " E

TESTS ON CELLULOIDS OF VARYING COMPOSITION

From preliminary tests it appeared that homogeneous celluloid of different chemical compositions could be obtained only by varying its composition when manufactured. Different samples of celluloid were prepared, care being taken to use raw materials of the same origin and to put them through the same manufacturing processes, varying the content in camphor and adding ester gum in one case.

The stress-strain curves were determined on specimens of rectangular cross section measuring 1 inch by 0.25 inch, and 4 inches in gage length.

The results, together with the relative content of camphor and ester gum, are summarized in Table I and Figs. 1 and 2.

The elastic limit was taken at the point where the stress-strain curve departs from a straight line. A more accurate definition of the elastic limit, such as a given increment of the elongation per unit of charge, could not be made on account of the plasticity of the materials. Single variations of the elongation differed appreciably, while the mean slope of the stress-strain curve was still constant.

TABLE I

Sample	Camphor Per cent	Ester gum Per cent	Young's modulus of elasticity Lbs./sq. in.	Elastic limit Lbs./sq. in.
A	9.5	0	350,000	2450
B	8.8	7.2	337,000	2025
C	17.8	0	357,000	2425
D	24.2	0	308,000	1875
E	38.6	0	254,000	1525

Although the elastic limits should, therefore, not be considered too accurate, the moduli of elasticity are more reliable, since for a given stress-strain curve a slight displacement of the elastic limit will affect the value of the modulus much less.

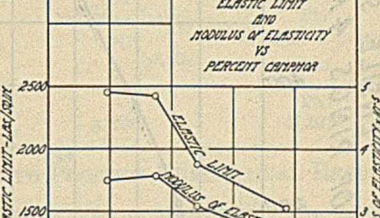

FIG. 2
ELASTIC LIMIT AND MODULUS OF ELASTICITY VS PERCENT CAMPHOR

Comparing Samples *A* and B, in which the ratio of camphor to nitrocellulose is the same, the only difference being the addition of ester gum, it is seen that ester gum lowers the elastic limit and the modulus of elasticity. Samples *A*, *C*, *D*, and *E* constitute a series in which the percentage of camphor varies from 9.5 to 38.6. Fig. 2 shows the effect of the camphor content on the elastic limit and the modulus of elasticity. It is seen that the modulus of elasticity does not vary constantly with the percentage of camphor. A maximum is reached at

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[1] Presented before the Division of Cellulose Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] This work was undertaken by the Photoelastic Laboratory of the Massachusetts Institute of Technology at the request of the Research Laboratory of the General Electric Company.

[3] Heymans, *Am. Mech. Eng.*, **44**, 513 (1922).

[4] THIS JOURNAL, **8**, 1099 (1916).

TABLE II—STRESS-STRAIN PROPERTIES OF CELLULOID SAMPLES *A* TO *E*

(Gage length 4 inches; cross section 1 × 1/4 inch. *S*, strain in pounds per square inch; *E*, elongation in inches per inch)

A		*B*		*C*		*D*		*E*	
S	*E*	*S*	*E*	*S*	*E*	*S*	*E*	*S*	*E*
106.5	0	81	0	116	0	988	0	76.1	0
213	0.00027	161	0.00027	232	0.00025	198	0.00031	152	0.000279
320	0.00053	242	0.00045	348	0.00057	296	0.00060	228	0.000587
426	0.00086	322	0.00071	463	0.00089	395	0.00090	304	0.000883
532	0.00115	403	0.00095	579	0.00119	494	0.00120	381	0.001180
638	0.00143	484	0.00118	695	0.00151	593	0.00150	457	0.001467
745	0.00171	575	0.00142	811	0.00185	692	0.00180	533	0.001745
873	0.00209	646	0.00164	926	0.00219	790	0.00220	609	0.002060
957	0.00236	727	0.00188	1040	0.00250	889	0.00250	685	0.002370
1064	0.00267	807	0.00216	1158	0.00273	988	0.00280	762	0.002655
1170	0.00294	888	0.00240	1273	0.00319	1087	0.00320	837	0.002960
1278	0.00327	968	0.00261	1390	0.00353	1186	0.00350	914	0.003070
1384	0.00362	1050	0.00285	1506	0.00388	1284	0.00390	989	0.003611
1490	0.00393	1130	0.00308	1620	0.00424	1382	0.00420	1065	0.003910
1598	0.00427	1210	0.00335	1738	0.00460	1481	0.00460	1140	0.004240
1704	0.00459	1290	0.00362	1853	0.00495	1580	0.00500	1216	0.004620
1810	0.00492	1372	0.00384	1970	0.00530	1679	0.00535	1294	0.004940
1917	0.00527	1452	0.00411	2083	0.00567	1778	0.00580	1368	0.005240
2020	0.00561	1533	0.00438	2200	0.00604	1876	0.00610	1445	0.005580
2130	0.00598	1613	0.00468	2320	0.00642	1995	0.00670	1521	0.005940
2235	0.00635	1695	0.00495	2430	0.00683	2075	0.00700	1598	0.006275
2340	0.00672	1773	0.00519	2550	0.00734	2173	0.00750	1675	0.006620
2450	0.00738	1855	0.00545	2665	0.00772	2271	0.00790	1750	0.006980
2560	0.00749	1936	0.00573	2780	0.00815	2370	0.0084	1827	0.007370
2660	0.00784	2020	0.00601	2895	0.00855	2470	0.0089	1900	0.007800
2770	0.00831	2100	0.00628	3010	0.00900	2570	0.0093	1978	0.008000
2875	0.00868	2180	0.00656	3125	0.00946	2660	0.0098	2055	0.008670
2980	0.00910	2260	0.00681	3245	0.00995	2763	0.0102	2130	0.009160
3085	0.00953	2340	0.00704	3360	0.01044	2660	0.0107	2205	0.009480
3195	0.00997	2420	0.00745	3475	0.01107	2960	0.0113	2280	0.010050
3300	0.01043	2500	0.00772	3590	0.01158	3060	0.0118	2360	0.010530
3410	0.01085	2580	0.00801	3710	0.01221	3160	0.0125	2435	0.01100
3510	0.01130	2660	0.00831	3820	0.01270	3260	0.0132	2510	0.01161
3620	0.01186	2740	0.00867	3940	0.01340	3360	0.0140	2585	0.01224
3725	0.01234	2823	0.00893	4050	0.01400	3455	0.0147	2665	0.01295
3835	0.01295	2905	0.00928	4170	0.01478	3555	0.0156		
3940	0.01349	2985	0.00962	4280	0.01539				
4045	0.01394	3065	0.00993	4400	0.01618				
4150	0.01457	3145	0.01020	4520	0.01695				
4260	0.01539	3225	0.01040	4630	0.01850				
		3310	0.01088						
		3390	0.01120						
		3470	0.01150						
		3550	0.01187						
		3630	0.01225						
		3710	0.01261						
		3790	0.01300						
		3875	0.01340						
		3950	0.01383						
		4030	0.01433						

about 18 per cent of camphor. Below and above this content the modulus decreases again, but faster on one side than on the other.

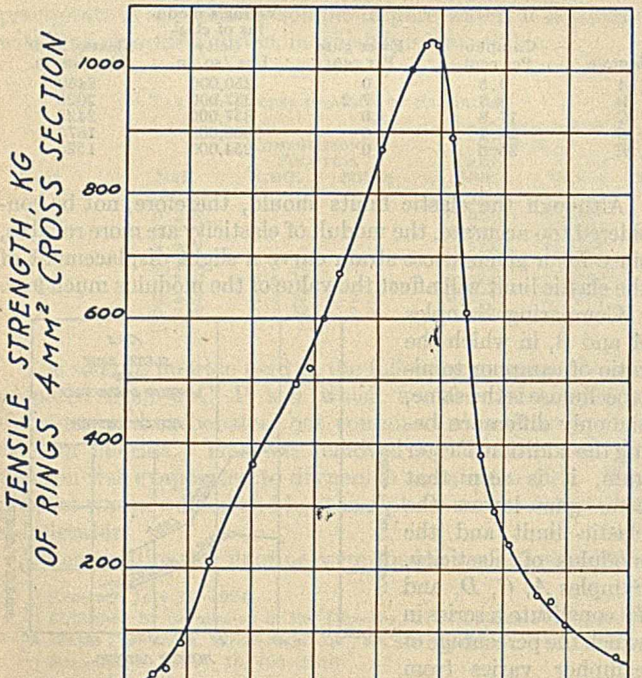

FIG. 3—TENSILE STRENGTH OF VULCANIZED RUBBER

DISCUSSION

The existence of a maximum in the modulus of elasticity and the elastic limit when the content of camphor is varied is comparable with similar observations well known by the rubber industry. A curve is given in Fig. 3, where the tensile strength of vulcanized rubber is plotted against the percentage of combined sulfur.[5]

In rubber, as in celluloid, if the resultant material were a simple mixture, its physical properties would be expected to vary proportionally with its composition. In the case of rubber, it seems to be well agreed at present that a chemical reaction takes place between the rubber hydrocarbon and the sulfur, which accounts for the maximum tensile strength at a definite percentage of combined sulfur.

In the case of celluloid, very little investigation has been made concerning the nature of the nitrocellulose-camphor mix. The present work, therefore, suggests that there is at least an indication of something more complicated existing in such a mix than a simple solution of two miscible constituents. It also shows that the use of physical tests can be of great help in investigating the chemical constitution of celluloid.

Regarding the more practical purpose of forecasting the elastic properties of celluloid, the curves in Fig. 2 are smooth enough to allow interpolation with a fair degree of accuracy. It will be possible, therefore, using the same nitrocellulose and the same process, to make celluloid of any desired elastic properties between the limits given for Samples *A* to *E*, the concentrations in camphor used here being about the permissible limit, without obtaining a product that is either brittle or plastic. It can be expected that, the elastic properties of any given sample of celluloid being determined, their variation with the percentage of camphor can also be predicted from the foregoing data.

The authors wish to thank the Research Department of E. I. du Pont de Nemours and Company for coöperation in making up the samples used in this investigation.

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[5] Whitby, "Plantation Rubber and Testing of Rubber," p. 316.

Preparation of a Basic Arsenate of Lead of Definite Composition[1]

By L. R. Streeter and R. W. Thatcher

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A basic arsenate of lead having the composition indicated by the formula $Pb_4(PbOH)(AsO_4)_3$ can be prepared by the reaction between lead subacetate and disodium arsenate in theoretical amounts.

In practice, in order to secure a product of satisfactory physical properties, it is desirable to use a slight excess of the arsenate, which invariably results in the conversion of a small proportion of the basic arsenate of lead into the normal orthoarsenate, the amount of the change depending upon the excess of disodium arsenate used and the time it is left in contact with the precipitate before filtering.

In preparation for some further studies of the insecticidal and fungicidal effects of various mixtures of lead arsenate with other spray-forming materials, the writers desired to prepare stocks of the different arsenates of lead in pure form and of known composition. No difficulty was experienced in securing a satisfactory supply of the acid arsenate ($PbHAsO_4$), but attempts to produce a basic arsenate of lead by the different methods which had been suggested by Robinson and Tartar[2] or McDonnell and Smith[3] failed to give a product which had a uniform composition from different successive trials, even when repeated under as nearly uniform conditions as could be obtained in this laboratory. None of the possible conditions or processes for the action of ammonia on di-lead arsenate gave a product sufficiently uniform in composition and properties to be satisfactory for these investigations.

Recourse was finally taken to the lead subacetate method. A product of satisfactory physical form, which showed identical composition by each of several preparations, was obtained. It is believed, therefore, that this offers a method for the preparation of a basic arsenate of lead of definite and uniform composition the usefulness of which, for studies of reactions of this compound with other spray-forming materials, justifies its publication in this paper.

As early as 1910, Thatcher found that an arsenate of lead having a very high ratio of lead to arsenic could be produced by mixing solutions of sodium hydrogen arsenate and lead subacetate. It was planned at that time to test out the physical, chemical, and insecticidal properties of this form of lead arsenate, but a change in professional engagements interrupted the work and no opportunity was found to resume it until the present studies were inaugurated early in 1923. In the meantime, other workers had apparently discovered this method of producing a basic arsenate of lead, since Cook and McIndoo,[4] in a bulletin issued after the present work of the writers was well under way, state that "basic lead arsenate may be prepared as follows: Produce basic lead acetate * * *. Then, mix it with arsenic acid, thus forming basic lead arsenate." However, no literature reference to the details of this procedure or to the kind of product obtained from this reaction has been found.

PROCEDURE

A dilute solution of lead subacetate was prepared according to the method used in sugarhouse laboratories, as outlined by Spencer,[5] which is briefly as follows:

> Heat nearly to boiling, for about one-half hour, 430 grams of neutral acetate of lead, 130 grams of litharge, and 1000 cc. of water. Cool, settle, and decant the clear solution.

To 100 cc. of this solution, diluted with 1500 cc. of water, a solution of disodium arsenate was added in slight excess, the mixture being kept at ordinary room temperature. The precipitate was washed several times with water, by decantation after centrifuging, until free from soluble ions.

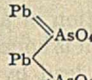
RESULTS

Several lots were made by this process on various occasions, with no special care to keep the conditions exactly uniform—in fact, at least one preparation was made with quite different concentrations of solutions than were used in other cases. The precipitates obtained were uniformly satisfactory in physical properties and, when filtered off, dried, and analyzed, showed uniform composition within the limits of experimental error. Five lots showed the following composition of the dry material:

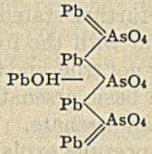
Sample	Lead oxide Per cent	Arsenic oxide Per cent	Ratio PbO to As_2O_5
1	74.45	23.60	3.155
2	74.71	23.64	3.156
3	74.72	23.60	3.166
4	74.50	23.47	3.170
5	74.64	23.58	3.161
Theoretical for $Pb_4(PbOH)(AsO_4)_3$			3.239

These figures indicate that the product obtained by this procedure apparently does not contain quite so high a ratio of lead to arsenic as would the theoretical monohydroxy lead arsenate of the formula $Pb_4PbOH(AsO_4)_3$. This formula is the simplest one and requires the lowest ratio of PbO to As_2O_5 of any that can be assigned to a monomolecular basic arsenate of lead, as shown by the following formulas:

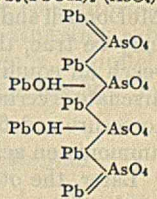
$Pb_3(AsO_4)_2$



$Pb_4(PbOH)(AsO_4)_3$



$Pb_5(PbOH)_2(AsO_4)_4$



Ratio PbO to As_2O_5 2.911 3.239 3.397

REASONS FOR FAILURE TO PRODUCE THEORETICAL RESULTS

Two possible explanations for the apparent failure of this product to conform in composition to the simplest theoretical composition of basic arsenate of lead suggested themselves. One is that the methods of determination of lead and arsenic available for the analysis of this kind of products do not give exactly true values, as has been claimed by some investigators. The other is that the product itself, instead of being a definite compound, is actually a "solid solution" of neutral

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[1] Presented before the Division of Agricultural and Food Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] Oregon Agr. Expt. Sta., *Bull.* **128** (1915).

[3] *J. Am. Chem. Soc.*, **38**, 2027 and 2366 (1916); **39**, 937 (1917).

[4] *U. S. Dept. Agr., Bull.* **1147** (1923).

[5] "A Handbook for Chemists of Beet Sugar Houses and Seed Culture Farms," **1897**. John Wiley & Sons, Inc.

and basic arsenates of lead, as suggested by McDonnell and Smith.

To clear up this point, the products were submitted to the action of ammonia under varying conditions in order to determine whether either a basic arsenate of a higher ratio of lead to arsenic or one that would be uniform in composition and would have a ratio of lead to arsenic to correspond to one of the theoretical simple formulas could be obtained in this way. Several typical results, selected from a considerably larger number of experiments, are shown in Table I, the results being the average of closely agreeing duplicate or triplicate determinations in each case.

TABLE I—EFFECT OF ACTION OF AMMONIA UNDER VARYING CONDITIONS UPON BASIC ARSENATE OF LEAD

Preparation	Water Cc.	Ammonia (10%) Cc.	Time of heating	Changes of ammonia	Composition of Product: PbO %	As_2O_5 %	Ratio PbO to As_2O_5
A	500	25	3 hrs.	1	75.75	23.15	3.276
		10	3 hrs.	1	75.97	23.03	3.299
B	500	50	3 hrs.	1	75.18	23.27	3.231
		25	24 hrs.	1	75.11	23.30	3.224
		25	3 days	1	75.61	23.18	3.262
		25	7 days	1	75.58	22.98	3.289
		25	14 days	Many	76.23	22.67	3.362
C	500	25	5 hrs.	2	75.64	23.07	3.278
	2000	100	3 hrs.	1	75.54	23.38	3.231
	500	25	8 hrs.	3	75.46	23.16	3.258

A—50 grams freshly precipitated paste; heated to 80°–85° C.
B—25 grams dry solid, Sample 5; heated to 80°–85° C.
C—50 grams freshly precipitated paste, Sample 4; heated to boiling.

These data clearly indicate that the failure of the original products to show a composition which approximates the theoretical for monohydroxy arsenate is not due to faulty analytical methods. The same products, after boiling with ammonia, invariably gave higher percentages of PbO and lower percentages of As_2O_5, with the alterations in these percentages in the direction and of the magnitude which would be required by a progressive extraction of the arsenate radical and change of lead to basic (PbOH) groups in the compound. Hence, it is concluded that a chemical change in the products toward the theoretical composition of more basic arsenates was produced by the action of ammonia on them.

On the other hand, the data fail to indicate any possibility of securing in this way a definite compound agreeing with any simple theoretical formula for a basic orthoarsenate of lead. It will be seen that in most cases, after heating with ammonia for a few hours, the ratio of PbO to As_2O_5 in the products exceeds that required by the formula $Pb_4(PbOH)(AsO_4)_3$; but that, even after 2 weeks' heating on a boiling water bath, with frequent changes of ammonia to insure the constant presence of a considerable excess of the reagent, the product did not reach the basic composition represented by the formula $Pb_5(PbOH)_2(AsO_4)_4$. Hence it appears that, while McDonnell and Smith's statement concerning "solid solutions" may be true, their further statements that the reaction will reach an equilibrium with the formation of a definite basic arsenate is certainly not true, and that it is hopeless to attempt to secure a definite basic arsenate of lead by the action of ammonia on acid lead arsenate.

Later, the other possible explanation of the failure of our products to conform exactly to the theoretical composition on monohydroxy lead arsenate was investigated. It seemed likely that, since disodium arsenate (HNa_2AsO_4) contains replaceable hydrogen and is therefore an acid salt, the excess of this salt in the mixtures might react with the basic lead arsenate, producing an equivalent amount of neutral lead arsenate and thereby lowering the ratio of PbO to As_2O_5 in the precipitated material. It had previously been found not feasible to carry on the reaction with an excess of the subacetate of lead, since under these conditions the precipitated lead arsenate is more or less colloidal in character, and it is impossible to filter and wash it satisfactorily for the purpose of securing the kind of pure materials desired for this work. It is necessary to carry on the reaction with a slight excess of disodium arsenate in order to get a rapid-settling, easily washable material, and there is, therefore, the possibility that this excess may react with the basic arsenate of lead as previously indicated.

A series of tests of this reaction was therefore carried out, using varying excessive amounts of disodium arsenate for the precipitation in some cases and in others allowing the precipitated basic arsenate of lead to stand for longer periods of time in contact with the mother liquor containing the excess of disodium arsenate. The resulting precipitates were filtered, washed, dried, and analyzed as before, except that in this case the combined water was determined by loss on ignition, in order to secure a check upon the accuracy of the other determinations. The results of some of these tests are shown in Table II.

TABLE II—EFFECT OF ACTION OF EXCESS OF DISODIUM ARSENATE UPON BASIC ARSENATE OF LEAD

Test No.	CONDITIONS	Composition of Product: PbO %	As_2O_5 %	Combined water %	Total %	Ratio PbO to As_2O_5
6*A*	Considerable excess arsenate, filtered immediately	74.64	24.32	0.76	99.72	3.070
6*B*	Same as 6*A*, but stood in mother liquor 3 hours	73.93	25.10	0.77	99.80	2.945
11*A*	Slight excess arsenate, filtered immediately	75.08	24.07	0.85	100.00	3.116
11*B*	Same as 11*A*, but stood in mother liquor 3 hours	75.03	24.30	0.86	100.19	3.087
10*A*	Very slight excess arsenate, filtered immediately	75.20	23.94	0.88	100.02	3.141
10*B*	Same as 10*A*, but stood in mother liquor 3 hours	75.14	24.18	0.95	100.27	3.107

These results clearly show that an excess of disodium arsenate reacts with precipitated monohydroxy lead arsenate, converting it into neutral lead arsenate. In Test 6*B* sufficient excess of the disodium arsenate was present and sufficient time elapsed for the reaction to go nearly to the point of complete transformation of the basic arsenate of lead into the neutral form (ratio PbO to As_2O_5 equals 2.911).

CONCLUSION

It seems to be clear, therefore, that the reaction between lead subacetate and disodium arsenate in theoretical proportions undoubtedly produces monohydroxy lead arsenate. But since the precipitate is more or less colloidal in form and difficult to free from impurities unless a slight excess of the disodium arsenate is used, in actual practice there will always be a slight admixture of the neutral arsenate of lead with the monohydroxy lead arsenate, the amount of this being determined by the quantity of excess of disodium and the time of contact of this excess with the original precipitate. The writers have shown, however, that, working under feasible laboratory conditions, it is possible to secure a product which is uniform in composition in successive preparations, of fine physical properties, and generally satisfactory for chemical and insecticidal studies in which a basic arsenate of lead is desired.

Gas Engineering Chair at Hopkins

The establishment of a chair of gas engineering at Johns Hopkins University by the Southern Gas Association has recently been announced by W. H. Taylor, vice president of the Georgia Railway and Power Company, Atlanta, Ga., and president of the Southern Gas Association, which is financing the project. Plans for the course have been worked out by a special committee under Edward L. Rieha, gas engineer of Baltimore, and approved by the Johns Hopkins authorities.

Examination of Liquid Glue[1]

By Donald K. Tressler

Mellon Institute of Industrial Research, Pittsburgh, Pa.

Inasmuch as the various brands of liquid glue vary widely in their properties, standard tests for the grading of these glues should be adopted. Permanence, adhesiveness, and hygroscopicity are properties of first importance in glues to be used for joining wood. The breaking of joints at various conditions of temperature and humidity gives an accurate measure of the hygroscopicity and strength of a glue. Determinations of adhesiveness (strength) are of little value unless the temperature and humidity at which the joints were dried are known. The permanence of a liquid glue may be determined by storing a sample at 37.5° C. for a short period.

The quality of the various brands and grades of liquid glue on the market varies greatly. The best liquid glues possess strength and all-round qualities equal to those of a good grade of hide glue. Some liquid glues which are sold at approximately the same price are of little value save when used as size or mucilage. An expert accustomed to handling large quantities of liquid glue may find defects by merely making a superficial examination, but a careful chemical and physical examination is required to estimate accurately the value of any glue, either solid or liquid.

Properties Controlling Quality of Liquid Glue

The properties desired in a liquid glue depend upon the use to which it is put. Glue suitable for joining work is considered the best type of liquid glue for general use. Therefore, the discussion of properties will be interpreted from the viewpoint of the joiner. If the general properties of a liquid glue are determined, the uses to which it is suited may readily be seen.

Liquid glues used for joining work should possess a high tensile and shearing strength under all ordinary weather conditions. Properties controlling strength include hygroscopicity, chemical composition, viscosity, and permanence. The gel point determines the viscosity and flow at low temperature. If a liquid glue is to be used in cool rooms, its gel point must be relatively low. The color and opacity of the liquid glue affect the appearance of the joint. Clear glues appear darker on wood than opaque glues provided the opacity is not caused by dark-colored pigments—viz., blues, blacks, or browns.

Determination of Viscosity and Flow

The terms "viscosity" and "flow" as ordinarily used are nearly synonymous. By a good flow is usually meant a low viscosity. Certain other factors influence the flow of glue, the chief of these being the amount of suspended matter present, which causes uneven flow. A semigelatinous condition also causes a poor, uneven flow. Thus, a liquid glue may have an excellent flow at 30° C., but its flow may be irregular at 15° C. Therefore, we may consider the flow of a liquid glue as dependent upon the viscosity, the gel point, and the number and size of suspended particles contained in it.

The viscosity of liquid glues is dependent upon the temperature, concentration, and chemical composition. The higher the temperature, the lower the viscosity becomes. As the concentration of dry glue in the solution becomes greater, the viscosity of the glue increases. In general, the greater the average molecular weight of the gelatins, gelatoses, gelatones, and peptides, the higher the viscosity of the liquid glue. The presence of foreign substances in the liquid glue alters the viscosity. Certain substances, such as some nitrates, chlorides, and salicylates, lower the viscosity of the liquid glues; while others, such as borates and some fluorides, increase the viscosity of the solution. The presence of these foreign substances in the solution also affects the gel point of the glue, and therefore alters the flow of the glue, because of the change in viscosity and gel point.

The viscosity of most liquid glues is easily determined in a Stormer viscometer at ordinary temperatures. At elevated temperatures a MacMichael instrument will give more accurate results than can be obtained with the Stormer instrument. The ordinary Stormer viscometer is equipped with a 100-gram weight. This weight is too light for use in determining the viscosity of most liquid glues at temperatures below 25° C. A 500-gram weight may be used in place of the lighter capsule for the more viscous liquid glues.

A viscosity determination is of no value unless the temperature at which the determination is made is noted. Viscosity determinations are of most value when the viscosity of a given glue is determined at two or more temperatures. For instance, let us suppose that the viscosity of a liquid glue at 25° C. is 50 revolutions per minute in a Stormer viscometer equipped with a 500-gram weight. This is a relatively low viscosity. But if the viscosity of this same glue is determined at 15° C. in the same machine and found to be 5 revolutions per minute, which is a high viscosity, we can draw the following conclusions: Since its viscosity increases so rapidly with decreasing temperatures and since it becomes so viscous at 15° C., its gel point is slightly below 15° C. (probably about 13° C.). Its low viscosity and high gel point indicate that it has a relatively high water content; therefore a large amount of it would have to be applied in gluing joints.

If the viscosity of a glue from 5° to 50° C. is plotted against the temperature on coördinate paper, the curve obtained is of considerable value. It gives much information as to the flow of the glue at various temperatures, the concentration of the glue solution, and the presence of gel-inhibiting substances. Moreover, the gel point of the glue is accurately indicated by the point at which the viscosity reaches "infinity."

Ash Content and Composition of the Ash

It is very difficult to obtain glue ash free from carbon without volatilizing some chlorides and other easily volatilized inorganic substances. For this reason the simple ignition of a weighed sample of glue does not give a true sample of ash.

The samples used in the determination of solid matter may be used for the ash determinations. They should be moistened with standard calcium acetate solution according to the method adopted by the Association of Official Agricultural Chemists.[2] After drying on a water bath the samples should be ignited, gently at first and then more vigorously,

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[1] Presented before the Division of Leather and Gelatin Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] *Bur. Chemistry, Bull.* **107**, 21 (1907).

until all the carbon is burned. The addition of the calcium acetate prevents the fusion of the ash and thus permits complete ashing. The weight of the ash must be corrected for lime and carbon dioxide.

Aside from indicating the presence of inorganic materials in the glue, the total ash content is of little value as an index of the quality of the liquid glue. An examination of the ash is of much more value to the chemist. The presence of large amounts of chlorides in the ash indicates that the glue is hygroscopic because of the presence of hygroscopic chlorides. Calcium and magnesium chlorides absorb moisture rapidly; sodium and potassium chlorides are much less hygroscopic yet even their presence weakens glues in damp weather. The chloride content of liquid glue is considered of such importance by some fish glue manufacturers that a chloride determination is made on the ash of a sample of each batch of glue. The fish glues are then graded according to the percentage of chlorides that they contain. The best fish glues should not contain more than 0.02 per cent of chlorine as chlorides.

DETERMINATION OF DRYING PROPERTIES

The relative rate of drying may be judged fairly by comparing the drying properties of a sample of liquid glue when spread on a glass plate with those of a standard sample. The time required for a layer 0.2 cm. in depth to dry, at a given humidity and temperature—e. g., 25° C. and 70 per cent humidity—should be noted and compared with the standard. The properties of the dried film should be observed. The best grades of liquid glues dry to transparent, glossy films, which are strong and brittle. If the dried film is easily powdered, the glue is of little value for most purposes.

DETERMINATION OF HYGROSCOPIC PROPERTIES

If the completely dried film of glue is placed in a constant-temperature, constant-humidity room, or in a humidor over a sulfuric acid solution, it absorbs some moisture. The gain in weight is an index of the hygroscopic properties of the glue. For example, if a small amount of liquid glue is dried to constant weight on a watch glass over concentrated sulfuric acid, and then placed on a humidor at 25° C. over 80 per cent sulfuric acid and allowed to remain until its weight is constant, the gain in weight is an excellent index of the hygroscopicity of the sample of glue. Single determinations of this sort are not of great value, but if a record is kept of the results obtained from a series of liquid glues, the data increase in value.

DETERMINATION OF THE JOINT STRENGTH OF LIQUID GLUES

In the manner in which strength tests are ordinarily carried out on glues, they are of little value. Even careful, accurate experimenters are unable to check their results closely. One factor of extreme importance has heretofore been neglected. Weather conditions—temperature and humidity—have an important influence on the strength of all glues (hide, bone, fish, etc.).

TENSILE STRENGTH OF GLUES UNDER VARIOUS CONDITIONS OF TEMPERATURE AND HUMIDITY

Liquid glue	15° C. and 50% humidity Kg./sq. cm.	20° C. and 75% humidity Kg./sq. cm.	25° C. and 90% humidity Kg./sq. cm.	25° C. and 95% humidity Kg./sq. cm.
A	49.6	45.8	35.4	26.4
B	45.7	44.1	39.1	29.0
C	31.7	31.3	31.1	30.3
D	42.7	41.2	39.4	37.7

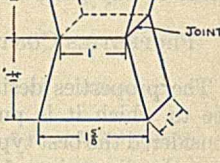
Note.—All joints were made up and dried at 20° C. and 75 per cent humidity. After drying 3 days, the joints were removed to the conditions at which they were broken and allowed to remain 7 days before breaking the joints.

The data presented in the table indicate the great importance of temperature and humidity as factors in controlling the strength of hygroscopic glues. Liquid glues *A* and *B* are very hygroscopic, whereas *C* and *D* are much less hygroscopic. Although *A* and *B* are much stronger than *C* and *D* at 15° C. and 50 per cent humidity, they are much weaker than *C* and *D* at 25° C. and 95 per cent humidity. Thus it is seen that strength tests at relatively high humidity and temperature are more valuable than similar tests conducted at low temperatures and humidities.

To obtain uniform results, the testing of the strength of glues must be carried out in constant-temperature, constant-humidity rooms, regardless of what strength is determined—i. e., shearing, tensile, or breaking strength tests must all be carried out under uniform humidity conditions. Fair results may be obtained by placing the joints in a humidor at 25° C. over 90 per cent sulfuric acid.

No tensile strength machine designed especially for glue-testing was available for use in this work, so a Fairbanks tensile strength cement tester was utilized. Oak blocks were sawed which, when joined with glue, just fitted the machine. These blocks were made so that the joint had an area of 6.46 sq. cm. (1 square inch) and was at right angles to the direction of the strain. When joined the blocks had a total length of 6.35 cm. (2.5 inches); the top and bottom of the joined block were 2.54 cm. (1 inch) by 4.1275 cm. (1.625 inches).

Rough tensile strength tests may be run by brushing a thin coat of glue on the smooth face of the blocks, allowing the glue to dry until it becomes very viscous, and then applying a second coat of glue. The excess of glue is wiped off and then the blocks are joined and clamped together. The joined blocks are placed in a humidor at a known temperature and humidity. After drying for a week the joints are broken in the Fairbanks tensile strength briquet machine.



JOINED BLOCKS 1" THICK.

THE JOINT

JOINT FOR TENSILE STRENGTH TEST.

More accurate results may be obtained by clamping the blocks under a definite pressure in a constant temperature and humidity room during the drying process.

SHEARING STRENGTH TEST

This strength test has been perfected by the U. S. Forest Products Laboratory, and consists in joining hard maple blocks, allowing the glue to set under definite pressure, and then bringing a shearing strain to bear on the layer of glue between the two wooden halves of the joint in an Olsen Universal testing machine.

The chief trouble with this shearing strength test is that, because of variations in humidity and temperature, the glues show a variable strength from day to day and from season to season. Moreover, most strong glues pull a larger or smaller proportion of the wood out, and thus the test may not indicate the full shearing strength of the glue.

DETERMINATION OF COLOR

The color of liquid glues is most easily determined by clarifying the glue with egg albumin and then matching the color in a Lovibond tintometer. The clarification is most easily effected by dissolving 1 per cent of powdered egg albumin in the glue at ordinary temperatures. This requires a considerable period of time. The finely powdered albumin should be slowly stirred into the glue, and the solution allowed to stand overnight. The glue should then be stirred for several minutes or until the albumin is dissolved. Upon heating to 90° C. for 15 minutes the albumin coagulates and brings down with it all suspended matter. The glue may be filtered while hot through either cotton or porous filter paper. The color of the clarified glue may be easily determined by placing a sample in a Lovibond tintometer cell and matching the color with the standard red and yellow tintometer glasses.

PERMANENCE

This is another point of first importance in the consideration of the value of any liquid glue. Not only should it retain its adhesive power indefinitely, but it must retain its original appearance—i. e., no coagulation, precipitation, or discoloration should appear on storage for long periods of time. The glue must, therefore, be preserved to prevent bacterial and mold growth, and it must not contain any suspended matter that will settle out on standing.

One of the best tests that may be applied to a liquid glue to determine its permanence is its storage at a slightly elevated temperature—e. g., 37.5° C. If liquid glue remains free from bacterial decomposition and other changes during a month's storage at this temperature, it is likely that it will keep indefinitely at ordinary room temperatures, provided it is properly preserved to prevent mold growth.

CHEMICAL COMPOSITION

The permanence of a liquid glue is partly dependent upon its chemical composition. If the glue is either strongly acid or alkaline, hydrolysis will take place slowly and the glue will gradually lose its strength. The proper reaction for glues is neutral to litmus and very slightly acid to phenolphthalein.

The presence of chlorides has already been considered. Other impurities in liquid glue may be exceedingly objectionable; for instance, the presence of substances corrosive to tin or iron causes many liquid glues to be of little value, although they may be splendid in other respects.

A complete chemical analysis of the glue itself is of considerable value in the examination of a liquid glue, provided the amounts of gelatins, gelatoses, gelatones, and amino acids are determined. Only chemists who have had considerable experience in the examination of glues are able to interpret the results of such an analysis correctly. The writer has not done sufficient work along this line to state definitely the maximum and minimum amounts of these substances that good liquid glues should contain, but the gelatin and gelatose content must be high and the gelatin and amino acid content should be low. This is obvious, for gelatones and amino acids have little adhesive power.

If a liquid glue is to be used for joining work, the properties of prime importance are permanence, adhesiveness or strength, and hygroscopicity. If the glue is lacking in any one of these three qualities, it is of no value for use in joining wood. Other properties, such as gel point, viscosity, color, and odor, are of minor importance in most cases. Where the glue is to be used for special work, such as joining glass, other properties—for instance, color and elasticity—become of importance.

In buying glue, viscosity, moisture content, and speed of set should be taken into consideration, for these properties determine the relative cost of liquid glues. Obviously, more glue must be used on joints in the case of liquid glues of low viscosity and high moisture content than when glues of high viscosity and low moisture content are used. If the liquid glue sets too quickly after it is applied, it will be impossible to spread uniformly, and therefore more glue must be applied in making the joint than would be the case if a slower setting glue were used.

A Titration Method for the Determination of Silver in Photographic Preparations[1]

By **Martin Marasco**

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THE possibility of quantitative determination of the reactions between soluble cyanides and silver salts, especially silver nitrate, has been known for a long time. The method was probably first tried by Liebig for the estimation of cyanogen by adding standard silver nitrate solution to cyanide in solution until a permanent turbidity of silver cyanide was formed, or, if some soluble halide was also present, by adding the silver nitrate solution until a precipitate of silver halide was formed which occurred as soon as all the cyanide had been converted to the double salt. In the photographic industry a reasonably accurate and rapid method of estimating silver halides in emulsions is important, but until recently no satisfactory way of doing this has been published.

Such a method has been used successfully in this laboratory for determining the silver content of photographic emulsions (emulsion noodles and dry emulsions on photographic plates and films). It is similar to, but more rapid and accurate than one recently described by Eggert.[2] The procedure suggested by Eggert is the same as that given by Rabiere,[3] and is probably better known as Denigès' method which is based on adding an excess of 0.1 *N* potassium cyanide solution to the neutral silver solution (about 0.2 gram in 200 cc.), then 5 cc. ammonium hydroxide, about 0.05 gram potassium iodide, and titrating back with 0.1 *N* silver nitrate solution until just turbid (due to silver iodide).

Comparing the equations representing both methods in their working order, we have for Eggert's method

$$q\ \mathrm{AgBr} + m\ \mathrm{KCN}\quad (\text{excess}) = q\ \mathrm{AgK(CN)_2} + n\ \mathrm{KCN} + q\ \mathrm{KBr} \qquad (1)$$

$$q\ \mathrm{AgK(CN)_2} + n\ \mathrm{KCN} + n/2\ \mathrm{AgNO_3} = (q + n/2)\ \mathrm{AgK(CN)_2} + n/2\ \mathrm{KNO_3} \qquad (2)$$

$$\mathrm{KI} + \mathrm{AgNO_3} = \mathrm{AgI} = \text{turbid solution} \qquad (3)$$

(q, m, and n represent the number of chemical equivalents, and $q = m - n$)

and for the method described here

$$\mathrm{AgBr} + 2\,\mathrm{KCN} = \mathrm{AgK(CN)_2} + \mathrm{KBr} = \text{clear solution} \qquad (1)$$

That the second method is far simpler and quicker is obvious at once from the equations; it remains to show that it is at least as accurate. By Eggert's method the emulsion is dispersed in hot water, then a mixture of ammonia and potassium iodide in water is added, followed by an excess of standard potassium cyanide solution. The excess of potassium cyanide is titrated with standard silver nitrate solution until a faint turbidity due to a permanent precipitate of silver iodide appears. Eggert's article might lead one to suppose that the ammonia is added to keep silver cyanide in solution at the end point, which, of course, is not the case. The real advantages of having ammonia present are:

(1) It keeps the solution alkaline and so prevents the liberation of traces of hydrogen cyanide during titration. Without the ammonia, after several hours of continuous work with cyanide solutions in an ordinary laboratory, the eyes become dull and there is a feeling of internal pressure about the temples, with occasional dizzy spells, but when a little ammonia is added to the mixture or the cyanide before titration these effects are no longer noticed.

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[1] Received May 24, 1924.

[2] *Z. wiss. Phot.*, **22**, 209 (1924).

[3] *Bull. soc. chim.*, **17**, 306 (1915).

(2) It favors the formation of very finely divided suspensions instead of clots during titration.

The second effect is particularly favorable for satisfactory results by the procedure described by the writer, of titrating to a clear end point, especially while standardizing the standard cyanide solution against pure silver nitrate.

Except in rare cases, the usual procedure by this method is to add 0.1 *N* potassium cyanide solution, containing 5.0 cc. ammonium hydroxide per liter, to the liquid emulsion dispersed in hot water until it becomes clear, which indicates the end of the titration. The trace of ammonia in the cyanide doubtless has a slight solvent action on the silver halides, but allowance is made for this when standardizing the cyanide solution.

In order to be successful by this method, there are certain precautions to be taken and several points with which the operator should be familiar.

(1) Although pure potassium cyanide solutions are fairly stable, standardization requires only a few minutes and should be repeated at least every other day in order to be sure that the solution has not decomposed to any important extent.

(2) The end of the titration is indicated by complete solution of the silver halides, but at this point the liquid is often slightly opalescent, depending on the amount and state of the gelatin in the sample. The end point of the titration is taken where two or three drops of the standard potassium cyanide solution cause no further decrease in turbidity. This is not difficult to see and is important since an attempt to overcome turbidity due to gelatin leads to high results.

(3) In the rare cases of coagulated emulsions or other silver halide precipitates, an excess of potassium cyanide is added as in the first part of Eggert's method until all the silver halides are dissolved. A known amount of silver nitrate is then precipitated in about 50 cc. of water in a separate beaker by a small excess of potassium bromide and the freshly prepared silver bromide suspension poured into the clear sample. Titration is then continued as before with standard potassium cyanide solution to a clear end point. Back titration of the excess potassium cyanide with standard silver nitrate solutions in the presence of gelatin as in Eggert's method gives low results.

(4) The rate of reaction between the silver halides and the entering cyanide varies somewhat with the size of the silver halide particles and the volume of liquid in which the silver halide is dispersed. In nearly every photographic emulsion the crystals are small enough to react instantly, but volume changes of 300 per cent increase the error of a determination by about 1 per cent. Cautious titration and reasonably uniform dilution are desirable to obtain best results.

STANDARDIZATION OF KCN SOLUTION

Dissolve a known weight (0.25 to 0.300 gram) of silver nitrate in about 150 cc. of hot distilled water (50° to 90° C.). Add about 0.4 gram of powdered potassium bromide (too much potassium bromide coagulates the silver bromide formed) stirring the mixture by the aid of a rubber-tipped rod and then run in approximately 0.1 *N* slightly ammoniacal potassium cyanide solution until the mixture becomes nearly clear; then add the potassium cyanide solution carefully by drops to a clear end point. If coagulated silver bromide or silver cyanide is formed, it is easily seen at the end of the titration as quick-settling white particles, and indicates that the work has not been done properly.

ANALYSIS OF EMULSIONS

Completely disperse a known weight or area of emulsion containing about 0.2 gram silver in about 150 cc. hot water, and titrate with standard potassium cyanide solution to a clear end point in the same way as in titrating the silver when standardizing the potassium cyanide solution. Remember that the gelatin, especially if present in large amounts, may cause an appreciable turbidity. Unless lumps or clots of emulsion are present, a reading taken before the first addition which causes no decrease in turbidity represents the end point.

If coagulated emulsion is encountered, add a known excess of potassium cyanide and stir until the silver halides in these clots are dissolved. Take more than sufficient silver nitrate to correspond to the excess potassium cyanide employed in about 30 cc. of water in another vessel, add a slight excess of potassium bromide solution to precipitate all the silver as bromide, and pour this into the clear sample, and titrate again with the standard potassium cyanide solution to a clear end point.

COMPARISON OF RESULTS BY BOTH METHODS

Since Eggert's procedures and the one described here are nearly identical, the only way to compare them is to analyze emulsions by both methods. Both methods give sharp end points in the standardization of the potassium cyanide solution. The following results, however, indicate that the presence of gelatin strongly impairs the accuracy of Eggert's method, and is responsible for the discrepancy between the true silver content and the results obtained by either method. This method gives results approximately 1 per cent high, while under the same conditions by Eggert's method the results are 2 to 5 per cent low, according to the amount of gelatin present.

STANDARDIZATION OF 0.1 *N* KCN SOLUTION

Direct titration method

$AgNO_3$ taken Grams	KCN soln. used Cc.	Ag equiv. per cc. of KCN soln. Grams	Average difference Per cent
0.2256	27.30	0.005247	−0.10
0.2519	30.43	0.005255	+0.06
0.2732	33.00	0.005253	−0.02
	Av.	0.005252	

Eggert's method

		Back titration[a]			
$AgNO_3$ taken Grams	KCN soln. added Cc.	$AgNO_3$ soln. used Cc.	KCN soln. used Cc.	Ag equiv. per cc. KCN soln. Grams	Average difference Per cent
0.2238	45.00	8.35	27.55	0.005158	+0.12
0.2512	45.00	6.70	31.00	0.005145	−0.14
0.2735	45.00	5.40	33.72	0.005153	+0.02
			Av.	0.005152	

ANALYSIS OF SILVER BROMIDE-GELATIN EMULSION

DIRECT TITRATION METHOD			EGGERT'S METHOD				
					Back titration		
Emulsion taken Grams	KCN soln. used Cc.	Ag in emulsion Per cent	Emulsion taken Grams	KCN soln. added Cc.	$AgNO_3$ soln. used Cc.	KCN soln. used Cc.	Ag in emulsion Per cent
3.232	18.55	3.015	3.400	40.02	9.95	19.27	2.92
4.672	26.85	3.017	4.645	40.00	13.63	26.37	2.92
6.337	36.30	3.007	6.135	45.00	10.22	34.78	2.90
	Av.	3.013				Av.	2.91

True per cent Ag = 2.980
Per cent error = +1.10

True per cent Ag = 2.98
Per cent error = −2.35

[a] Ratio of $AgNO_3$ solution to KCN solution was 1:2.090

COMPARATIVE RESULTS SHOWING EFFECT OF ADDED GELATIN

Gelatin in sample Grams	Error by direct method Per cent	Error by Eggert's method Per cent
None	0.06	0.09
0.4	+1.1	−2.2
1.5	+1.1	−4.4
1.2	+1.6	−3.3
2.0	+0.8	−5.2

ACKNOWLEDGMENT

The writer wishes to express his appreciation to F. F. Renwick for kindly criticisms.

Announcement of Chemical Exposition Date

Owing to some confusion which is believed to exist in a few quarters regarding the holding of the next chemical exposition, an announcement has been sent out by the International Exposition Company, under whose management the Exposition of Chemical Industries has been held since 1915. This announcement states that there will be no chemical exposition in 1924. The next Exposition of Chemical Industries will be held September 28 to October 3, 1925, at the Grand Central Palace, New York, N. Y.

Modified Method for Determining Cellulose in Wood[1]

By G. J. Ritter

Forest Products Laboratory, Madison, Wis.

On account of a slightly gelatinous property acquired by cellulose during its isolation by the Cross and Bevan method, the thorough removal of the chemicals used in the process is frequently difficult. The undesirable gelatinous property of cellulose is often associated with a subsequent darkening of color while the product is drying. The discoloration developed during drying has been ascribed to an improper removal of the reduced permanganate residues which form during the bleaching process. The work described in this paper was undertaken with a view to modifying the present method of preparing cellulose, so as to minimize, if possible, these troublesome features.

The modifications studied may be classified under three headings—namely, (1) decreasing the length of the chlorination periods, (2) trying different bleaching agents, and (3) digesting the cellulose on a hot water bath before final washing.

It was planned to compare the samples of cellulose isolated by the modified and regular Cross and Bevan methods as to both physical and chemical characteristics. For a chemical characteristic the hot water–soluble content[2] of cellulose was to be substituted for alpha, beta, and gamma cellulose. It was soon learned, however, that the hot water–soluble portion could not be used as a constant on cellulose prepared by either the regular or modified methods, for the value of the soluble portion on the same wood ranged from 3.5 to 15 per cent.

The experimental work was confined to redwood-heartwood sawdust 80 to 100 mesh. The procedure for preparing the cellulose was the same as described in previous papers,[3] with the modifications to be explained in the present paper.

Length of Chlorination

Modification 1 is based on results reported in a previous paper[3] of this series. The chlorination periods were reduced from 5 to 4 minutes, and finally to 3 minutes, without any noticeable difference in cellulose yields. It was decided to drop this phase of the work inasmuch as 15 to 20 seconds are required to displace the air with chlorine in the reaction chamber. A period of 3 minutes for the sawdust in the reaction chamber after the chlorine enters is as efficient for removing lignin from cellulose as 5-minute periods. This would indicate that any time above 3 minutes results in overexposure of cellulose to the chlorine gas. In the previous paper[3] it was shown that the pentosans and lignin content of cellulose prepared by the short and long chlorination periods agree closely. Accordingly, these determinations of the cellulose were omitted. The results obtained by decreasing the chlorination periods are shown in Table I.

Effect of Different Bleaching Agents on Yields and Composition of Cellulose

This phase of the work was undertaken in order to determine whether the permanganate is the cause of frequent discolorations of the isolated cellulose. Two other bleaching agents, hydrogen peroxide and sulfur dioxide, were therefore used.

By being reduced to water and oxygen, hydrogen peroxide would eliminate the addition of new salts to be removed by subsequent washing. Since sulfur dioxide is used in reducing the excess permanganate, it was also used for reducing the excess hydrogen peroxide. It was found that the occasional discoloration of the cellulose during drying was not eliminated by bleaching with hydrogen peroxide instead of permanganate.

Table I—Cellulose in Redwood Heartwood, Isolated by Varying Lengths of Chlorination Periods

(Results based on oven-dry weight (105° C.) of material)

Chlorination periods Minutes	Cellulose Per cent
5, 5, 5, 5, 2	42.2
5, 5, 5, 5, 2	41.9
5, 5, 5, 5, 2	42.4
5, 5, 5, 5, 2	42.5
4, 4, 4, 4, 2	41.9
4, 4, 4, 4, 2	42.3
4, 4, 4, 4, 2	42.2
4, 4, 4, 4, 2	42.0
3, 3, 3, 3, 2	42.1
3, 3, 3, 3, 2	42.3
3, 3, 3, 3, 2	42.4
3, 3, 3, 3, 2	42.2

Naturally, the presence of sulfur dioxide as an addition compound with cellulose or absorbed by the cellulose suggested itself. Its presence in either of these forms might be the influential factor in the discolorations. Sulfur dioxide was next used for bleaching cellulose, and showed the same occasional undesirable discoloration of the dried cellulose. From these results sulfur dioxide seems to be the principal agent in causing discoloration of the cellulose. Further evidence of this effect is shown under Modification 3.

The effect of the three bleaching agents on the yield and chemical properties of the cellulose isolated was studied. An attempt was made to compare the chemical properties of the various samples by determining the hot water–soluble content of the cellulose. As previously noted, however, the hot water–soluble content was so variable as to make this comparison unreliable. Table II contains the results.

Table II—Effect of Different Bleaching Agents on Cellulose from Redwood Heartwood

(Yields based on oven-dry weight (105° C.) of material)

Bleaching agent	Total cellulose Per cent	Hot water–soluble content of total cellulose Per cent
$KMnO_4$	42.7	3.5
	41.9	13.8
	42.0	10.2
	41.7	11.9
	42.4	9.7
	41.6	8.3
H_2O_2	42.6	3.6
	41.9	15.1
	42.0	12.1
	41.9	12.6
	42.0	9.0
SO_2	41.9	15.1
	42.4	13.8
	42.0	9.7
	42.5	10.2

Digestion of Cellulose on a Hot Water Bath before Final Washing

The gelatinous characteristic hinders final washing of the cellulose. Any salts or acids on the cellulose would tend to concentrate during the drying process and promote formation of hydrolyzed material. The amount of such hydrolyzed material might then account for the varying water–soluble content which was found with separately prepared samples of cellulose. That such would be the result has been shown by

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[1] Presented under the title "Some Modifications in the Method of Determining Cellulose in Wood" before the Division of Cellulose Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] Sherrard and Blanco, This Journal, **15**, 1166 (1923).

[3] Ritter and Fleck, *Ibid.*, **16**, 147 (1924).

Sherrard and Blanco.[2] In order to eliminate the gelatinous condition of the cellulose the material was digested in water on a hot water bath for varying periods. The cellulose could then be washed with water and filtered easily. This is in accord with some of the later results by Sherrard on the partial hydrolysis of wood cellulose. The hot water–soluble content was reduced, progressively, to approximately 1 per cent, as shown in Table III.

Table III—Effect of Heating Redwood-Heartwood Cellulose in Water Bath for Varying Periods of Time before Final Washing
(Results on basis of oven-dry weight)

Heating periods Hours	Total cellulose Per cent	Hot water–soluble content of total cellulose Per cent
1/2	42.9	7.9
1/2	42.7	6.5
1	42.4	4.0
1	42.4	3.0
2	42.4	0.8
2	42.5	0.6
2	42.5	1.6
2	42.3	1.3
2	42.2	1.0

Samples of cellulose prepared by the regular method (with high hot water–soluble content) and others prepared by the modified method (with low hot water-soluble content) were boiled with water 20 minutes, filtered, and the residues and filtrates tested for traces of acids.

The moist residue from cellulose with high hot water–soluble content gave a distinct acid reaction on remaining in contact with blue litmus for a few minutes. The filtrate from the same cellulose, on oxidation with bromine water and the addition of barium chloride, produced a white precipitate insoluble in hydrochloric acid. These two tests indicate that some sulfur dioxide remained on the cellulose and some was taken up by the water on boiling. The presence of sulfur dioxide with the cellulose at temperatures of 100° to 105° C. during drying would cause hydrolysis and the subsequent appearance of hot water–soluble material.

The moist residues from cellulose with low hot water–soluble content (prepared by the modified method) showed no test for acid with litmus. The filtrate from the same cellulose on oxidation with bromine water developed a very slight cloudiness.

The advantages gained by a slow digestion of the cellulose with hot water can be stated as follows: (1) The elimination of the undesirable gelatinous property of the cellulose is accompanied by facility in washing and filtering. (2) By a more thorough removal of acids and salts, a more highly hot water–resistant product is obtained.

Titration of Aniline and Homologs[1]

By D. O. Jones and H. R. Lee

The Newport Co., Milwaukee, Wis.

The usual nitrite titrations of aniline, *o*- and *p*-toluidines, and xylidine require a temperature of 0° to 5° C. on account of the instability of the diazo compounds. The slow rate of diazotization of these amines makes their analysis by this method both tedious and inaccurate.

This investigation was started to determine whether the principle of the back titration method,[2] as applied to the analysis of dehydrothio-*p*-toluidine, could be applied to this class of compounds.

Preliminary Titrations

Preliminary titrations made on a sample of purified *p*-toluidine yielded low results. In these titrations a sufficient quantity of the amine to require approximately 40 cc. 0.1 *N* sodium nitrite solution was diluted to 400 cc., 25 cc. concentrated hydrochloric acid added, the solution cooled to 0° C., and approximately 10 cc. excess of 0.1 *N* nitrite added. Back titrations were made after allowing to stand from 2 to 5 minutes.

The results indicated at once that a longer time would be necessary for complete diazotization. Upon extension of the time allowed for diazotization, in the presence of the excess nitrite, a maximum absorption was reached in 30 minutes. The values corresponding to this nitrous acid absorption were, however, over theory, which suggested a loss of nitrous acid. A measure of this loss is shown in Table I.

Table I—Loss of Nitrous Acid from Solution at 0° C.

No.	0.1 *N* $NaNO_2$ solution taken Cc.	*p*-Nitroaniline Used: Immediate titration Cc.	*p*-Nitroaniline Used: Titrated after 30 min. Cc.
1	10.00	10.11	9.85
2	10.00	10.11	9.80

The expression $3\ HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$, commonly given for the decomposition equilibrium of nitrous acid in solution, suggested the use of nitric acid for suppressing the loss of nitrous acid in this titration.

Stability of Nitrous Acid Solutions

The stability of nitrous acid solutions of different concentrations was then studied. Solutions containing different quantities of 0.1 *N* nitrite in a volume of 400 cc. containing 25 cc. concentrated hydrochloric acid were allowed to stand at 0° C. for various lengths of time with and without nitric acid present, and the nitrous acid remaining was then titrated with *p*-nitroaniline solution. The results are shown in Table II.

Table II—Stability of Nitrous Acid Solutions

No.	HNO_3 used Cc.	*p*-Nitroaniline solution used in back titration	Time allowed to stand with excess nitrite before back titration—Min.
		Part 1[a]*—10 cc. 0.1 N* $NaNO_2$ *taken*	
1	None	10.20	None
2	None	10.22	
3	5	10.25	
4	10	10.22	
5	None	9.93	30
6	None	9.90	
7	5	10.15	
8	10	10.18	
		Part 2—20 cc. $NaNO_2$ *taken*	
9	5	21.16	None
10	10	21.16	
11	None	20.20	20
12	5	20.78	
13	5	20.77	
14	10	20.91	
15	20	21.05	

[a] In Parts 1 and 2 different *p*-nitroaniline solutions were used.

The presence of nitric acid was found to have no injurious effect upon the diazotization reaction or upon the end point. In Table II it is shown that check results are obtained with

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[1] Presented before the Division of Dye Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

[2] Lee and Jones, "An Accurate Method for the Analysis of Dehydrothio-*p*-toluidine," presented before the Division of Dye Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923. (See page 930, this issue.)

or without nitric acid if the back titrations are made immediately. Furthermore, 10 cc. nitric acid are effective in preventing the loss of nitrous acid by dissociation when 10 cc. 0.1 *N* nitrite are allowed to stand at 0° C. in a volume of 400 cc. for 30 minutes. For larger quantities of nitrite more nitric acid is required, 20 cc. excess nitrite requiring at least 20 cc. nitric acid.

An excess of approximately 10 cc. 0.1 *N* nitrite and the addition of 10 cc. concentrated nitric acid are therefore the most suitable conditions.

Samples of the purified *p*-toluidine, previously referred to as yielding low results in the preliminary titrations, were then analyzed in the same manner except that they were allowed to stand for 30 minutes before making the back titration. Titrations were made with and without nitric acid. The results are shown in Table III.

TABLE III—ANALYSIS OF *p*-TOLUIDINE WITH AND WITHOUT NITRIC ACID

Without HNO_3 Per cent	With 10 cc. HNO_3 Per cent
100.52	99.72
100.12	99.92
100.07	

TIME REQUIRED FOR COMPLETE DIAZOTIZATION

The time required for complete diazotization of technical samples of aniline and homologs was then determined, using 10 cc. concentrated nitric acid and approximately 10 cc. 0.1 *N* nitrite in excess. The results are shown in Table IV.

TABLE IV—DIAZOTIZATION AFTER VARYING PERIODS OF TIME

Time allowed before back titration—Min.	*p*-Toluidine Per cent	*o*-Toluidine Per cent	Aniline Per cent	Xylidine Per cent
10	98.15	98.78 98.78	99.54	98.51
20	99.20	98.83 98.74	99.75 99.78	98.63
30	99.40	98.88 98.81	99.72 99.78	99.01
45	99.40	98.81	99.78	99.01
Average cc. 0.1 *N* $NaNO_2$ present in excess for 30-min. titration..........	10.53	10.53	11.05	11.21

The data clearly show that in all cases maximum nitrite absorption is obtained by allowing 30 minutes' standing before making the back titration.

PREPARATIONS AND ANALYSIS OF PURIFIED SAMPLES

In order to show that this method gives theoretical results for this class of compounds, pure samples of each were prepared and analyzed.

p-TOLUIDINE—The technical product was recrystallized from alcohol, distilled, and sublimed *in vacuo*. The purified product had a crystallizing point of 43.57° C.

Analysis by Nitrite. A 4.4979-gram sample was dissolved, diluted to 500 cc., and 50-cc. aliquots taken.

0.1 *N* factor nitrite, 1.0432
0.1 *N* factor *p*-nitroaniline, 0.9964

				p-TOLUIDINE	
No.	Nitrite taken Cc.	*p*-Nitroaniline required Cc.	0.1 *N* nitrite consumed Cc.	Found (m. w. 107.11) Per cent	Analysis by Kjeldahl nitrogen (m. w. 107.11) Per cent
1	50.00	10.19	42.01	100.03	99.87
2	50.00	10.23	41.97	99.94	99.87

o-TOLUIDINE—The technical product was purified by the method of Rosenstiehl,[3] redistilled, and the constant boiling middle fraction taken for analysis.

Analysis by Nitrite. A 4.0306-gram sample was dissolved, diluted to 500 cc., and 50-cc. aliquots taken.

0.1 *N* factor nitrite, 1.0269
0.1 *N* factor *p*-nitroaniline, 0.9870

No.	Nitrite taken Cc.	*p*-Nitroaniline required Cc.	0.1 *N* nitrite consumed Cc.	*o*-Toluidine found (m. w. 107.1) Per cent
1	47.00	10.81	37.60	99.91
2	50.00	13.92	37.61	99.92

ANILINE—The technical product was redistilled three times *in vacuo*. The second and third distillations gave products having a freezing point of −6.29° C., which corresponded[4] to 99.92 per cent.

Analysis by Nitrite. A 3.7115-gram sample was dissolved, diluted to 500 cc., and 50-cc. aliquots taken.

0.1 *N* factor nitrite, 1.0684
0.1 *N* factor *p*-nitroaniline, 1.0064

No.	Nitrite taken Cc.	*p*-Nitroaniline required Cc.	0.1 *N* nitrite consumed Cc.	Aniline found (m. w. 93.1) Per cent
1	47.50	10.90	39.78	99.78
2	47.50	10.88	39.80	99.84
3	47.50	10.88	39.80	99.84

XYLIDINE—A sample of technical *m*-xylidine was converted into the hydrochloride, which was then recrystallized and converted into the base. The base was distilled *in vacuo* and a constant-boiling middle fraction taken for analysis.

Analysis by Nitrite. A 4.7620-gram sample was dissolved, diluted to 500 cc., and 50-cc. aliquots taken.

0.1 *N* factor nitrite, 1.0684
0.1 *N* factor *p*-nitroaniline, 1.0064

No.	Nitrite taken Cc.	*p*-Nitroaniline required Cc.	0.1 *N* nitrite consumed Cc.	Xylidine found (m. w. 121.14) Per cent
1	49.00	13.00	39.27	99.90
2	49.00	12.99	39.28	99.93

METHOD OF ANALYSIS—Measure with a dry Mohr pipet or transfer—depending upon whether the sample is liquid or solid—a sufficient quantity of the sample into a tared weighing bottle, such that one-tenth of it will require approximately 40 cc. 0.1 *N* sodium nitrite solution, and weigh. Transfer to a 500-cc. volumetric flask, using 5 per cent hydrochloric acid to wash the weighing bottle; then dissolve by further addition of acid and dilute to volume. Pipet a 50-cc. aliquot into a 600-cc. beaker, dilute to 300 cc., add 25 cc. concentrated hydrochloric acid, surround with ice, and cool to 0° C. Add chipped ice to the solution and, while stirring, add 50 cc. 0.1 *N* sodium nitrite solution, then immediately add 10 cc. concentrated nitric acid (N_2O_3 free). Cover with a watch glass and allow to stand for 30 minutes with occasional stirring. Titrate back the excess nitrous acid with the standard *p*-nitroaniline solution, as described in the analysis of dehydrothio-*p*-toluidine.[2]

STABILITY OF THE 0.1 *N* *p*-NITROANILINE SOLUTION—An approximately 0.1 *N* solution of *p*-nitroaniline was standardized daily against 10 cc. of a 0.1 *N* solution of sodium nitrite for a period of 16 days. Assuming that the nitrite solution was stable, no regular change occurred in the *p*-nitroaniline solution. The largest difference in the *p*-nitroaniline solution required for titration during this period was 0.15 cc. This was apparently due to different observations of the end point, for when these standardizations were applied to the analysis of a sample of sulfanilic acid by the back titration method on the corresponding days, identical values were obtained.

DISCUSSION OF THE METHOD

Analyses of samples of commercial aniline by the freezing point method[4] have been in very close agreement and usually slightly lower than by the procedure herein described. This relation would be expected because of the presence of a small quantity of homologs.

The method described is not only suitable for the analysis of aniline and its homologs in the pure state, but is especially valuable for technical samples, liquors, extractions from residues, etc., the amino values of which are frequently required in commercial work.

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[3] Lunge, "Technical Methods of Analysis," Vol. II, Part II, p. 855.

[4] THIS JOURNAL, **12**, 882 (1920).

The Determination of Free Calcium Hydroxide in Commercial Calcium Arsenate[1]

By C. M. Smith and S. B. Hendricks

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Calcium arsenate, as used for the control of the cotton boll weevil, is not a single, definite chemical compound. As usually made, it contains, in addition to one or more forms of calcium arsenate, calcium carbonate and free calcium hydroxide. This complexity leads to difficulty in interpreting the analyses of commercial calcium arsenates as made by the recognized methods. Allowance may be made for the carbonate by making a carbon dioxide determination, but after this is done the remaining calcium oxide and the total arsenic oxide present give no information as to just what arsenate is present, because the distribution of the calcium between the hydroxide and the arsenate is indeterminate. The estimation of the quantity of free lime present seemed to offer the best means of determining this distribution, and this article outlines the method developed for that purpose.

It might seem at first that the free calcium hydroxide could be dissolved in water or in sugar solution, as recommended in various methods for the analysis of commercial lime. It must be remembered, however, that all the known calcium arsenates are dissolved, or hydrolyzed, to some extent in water, and that reactions may occur which will use up calcium hydroxide to form more basic compounds if the various components are not in equilibrium with each other. Experiments made by the authors on mixtures of lime with di- and tricalcium arsenates and with commercial samples confirmed the supposition that aqueous extraction gives erroneous results, at least in many cases.

It is very desirable to have a method that can be relied upon to determine accurately the free calcium hydroxide, even in the extreme case of a mixture of that compound with dicalcium arsenate, inasmuch as this salt is known to have occurred in some commercial calcium arsenates. The use of some non-aqueous medium which would operate to repress solubility and hydrolysis appeared to offer hope, and after experimenting with a number of organic liquids alcohol was adopted as the most satisfactory.

The method tested consisted in treating the sample with a known excess of standard acidified alcohol, followed by back titration with standard alkali in alcohol, it being hoped that the acid would attack the calcium hydroxide and not react with the other components. Preliminary tests showed that hydrochloric acid gave very poor results, acetic acid was considerably better, and benzoic acid gave excellent results. Consequently, benzoic acid was adopted and used in the form of an approximately 0.1 *N* solution in 93 per cent ethyl alcohol.

Procedure

A 1-gram sample of the material under examination, previously sifted through a 200-mesh screen, is put into a 200-cc. Erlenmeyer flask, 50 cc. of the alcoholic benzoic acid added, the flask stoppered, and the whole shaken vigorously for 5 to 6 minutes. Phenolphthalein solution is then added and the back titration begun with 0.1 *N* sodium hydroxide in 93 per cent alcohol solution. It was found to be necessary to agitate the solution violently during this back titration. For the most accurate results the titration should be stopped somewhat before the end point, the solution filtered through a folded filter paper, the latter washed once or twice with alcohol, and the clear filtrate then titrated to the first appearance of pink. This filtration is necessary to prevent a dragging end point due to reaction between the sodium hydroxide and the precipitate. However, results within about 0.15 per cent (low) of the true values can be obtained without filtration, and probably the adoption of a motor-driven stirrer would improve this.

Results

Table I shows the results obtained when this method was applied to the individual components which it is assumed may be present. The materials used here and in the subsequent experiments were as follows:

Calcium hydroxide: reagent containing about 96 per cent $Ca(OH)_2$
Calcium carbonate: C. P. reagent
Dicalcium arsenate: a C. P. salt of the formula $CaHAsO_4.H_2O$ prepared in the laboratory
Tricalcium arsenate: a C. P. salt of the formula $Ca_3(AsO_4)_2.8H_2O$ prepared in the laboratory

Table I

Material Analyzed	Weight of sample Grams	Per cent $Ca(OH)_2$ Present	Per cent $Ca(OH)_2$ Found	Error Per cent
$Ca(OH)_2$	0.1	96.1	96.1	0.0
$CaCO_3$	1.	0.00	0.02	+0.02
$CaHAsO_4.H_2O$	1.	0.00	0.02	+0.02
$Ca_3(AsO_4)_2.8H_2O$	1.	0.00	0.06	+0.06

It is seen that the calcium hydroxide is recovered quantitatively, while all the other components are not attacked.

Table II shows the results obtained from known mixtures of calcium hydroxide with the other components, the latter taken one, two, and three at a time.

Table II

Material Analyzed	Weight of sample Grams	Per cent $Ca(OH)_2$ Present[a]	Per cent $Ca(OH)_2$ Found	Error Per cent
$CaCO_3$ $Ca(OH)_2$	1. 0.1	9.81	9.83	+0.02
$CaHAsO_4.H_2O$ $Ca(OH)_2$	0.9 0.1	11.22	11.19	−0.03
$Ca_3(AsO_4)_2.8H_2O$ $Ca(OH)_2$	1. 0.1	9.88	9.90	+0.02
$CaHAsO_4.H_2O$ $CaCO_3$ $Ca(OH)_2$	0.8 0.1 0.1	10.89	10.81	−0.08
$Ca_3(AsO_4)_2.8H_2O$ $CaCO_3$ $Ca(OH)_2$	0.8 0.1 0.1	9.61	9.60	−0.01
$CaHAsO_4.H_2O$	0.4	0.00	0.02	+0.02
$Ca_3(AsO_4)_2.8H_2O$	0.4	1.44	1.41	−0.03
$CaCO_3$	0.1	4.06	4.06	0.00
$Ca(OH)_2$ (Various weights)		5.78 7.59	5.73 7.56	−0.05 −0.03

[a] The weights of calcium hydroxide given under "Weight of sample" in Tables II and III are only approximations; the figures given under "$Ca(OH)_2$ present" were, however, calculated on the basis of the exact quantities.

Here the average error is about 0.02 per cent, which is well within the experimental limits.

Finally, experiments were made with three commercial samples of calcium arsenate, one of which (Sample A) was presumed to contain no free lime, another (Sample B) very little, and the third (Sample C) a considerable proportion of free lime, as judged by their reaction to an alcoholic solution of phenolphthalein. These samples were run alone, in mixtures with lime, and in various combinations with each other,

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[1] Presented under the title "A Method for the Determination of Free Calcium Hydroxide in Calcium Arsenate" before the Division of Agricultural and Food Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

to see if the results on the mixtures agreed with the values calculated from the originals. The data obtained are given in Table III.

TABLE III

Material Analyzed		Reaction to Alcoholic Phenolphthalein	$Ca(OH)_2$ calc. Per cent	$Ca(OH)_2$ found Per cent	Error Per cent
Sample A		Not alkaline	..	0.04	..
Sample A + $Ca(OH)_2$			9.19	9.15	−0.04
Sample B		Faintly alkaline	..	0.20	..
Sample B + $Ca(OH)_2$			4.60	4.56	−0.04
Sample C		Strongly alkaline	..	8.60	..
Sample C + $Ca(OH)_2$			12.80	12.83	+0.03
Equal mixture	A+B		0.12	0.09	−0.03
	B+C		4.40	4.33	−0.07
	A+C		4.32	4.24	−0.08
	A+B+C		2.95	2.90	−0.05

These results on commercial samples are seen to be practically as satisfactory as those obtained when mixtures made from pure compounds were used. There is a tendency toward slightly low values, which could probably be lessened by more violent agitation during the titrations.

This method does not work so smoothly in the presence of magnesium compounds, and all the experiments outlined herein were made with materials that were practically free from them. It is hoped that the method can be modified to include products containing magnesium compounds, since commercial calcium arsenates sometimes contain a sufficient amount of the latter to affect the results.

Copper as Reducing Agent in Iron Determinations[1]

By J. M. Hendel

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COPPER gauze has been found very convenient in the reduction of ferric sulfate preparatory to titration by permanganate. It is rapid in action and requires no blanks, and is therefore of especial value to those who make iron determinations only occasionally.

The reductor consists of ordinary window screening of 15-mesh cold-drawn copper gauze, cut into squares 4 cm. on a side and attached to a copper wire or a glass rod. It is immersed in the gently boiling ferric sulfate solution until the color of ferric iron has disappeared. After allowing 3 minutes more to insure complete reduction, the gauze is washed with a stream of water and removed. If a total area of 64 sq. cm. of gauze is used, 25 mg. of iron may be reduced in 8 minutes and 150 mg. in 15 minutes; with 32 sq. cm. of gauze, 125 mg. of iron require 30 minutes for complete reduction.

Commercial grades of copper gauze that are 99.8 per cent pure may be readily obtained. The gauze used in this work contained not more than 0.015 per cent iron.

The reaction may be represented by the equation:

$$Cu + 2Fe^{+++} = Cu^{++} + 2Fe^{++}$$

However, the solutions titrated immediately after reduction and cooling to room temperature gave results for iron 0.4 per cent too high, probably due to the presence of cuprous ion, because the substance causing the high results was not removed by a stream of hydrogen. Aeration, however, always removed the source of error.

The stability of ferrous sulfate solutions toward oxidation by the air, even at the boiling point, has been previously observed.[2,3] In the presence of small amounts of cupric ion, however, the aeration of hot ferrous sulfate solutions, normal in acidity, causes appreciable oxidation of ferrous ion. The rate of aeration was 1 liter of air in 5 minutes, the air being drawn from outside the laboratory, through absorbent cotton, and thence into the ferrous solution.

To secure correct results for iron, then, all reduced solutions were cooled to room temperature, made normal in acidity, and aerated for from 1 to 10 minutes, after which they were titrated with standard permanganate solution. Table I shows the results obtained with the copper reductor with various amounts of ferric sulfate and varying aeration periods. The reduction was carried out in 0.1 *N* sulfuric acid, in a volume of 175 cc. The theoretical value for the iron was determined by careful reduction with the platinum-hydrogen reductor[2] and by the zinc reductor, followed by titration with permanganate.

TABLE I

No.	Aeration time Minutes	Iron taken Mg.	Iron found Mg.	Difference Mg.
1	3	24.65	24.62	−0.03
2	5	24.65	24.67	+0.02
3	10	24.65	24.75	+0.10
4	3	101.0	101.0	..
5	5	101.0	101.0	..
6	10	101.0	100.9	−0.1
7	3	126.1	126.2	+0.1
8	5	126.1	126.2	+0.1
9	10	126.1	125.8	−0.3
10	1	150.7	150.8	+0.1
11	1	150.7	150.7	..
12	3	150.7	150.3	−0.4
13	3	150.7	150.1	−0.6

From the table it may be observed that for 25 to 125 mg. of iron, aeration from 3 to 10 minutes gives correct results.

The acidity during the reduction must be no more than 0.25 *N*. Quantitatively complete reduction in 0.5 or 1 *N* sulfuric acid was never obtained, even after 1 hour. In all experiments described herein, however, the acidity during aeration and titration was normal.

The presence of titanium has no effect on the determination of iron. A hot solution of 56 mg. of titanium in 175 cc. of 0.1 *N* sulfuric acid was subjected to the reduction process for a half hour and titrated hot without previous aeration; 0.32 cc. of 0.07181 *N* permanganate was required, indicating, perhaps, traces of titanous ion, but more probably cuprous ion, formed by oxidation of copper metal in the hot acid. A hot solution of 5.5 mg. of titanium in 0.25 *N* acid was then reduced for 10 minutes, cooled to room temperature, aerated for 3 minutes, and tested with permanganate; none was required. Finally, two solutions were reduced, which contained 126.1 mg. of iron and 2.3 mg. of titanium in 175 cc. of 0.25 *N* acid. After reduction for 15 minutes and aeration of the cooled solution for 3 minutes, titration with permanganate showed, in one case, 126.1 mg., and in the other, 126.0 mg. of iron.

Any titanous ion that may have been formed was therefore reoxidized in the aeration. This confirms the results of many previous experiments, which showed conclusively that aerating cold solutions containing ferrous and titanous ions results in oxidation of the titanous ion only.[2]

The copper reductor is being applied to the determination of iron in the presence of vanadium, and of vanadium in steels and other alloys. Preliminary experiments with molybdate solutions indicate other possible applications of copper as reducing agent.

The author wishes to express his appreciation to Miss Clara Adlerblum for her careful performance of the experimental work herein described.

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[1] Received June 2, 1924.

[2] Hendel, Dissertation, Columbia University, **1922**.

[3] Baskerville and Stevenson, *J. Am. Chem. Soc.*, **33**, 1104 (1911).

Continuous Conductivity Method of Measuring Small Concentration of Chlorine in Air[1]

By T. B. Hine

Chemical Warfare Service, Washington, D. C.

THE method here described is one of several investigated in the attempt to develop an instrument for continuous measurement of small concentrations of chlorine in air, to be used in field experimentation. The method soon appeared to be unsuited to field use and was, therefore, not investigated in much detail, but as it may have value in laboratory or plant control, especially as it can be used with other gases than chlorine, it seems worth while to present the results of the experiments.

Electrical conductivity methods of following concentration changes of salts in liquids are well known, but the only extension of this method of measurement to gas analysis of which the author is aware is the determination of carbon dioxide in air by passing it into barium hydroxide solution and measuring the decrease in conductivity of this solution. In the method investigated, air containing small amounts of chlorine is continuously and rapidly scrubbed with distilled water, which then flows through a conductivity cell. The electrical resistance of the cell is a function of the chlorine concentration in the air and serves as a measure of this concentration.

From the beginning it was realized that the success of this method depended upon obtaining a rapid, uniform, and fairly efficient method of scrubbing the air, since low concentrations and rapid fluctuations in concentration were desired. Several familiar types of scrubbers were tried, but most of them require too large a volume of liquid in the scrubber. For instance, with a small tower filled with glass beads, if the water is run through rapidly enough to wash it out thoroughly every few seconds, the ratio of the volume of air to the volume of liquid is too small to permit accurate determination of very small concentrations of chlorine in the air, but if the sensitivity is increased by running the water more slowly, the rapidity of response to concentration changes is lost. For the present purpose very rapid response to concentration changes was necessary, but for many cases of laboratory or plant control this is not necessary and consequently tower-type scrubbers might well be employed.

In all the experiments reported here a glass scrubber operating on the principle of the Ceco sprayer was used. In this scrubber the water falling upon the center of a rapidly revolving horizontal disk is thrown off to the sides in a thin sheet through which the air to be scrubbed must pass. It is quite an efficient scrubber and has the especial advantage that the volume of liquid in the scrubber at any time is small and there is almost no resistance to gas flow.

EXPERIMENTAL[2]

The chlorine and air were run through separate flowmeters and then mixed and led through a long coil of glass in a thermostat to the scrubber. The water was also passed through a long glass coil in the thermostat before entering the scrubber. The chlorine was obtained from a cylinder of liquid chlorine. No check on its purity was made but as the chlorine flowmeter was calibrated with the chlorine from the cylinder by titrating the iodine liberated from a potassium iodide solution by the chlorine, the flowmeter reading gave the rate of flow of chlorine irrespective of the actual purity of the material in the cylinder. The concentrations of chlorine in the chlorine-air mixtures were calculated from the flowmeter readings, and the milligrams of chlorine per liter as reported are estimated not to be in error by more than 3 per cent.

Although it is desirable to use water of very low conductivity since the results show that the sensitivity is greater with such water, it is not possible to use very pure conductivity water as the water must be in contact with air. Several grades of distilled water were used in the course of the work. The best water used had a specific conductivity of 1 × 10^{-6} reciprocal ohms at 25° C., which compares with Kohlrausch's best water in equilibrium with air of specific conductivity 0.8 × 10^{-6} reciprocal ohms at 25° C.

The electrical resistance was measured with standard equipment of high quality, but no effort was made to attain extreme precision, since in the low concentration range of interest here the precision was easily greater than the accuracy of the gas concentration measurements required. The cell constant of the cell employed was 0.327.

With a fixed rate of gas and water flow and water of definite purity, measurements are regularly reproducible. The effect of varying these conditions is shown in Fig. 1, where the electrical resistance of the solution flowing from the scrubber is plotted against the concentration of chlorine in the air being scrubbed for the conditions tabulated below:

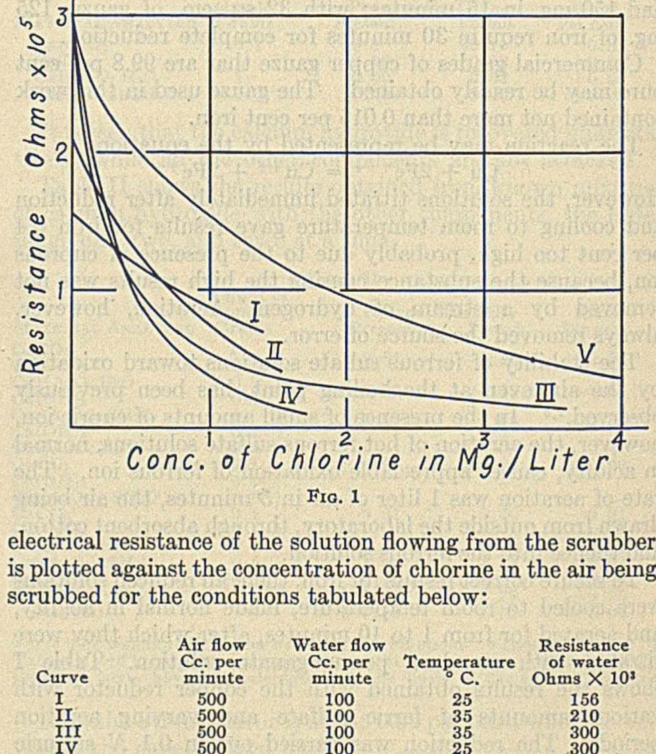

FIG. 1

Curve	Air flow Cc. per minute	Water flow Cc. per minute	Temperature ° C.	Resistance of water Ohms × 10^3
I	500	100	25	156
II	500	100	35	210
III	500	100	35	300
IV	500	100	25	300
V	650	120	30	300

The influence of the purity of the water used is very great, as may be seen by comparing Curves I and IV or Curves II and III. The greater the initial resistance of the water the more rapidly its resistance decreases with increasing amounts of chlorine in the air, but it is not possible to use water of

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[1] Received July 9, 1924.

[2] The experimental work was begun under the supervision of the author by D. H. Parker and completed by E. P. Cox with the coöperation of Simon Klosky.

greater resistance than that of pure water in equilibrium with air. The sensitivity of the method is greater at lower temperatures, as is seen by comparing Curves III and IV.

The sensitivity is dependent upon both the relative and absolute values of air and water flow, and this dependence is in turn a function of the scrubber and resistance cell construction. The optimum conditions can be readily determined by experiment with a given apparatus. The greater the ratio of air to water flow the greater the sensitivity, but the absolute value of the water flow should be kept low since increased water flow greatly decreases the sensitivity. This is shown by Curve V, where, in spite of the increased air-water ratio, the sensitivity is much less than in Curve III owing to the 20 per cent increase in water flow. When the water flow is decreased the time of response to a concentration change is lengthened; hence a compromise must be made for a given apparatus between sensitivity and time of response. In the experiments recorded here the time of response of the resistance change to the concentration change was between 5 and 10 seconds.

Laboratory Experimental Work on Ester Gum[1]

By F. M. Beegle

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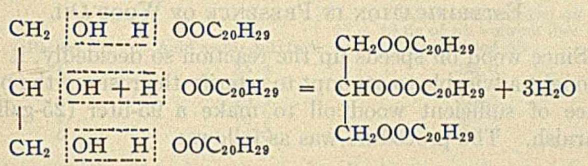
Experiments in the production of ester gum using both an open kettle and a partially closed kettle proved that a partially closed kettle with a stack to condense the glycerol vapors was essential. After trying such catalysts as iron, copper, cobalt, aluminium, and wood oil, the latter was found to be the best when used in limited amounts.

Varnishes made from ester of varying acid numbers were tested and it was proved that it is not necessary to carry the acid value below 14 to 18 in order to make a good waterproof product.

Synthetic ester gum is formed by the union of rosin with glycerol. Since the principal constituents of rosin are abietic acid and its anhydride, the reaction is essentially that of glycerol with abietic acid or its anhydride, whereby one molecule of water is eliminated for each molecule of the acid combined with the glycerol radical.



$$\begin{array}{l} CH_2\;\boxed{OH\;\;H}\;OOC_{20}H_{29} \\ \;| \\ CH\;\boxed{OH + H}\;OOC_{20}H_{29} \\ \;| \\ CH_2\;\boxed{OH\;\;H}\;OOC_{20}H_{29} \end{array} = \begin{array}{l} CH_2OOC_{20}H_{29} \\ \;| \\ CHOOOC_{20}H_{29} \\ \;| \\ CH_2OOC_{20}H_{29} \end{array} + 3H_2O$$

In the past, the method for removing the water of formation, which is essential to the progress of the reaction, had been to treat in an autoclave under pressure. The water formed was converted into steam and escaped through a pop-off valve when the internal pressure became sufficient. In an attempt to get away from this method which required an expensive installation of equipment, experiments were started to ascertain if it were possible to make ester gum in ordinary varnish equipment. Work was started in the laboratory with apparatus giving conditions similar to those obtained by using an open kettle and a partially closed kettle.

Series I

In order to secure a comparison between the open kettle and a covered kettle with a stack to act as a reflex condenser, 500 grams of W. W. rosin and 62.5 grams of glycerol were weighed into each of two 1000-cc. beakers, and two 1000-cc. Florence flasks with necks 2.5 cm. (1 inch) in diameter and 10 cm. (4 inches) long. Ten grams of aluminium foil were added to one beaker and one flask in order to determine if this metal had any catalytic effect on the reaction. All were heated to 271° C. (520° F.) in as nearly the same length of time as possible, and held at about this temperature for 3 hours. Samples were removed every half-hour and tested for acid number. This gave a measure of the progress of the reaction whereby the rosin with an acid number of 150 was changed into the ester which would have a theoretical acid number of zero.

The results of these experiments are given in Table I.

Experiments III and IV proved beyond a doubt that a product of low acid number cannot be made in an open vessel by this method. Experiments I and II prove that a good product of low acid number can be made in a covered vessel with a short chimney to act as a condenser for the glycerol vapors. A comparison of the acid values leads one to believe that the reaction proceeds faster toward completion in the presence of aluminium.

Table I

	1-liter flask		Open beaker	
Period	Expt. I No Al	Expt. II 10 grams Al	Expt. III No Al	Expt. IV 10 grams Al
1	70.1	56.0	97.7	82.2
2	47.0	38.7	91.3	..
3	36.0	30.2	90.4	79.9
4	31.0	23.4	..	..
5	24.0	19.2	..	..
6	19.0	13.7	..	..

Series II

The experiments of Series II were run to determine the catalytic effect of the metals, which could be used for making the kettles for the manufacture of ester gum, on the reaction and the resulting product. The vessels used were 1-liter glass flasks to which 10 grams of the various metals were added in the form of thin foil. The same reacting materials and procedure were used as in Series I.

Table II

Period	Expt. I Glass alone	Expt. II Glass-aluminium	Expt. III Glass-copper	Expt. IV Glass-steel
1	72.5	56.3	67.4	30.9[a]
2	42.8	37.0	42.8	16.3
3	31.9	22.1[a]	29.3	13.0
4	24.7[a]	16.9	23.9	11.4
5	19.5	13.3	21.8[a]	15.9

[a] Product clear after cooling on glass.

A comparison of the acid values given in Table II indicates that steel has the greatest catalytic effect of all the metals used. While a product of low acid value could be secured in the shortest time in a steel vessel, this advantage is offset by the disadvantage that the rosin acids attack the iron and give a very dark-colored product. It is also interesting to note that after a low acid value is obtained in the presence of this metal, the material starts to break down again and the acid number increases.

Aluminium has a greater catalytic action on the reaction than copper and also the advantage of yielding a much lighter

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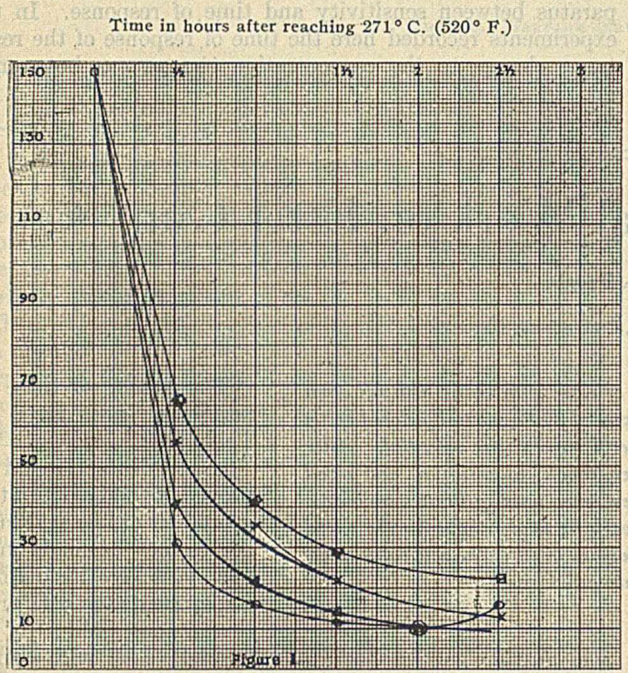
[1] Presented before the Section of Paint and Varnish Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

and clearer product. From this series of experiments it can be safely concluded that the ester should be made in an aluminium rather than a copper vessel, in order to secure a clear product and a low acid number in a given time.

The effect of the metals on the speed of reaction is represented graphically in Fig. I.



Action of Metals on Speed of Esterification

	Grams		Grams
× Aluminium foil	10	△ Lead acetate	5
⊙ Steel foil	10	⚠ Cobalt sulfate	5
⊡ Copper foil	10		

Series III

Series III was run in order to determine the effect of the rate of heating on the speed of reaction and also to ascertain the best time to add the glycerol to the rosin.

Table III

Aluminium foil in all flasks. 500 grams W. W. rosin, 62.5 grams glycerol
Temperature 271° C. (520° F.)

Period	Fast heat 21 min. to reach 271° C.	Slow heat 41 min. to reach 271° C.	Fast heat Glycerol added at 177° C. (350° F.)
1	83.0	73.5	80.5
2	41.0	40.0	45.9
3	30.5	28.3	34.4
4	24.7	19.8	Flask broke
5	17.2	15.6	..
6	12.4	12.0	..

The acid values shown in Table III indicate that the time required to attain 271° C. (520° F.) has little effect on the speed of reaction after the first half-hour period; also that there is only a slight difference between adding the glycerol to the rosin at the start or after the rosin has been melted. However, the difference is in favor of adding both to the kettle at once. These results are shown graphically in Fig. II.

Series IV

The fourth series was run to determine the effect of adding wood oil or the driers, lead acetate and cobalt sulfate, on the speed of esterification.

Table IV

Aluminium foil in all flasks. 500 grams W. W. rosin, 62.5 grams glycerol
Temperature 271° C. (520° F.)

Period	Aluminium	5 grams lead acetate	5 grams cobalt sulfate	28 grams wood oil
1	56.3	41.9	43.2	41.9
2	37.0	22.1[a]	23.4[a]	26.0
3	22.1[a]	14.3	13.6	17.1[a]
4	16.9	10.4	12.0	12.5

[a] Product clear on glass after cooling.

Lead acetate, cobalt sulfate, and wood oil all speed up the reaction to a marked degree. The presence of lead in the ester gum would be objectionable if it were to be cooked in oil for any length of time, and if a light-colored product were desired. The cobalt sulfate gave a dark-colored product. The ester made with wood oil was equal in clearness to that made in the presence of aluminium alone. The wood oil was as good a catalyst as the previously mentioned materials, had the advantage of being a normal constituent of any varnish, and had no apparent objectional qualities.

Series V

Series V was run to determine the quantity of wood oil that could be used to best advantage.

Table V

Aluminium foil in all flasks. 500 grams W. W. rosin, 62.5 grams glycerol
Temperature 271° C. (520° F.)

		Wood Oil		
Period	Aluminium	14 grams	28 grams	57 grams
1	67.5	60.7	50.8	34.2
2	37.1	32.8	28.0	17.9[a]
3	23.4	18.6[a]	17.3[a]	12.4
4	18.7[a]	13.6	12.7	9.7
5	14.8	10.5	9.8	8.4

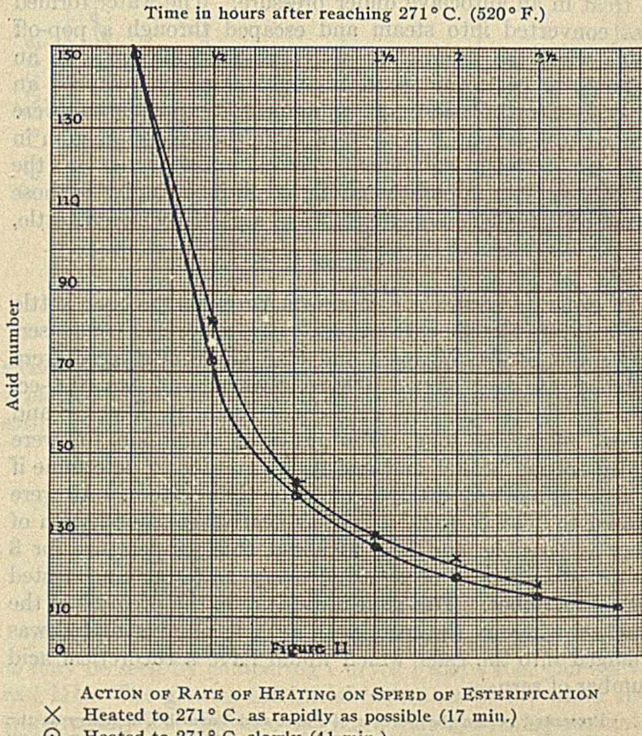
[a] Clear on glass after cooling.

These data show that wood oil had a decided catalytic effect on the esterification reaction and that by using 57 grams of wood oil to 500 grams of rosin a product of lower acid value can be secured in 1.5 hours than in 2.5 hours in the absence of the oil. The gum produced is very slightly darker in color, is not sticky, and could be stored very satisfactorily in the same manner as the raw rosin. The results of this series are represented graphically in Fig. III.

Esterification in Presence of Wood Oil

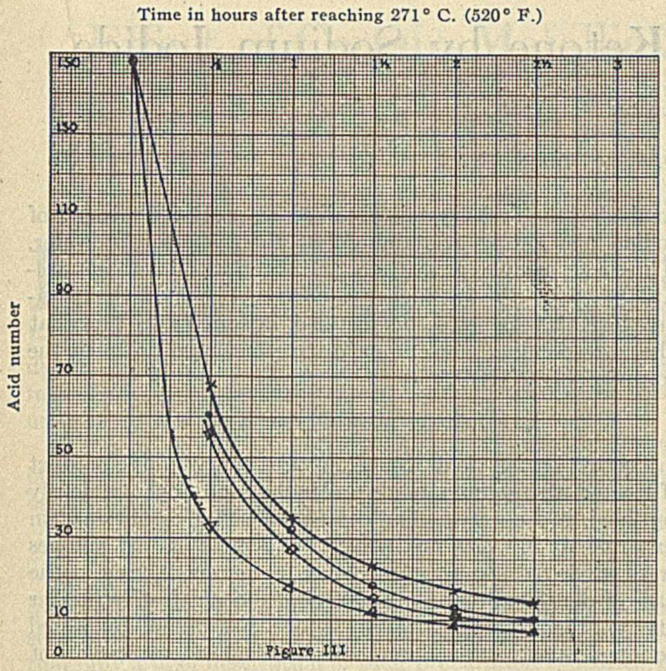
Since wood oil speeds up the reaction so decidedly, it was thought advisable to attempt to esterify the rosin in the presence of sufficient wood oil to make a 95-liter (25-gallon) varnish. The procedure was as follows:

1160 grams of W. W. rosin and 160 grams of glycerol were added to the flask at the same time, together with 2268 grams of



Action of Rate of Heating on Speed of Esterification

× Heated to 271° C. as rapidly as possible (17 min.)
⊙ Heated to 271° C. slowly (41 min.)
Heated to 177° C. before adding glycerol, curve between X and O.



Action of Wood Oil on Speed of Esterification
× Without oil
⊙ 14 grams oil in 500 grams rosin
⊡ 28 grams oil in 500 grams rosin
△ 57 grams oil in 500 grams rosin

wood oil. The contents were heated to 520° F. as rapidly as possible. Samples were removed every 15 minutes, after reaching 271° C. (520° F.), and their acid value determined.

Period	Acid value mixture	Acid value calculated on basis of no volume due to wood oil
1	35.4	90.0
2	26.2	65.5
3	20.1	50.5
4	16.2	40.5
5	14.0	35.0

Apparently this is too much oil, because the reaction is slowed down to a great extent. The actual acid number of the rosin present was greater in this experiment at the end of 2.5 hours than at the end of the first half-hour period, when only 57 grams of oil were present in 500 grams of rosin.

Water Test

Series of ester gums were now made up, using 1000 grams W. W. rosin, 125 grams glycerol, 10 grams aluminium foil, and 113 grams of wood oil, attaining acid numbers 6, 11, 15, 22, and 30. Each ester gum of this series was made up into a varnish.

It was interesting to learn that the rate of bodying of the oil is in direct proportion to the acid number of the ester gum. The ester gum with an acid value of 6 bodied very rapidly, while the one with an acid value of 30 bodied slowly.

Thirty cubic centimeters of white enamel drier were added to about 1 liter of each of the above varnishes, after which they were flowed on glass panels, air-dried 64 hours, then immersed in water for the water test.

Their drying time and order of waterproofness is as follows:

Glidden Ester Varnish

Acid value	Drying time Hours	Order of Waterproofness
6	7	Unaffected
11	7	
15	7	
22	7	Slight whitening on the fatty edges
30	7	

All the varnishes made from esters with acid values from 6 to 30 are very waterproof and the only sign of whitening after standing in water 4 days is along the fatty edges of 22 and 30. As a result of this series of tests the writer advises making an ester gum with an acid value anywhere between 10 and 18. While an ester with an acid value as low as 4 or 5 might prove better in a long endurance test under water, it is his opinion that this advantage is offset by the greater time required to make this low acid ester, with consequent loss in color, and by the increased difficulty in manipulating the wood oil with it.

Conclusions

1—A good grade of ester gum can be made without vacuum or pressure.

2—The vessel in which ester gum is made must have a tight-fitting cover, with a stack in the center sufficiently long to act as a reflex condenser for glycerol vapors and at the same time short enough to permit the water vapor to escape before condensation.

3—A clear product can be best obtained by using an aluminium kettle.

4—Aluminium has a catalytic action on the esterification reaction, and hence a kettle of this metal will help increase production.

5—Wood oil increases the speed of reaction. By use of 1.5 gallons per 100 pounds rosin a lower acid number can be secured in 1.5 hours less time than without it.

6—The higher the acid number of the ester gum, the more it retards the bodying of wood oil.

7—Any ester with an acid number ranging from 6 to 30 will produce a good waterproof varnish when used in connection with wood oil. This being the case, it is not believed advisable to carry on the esterification reaction beyond an acid value of 20 because of the time consumed and the darker product secured.

8—Heating the wood oil for an ester gum varnish at any temperature between 232° and 321° C. (450° and 600° F.) until the proper body is secured does not affect the waterproof properties of the varnish.

Enforcement of Naval Stores Act Begun

Work on the enforcement of the Naval Stores Act has been begun by the Bureau of Chemistry under an appropriation of $10,000 which was made during the last session of Congress and became effective on July 1.

The Naval Stores Act provides that the Secretary of Agriculture

> * * * shall examine, if practicable, upon request of any interested person, any naval stores and shall analyze, classify, or grade the same on tender of the cost thereof as required by him, under such regulations as he may prescribe. He shall furnish a certificate showing the analysis, classification, or grade of such naval stores, which certificate shall be prima facie evidence of the analysis, classification, or grade of such naval stores and of the contents of any package from which the same may have been taken, as well as of the correctness of such analysis, classification, or grade and shall be admissible as such in any court.

A request for analysis, classification, or grade of any lot of naval stores shall be made in writing, on a special form, to the Bureau of Chemistry or to the nearest Naval Stores Inspector. The charge for examining turpentine is fixed at $2 for each sample, with 4 cents per package additional for making; classifying, grading, and marking rosin, 10 cents per package, with a minimum charge of $1; with costs of traveling in addition, when this is necessary.

The Secretary of Agriculture is authorized to purchase from time to time samples of spirits of turpentine and of anything offered for sale as such, for the purpose of analysis, classification, or grading and of detecting any violation of the Act.

Application for analysis, classification, and grading of turpentine, or forms provided for the purpose, obtainable on request, may be made to the Bureau of Chemistry, Washington, or to S. W. Ahlmann, U. S. Food and Drug Inspection Station, Government Bldg., Cincinnati, Ohio, or to C. E. Smith, Room 1301, 15 Moore St., New York, N. Y. Application for the classification and grading of rosin should be made only to the bureau or to Mr. Smith.

Purification of Methylethyl Ketone by Sodium Iodide[1]

By H. L. Lochte

University of Texas, Austin, Texas

TECHNICAL methylethyl ketone is one of the cheap organic chemicals, while the pure ketone is a comparatively expensive material. This fact is not surprising to persons who have tried to purify technical methylethyl ketone by the usual sodium bisulfite method.

Shipsey and Werner[2] describe a method of purifying acetone by dry distillation of its sodium iodide addition compound. This method has been employed frequently since and has proved satisfactory although the rather low temperature required for a good yield requires considerable time. It is now found that methylethyl ketone may be purified even more conveniently by the same method.

The impure methylethyl ketone boiling between 70° and 77° C. is placed in a round-bottom flask and connected to a reflux condenser. The flask is heated in a water bath and enough sodium iodide added to leave a small amount undissolved after refluxing for an hour. The saturated solution is rapidly filtered through a hot-water funnel. The addition compound crystallizes out on cooling the solution to room temperature. To improve the yield of crystals, the solution may be cooled by an ice bath but it is not necessary to cool with a freezing mixture as in the case of the corresponding acetone compound. The mass of white needles is then separated from the remaining liquid by filtering through a Büchner funnel without filter paper. The solid product is next placed in a round-bottom flask connected with a short fractionating column and a condenser. On heating in a water bath the crystals melt at 73° to 74° C. and pure, moist ketone distils over. Toward the end of the distillation the boiling point gradually rises to about 77° C., but only a small amount distils over above 76° C. The ketone is dried in the usual manner. The residual salt or aqueous solution of iodide may be used for subsequent runs after driving over some, but not all, of the water. In a series of trial runs in which both the ketone and the sodium iodide had been carefully dried, no addition compound crystallized out, even on cooling to −10° C. by means of a salt-ice freezing mixture. A small amount of moisture is sufficient to permit the isolation of a small yield of crystalline product, but moisture enough to form the dihydrate of sodium iodide seems to be required for a maximum yield. This phase of the problem, as well as the determination of the vapor pressure and other physical constants, is being taken up by members of the department of physical chemistry of this university.

Analysis of Addition Compound

The analysis of the addition compound presents some difficulty, since the vapor pressure of ketone from the crystals is rather high and the substance is hygroscopic. The fact that no compound could be isolated in case carefully dried materials were employed made it difficult to obtain samples of compound not contaminated with dihydrate. A tentative formula for the compound was determined by means of a series of volatile matter determinations from a large number of different samples of material. The results show that, by varying conditions, mixtures may be obtained ranging in composition from pure sodium iodide dihydrate with 19.4 per cent volatile matter to practically pure $NaI.C_4H_8O$ with 32.43 per cent. The latter may most easily be obtained by analyzing the first crystals obtained on cooling a mixture of iodide and ketone containing less than 5 per cent water. Three such samples gave 31.45, 31.32, and 31.60 per cent volatile matter. Since no higher values were obtained, the tentative formula assigned seems justified, in spite of the fact that the corresponding acetone derivative has been assigned the formula $NaI.3C_3H_6O$.[2]

Experiment with Other Ketones

Diethyl ketone yields a small amount of crystalline product if treated with sodium iodide under the conditions previously outlined, but no crystalline compound could be obtained in experiments in which methylhexyl and methylnonyl ketones were employed instead of methylethyl ketone. Even in the case of diethyl ketone the small yield did not justify further study of the reaction. The only ketone that might be expected to interfere with the sodium iodide method of purification of methylethyl ketone is acetone. Experiments show that, if the mixture has been fractionated so that the boiling point lies within the limits indicated in this article, the common impurities encountered in the purification of methylethyl ketone do not interfere with this method.

Yield

The yield of ketone that may be obtained under laboratory conditions varies between 10 and 20 per cent of original ketone per run. Since the iodide as well as the filtrate or uncombined ketone may be used over and over, the total yield may be raised to about 75 per cent of the original amount of ketone. It is usually more convenient to obtain the desired quantity of ketone by making a few runs on large batches and recovering the uncombined part as technical ketone rather than making a large number of runs on a small batch. The iodide may be used an indefinite number of times, depending on the purity of the crude ketone.

Drying Methylethyl Ketone

The ketone obtained by this method is dried by the same methods as that obtained by the sodium bisulfite method. Although the use of calcium chloride is usually recommended as drying agent, experiments show that there is considerable loss due to the formation of an addition compound with the ketone. Probably because of mechanical interference by a layer of this compound, the product obtained from calcium chloride is usually not quite dry. Anhydrous copper sulfate was found to be best suited as a drying agent for small amounts of ketone.

Comparison of Untreated and Purified Products

Finally, the product obtained by the sodium iodide method was compared with the untreated ketone and with a sample of methylethyl ketone purified by means of the bisulfite method. The results in the table show that pure methylethyl ketone may be prepared cheaply and conveniently by dry distillation of its sodium iodide addition product.

Table I

Sample	Dried by	n_D^{25}	Density at 34°/4° C.	Boiling point ° C.	Pressure mm.
Technical	$CuSO_4$	1.3780	0.787	77 to 78	745
Purified by NaI	$CuSO_4$	1.3775	0.802	77 to 78.5	745
Purified by bisulfite	..	1.3780	0.803	77 to 79.5	745

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[1] Received June 25, 1924.

[2] *J. Chem. Soc.* (*London*), **103**, 1255 (1898).

Effect of Certain Metallic Soaps on the Drying of Raw Linseed Oil[1,2]

By L. L. Steele

Bureau of Standards, Washington, D. C.

LEAD, manganese, and cobalt and combinations of these metals in the form of their soaps are the commonly used driers for linseed and other drying oils. Iron and copper are two other metals which may be introduced through the heat treatment of a drying oil in kettles made from one of these two metals. In addition, iron has been used as a drier in the manufacture of black varnishes.

In this paper data are presented on the comparative effects of different proportions of these five metals and combinations of them on the drying time of raw linseed oil.

Preparation of Metallic Soaps

Fused metallic resinates were selected as a convenient form of the respective metals for introduction into raw linseed oil. They were prepared by customary methods,[3] so that only a brief description of their preparation is necessary.

The resinates were prepared by the fusion of water-white rosin with the acetates of lead, manganese, cobalt, and copper and freshly precipitated ferric hydroxide made from electrolytic iron containing less than 0.01 per cent manganese. The metallic acetates were C. P. reagents.

The lead resinate was light amber in color and contained 6.73 per cent of lead. The manganese resinate was amber colored and contained 2.93 per cent of manganese. The cobalt resinate was ruby colored and contained 3.29 per cent of cobalt. The copper resinate was deep emerald in color and contained 4.16 per cent of copper. The iron resinate was very dark brown and contained 2.76 per cent of iron. All these resinates dissolved to a clear solution in benzene, except iron, which showed traces of sediment.

Preparation of Samples Containing Different Amounts of Drier

A clear sample of raw linseed oil with an iodine number of 191, which conformed to the requirements of Bureau of Standards (*Circular* **82**, 2nd ed., U. S. Government Specification for Linseed Oil), was selected for use in all the drying tests. Stock samples of oil containing definite percentages of metal were prepared by incorporating the necessary amount of the respective metallic resinate in a weighed quantity of oil. The resinate and oil were heated to 150° C., thoroughly shaken, and allowed to cool. In this way thorough mixing was obtained without an appreciable alteration of the oil through heat treatment. Portions of these different stock solutions were diluted with definite amounts of raw linseed oil to give a series of samples with decreasing percentages of metal. These samples were all kept in tightly corked tubes, the air in which had been displaced by carbon dioxide to preclude any preliminary oxidation of the oil.

Determination of Drying Time of Samples

The linseed oil samples containing definite percentages of metals were flowed in streaks approximately 2 inches wide on thoroughly cleaned window-glass plates measuring 6 by 8 inches. The excess oil was drained by inclining the plates at an angle of approximately 45 degrees to the vertical for 15 minutes, the bottom edge wiped off, and the plates laid in a horizontal position. The drying tests were made in an evenly heated laboratory, free from combustion or chemical fumes, and lighted by northern exposure. A recording thermometer of the wet and dry bulb type yielded data concerning any fluctuations in temperature or humidity. The average relative humidity during the drying tests was 40 per cent, with a variation from 36 to 43 per cent, with the exception of one 24-hour period when the relative humidity reached 49 per cent. The average day temperature during the drying period was 23.3° C. (74° F.), with a variation from 22.2° to 23.9° C. (72° to 75° F.), while the average night temperature was 20° C. (68° F.), with a variation from 18.9° to 20.5° C. (66° to 69° F.).

The oil films were tested at regular intervals, approximately in the center, 2.5 cm. (1 inch) from the top. The oil was considered to be dry when the finger could be drawn lightly over the surface at an arbitrarily chosen point without marring it. Fairly definite end points could be obtained with the rapid drying oil mixtures; with the slow drying samples the exact length of time for the film to become dry could not be determined with a high degree of accuracy. It should be emphasized that this method for the determination of the drying time involves a considerable personal element, but the data presented are intended chiefly to show the relative catalytic drying effects of the five metals and combinations thereof.

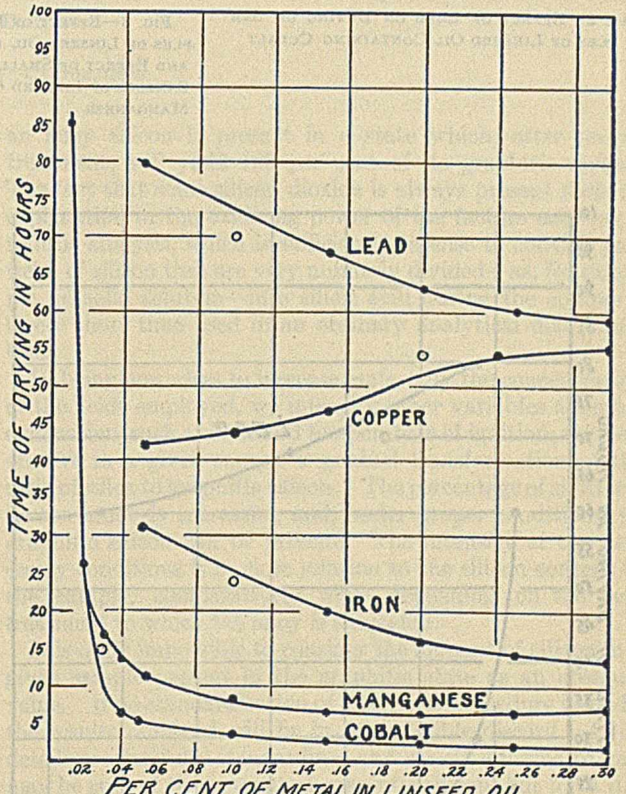

Fig. 1—Effects of Different Percentages of Lead, Copper, Iron Manganese, and Cobalt on the Drying of Linseed Oil

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[1] Received April 14, 1924. Presented before the Section of Paint and Varnish Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] Published by permission of the Director, U. S. Bureau of Standards.

[3] Educational Bureau of the Paint Manufacturers' Association of the United States, *Circular* **120**; Seeligmann and Ziecke, "Handbuch der Lacund Firnisindustrie," p. 701.

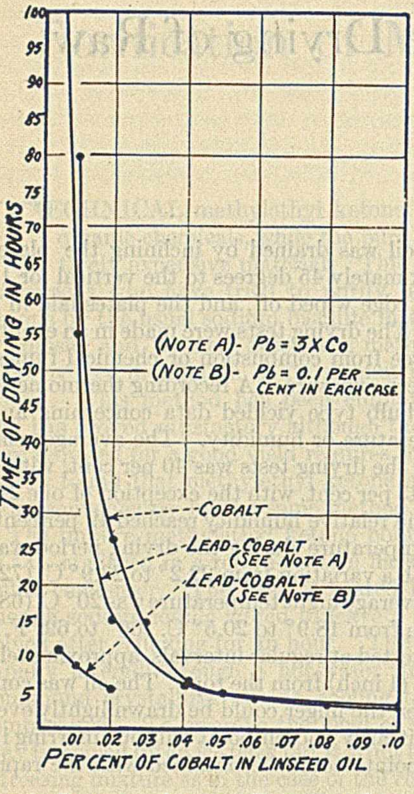

Fig. 2—Effect of Lead on Drying of Samples of Linseed Oil Containing Cobalt

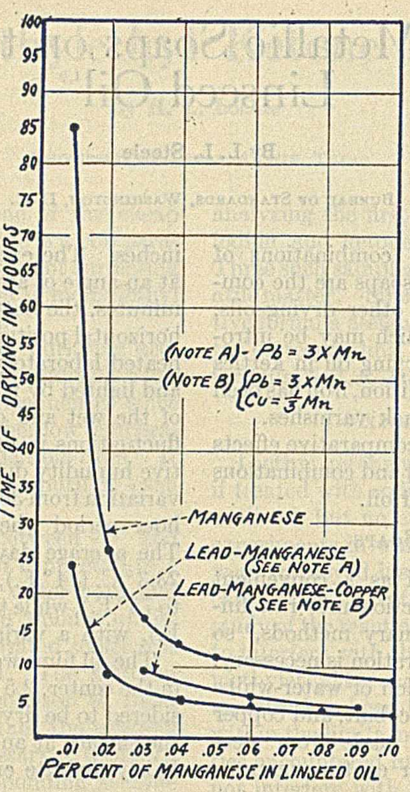

Fig. 3—Effect of Lead on Drying of Samples of Linseed Oil Containing Manganese, and Effect of Small Amounts of Copper on Samples of Linseed Oil Containing Lead and Manganese

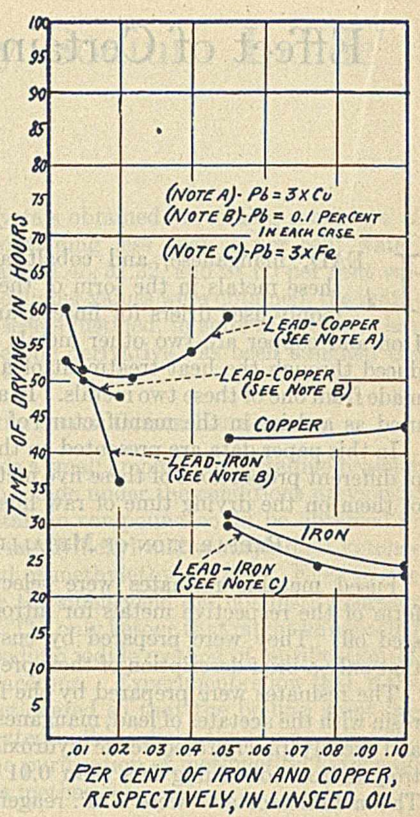

Fig. 4—Effect of Lead on Drying of Samples of Linseed Oil Containing Copper and Iron

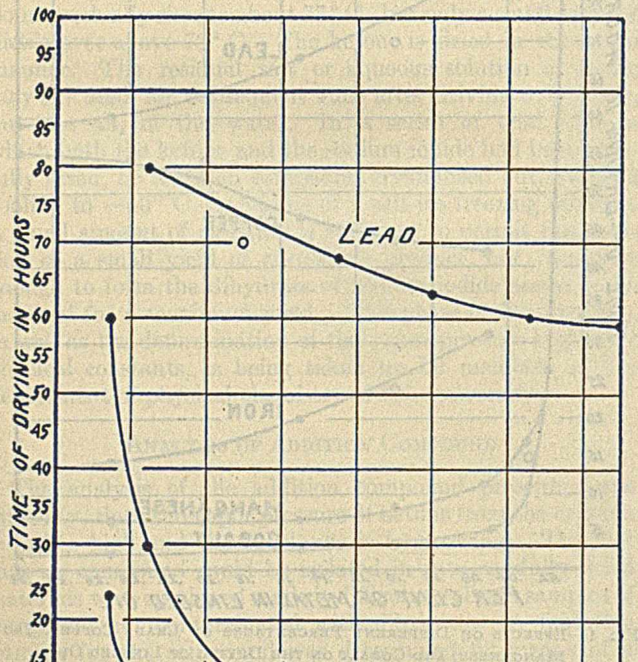

Fig. 5—Effect of a Constant Small Percentage of Manganese on the Drying of Samples of Linseed Oil Containing Different Amounts of Lead

Tabulation of Results

All the data on the drying effects of the different metals and their combinations on linseed oil are shown in graphic form in Figs. 1 to 5, inclusive.

Discussion of Data

From Fig. 1 it appears that neither copper nor lead resinate alone is an efficient drier for raw linseed oil. Of the five metals studied, copper is the only one that shows any marked increase in drying effectiveness with decrease in concentration. Iron seems to approach manganese and cobalt in effectiveness when used in comparatively high concentrations. The excessively dark color of the iron solutions would be a serious objection to their use. Cobalt appears to be somewhat more effective than manganese in concentrations ranging from 0.3 to 0.03 per cent; below this concentration these metals seem to be nearly equal in their catalytic action, which begins to diminish rapidly at this point with further decrease in concentration. There seems to be practically no advantage in the use of more than 0.05 per cent of either manganese or cobalt to dry linseed oil.

At a concentration of 0.05 per cent of metal, taking cobalt as 100, the relative catalytic effects of the other metals studied would be, roughly, manganese 46, iron 17, copper 13, and lead 6.5.

From Fig. 2 it is seen that if lead is added to samples of linseed oil containing cobalt in the proportion of 3 parts of lead to 1 part of cobalt, there is very little added catalytic effect when the concentration of cobalt is above 0.02 per cent. Lead in the same proportion seems to add effectiveness when cobalt is present in concentrations approximating 0.02 per cent. A greater concentration of lead adds catalytic effect in a marked degree to small concentrations of cobalt. With

0.1 per cent of lead present, an amount of cobalt as small as 0.005 per cent dries linseed oil in less than 12 hours. A more extended study of the effect of different concentrations of lead on small concentrations of cobalt is desirable.

From Fig. 3 it is seen that if lead is added to samples of linseed oil containing manganese in the proportion of 3 parts of lead to 1 part of manganese, there is a marked increase in the catalytic drying effect. A sample of linseed oil containing 0.01 per cent of manganese is changed in drying time from 85 to 24 hours by the addition of 0.03 per cent of lead.

The addition of small amounts of copper to an oil containing lead and manganese appears to have no appreciable effect upon the drying time. This point is of interest because of the possible entrance of copper into linseed oil which has been heat-treated in a copper kettle.

From Fig. 4 it is seen that if lead is added to samples of linseed oil containing iron in the proportion of 3 parts of lead to 1 part of iron, there is no appreciable increase in the catalytic drying action. In no case did samples of linseed oil containing 0.1 per cent of lead and 0.02 , 0.01, and 0.005 per cent of iron, respectively, dry in less than 35 hours. This fact indicates that iron cannot be classed with manganese and cobalt in catalytic drying action.

The addition of lead to samples of linseed oil containing copper in the proportion of 3 parts of lead to 1 part of copper seemed to have a marked retarding effect upon the drying time. In a similar manner, larger amounts of lead with comparatively small amounts of copper did not produce an effective catalytic drying action.

Fig. 5 shows in a marked way the large increase in drying effect obtained by the addition of relatively small percentages of manganese to samples of linseed oil containing different percentages of lead.

There appears to be no advantage in using more than 0.05 per cent of lead in combination with 0.01 per cent of manganese or more than 0.1 per cent of lead in combination with 0.005 per cent of manganese.

In conclusion, it should be emphasized that the data shown in the paper apply to the relative drying effects of certain metals and combinations of these metals when incorporated with raw linseed oil in the form of metallic resinates. The effect of heat treatment during incorporation of the different metals in the manufacture of a true boiled linseed oil has not been considered. Such heat treatment might have a very considerable modifying effect on the catalytic action of the five metals studied.

Silicon in Aluminium-Silicon Alloys[1]

By John D. Gat

405 Second St., N. W., Canton, Ohio

An analytical chemist who deals with this class of alloys is sometimes at a loss when his results do not agree, and although all probable variables have been kept practically constant, he frequently desires considerably more accuracy. The general rule in such a case is to attribute the discrepancies to the lack of uniformity of the sample. Though the lack of uniformity in the aluminium-silicon series is sometimes very pronounced, a wrong assumption seems to be responsible for devising the methods now in general vogue, and which are therefore inherently inaccurate.

In textbooks of inorganic chemistry and, to the author's knowledge, in all treatises on analysis, it is generally stated that so-called "graphitic" silicon obtained in the course of analysis cannot be oxidized to silicon dioxide by ignition and remain unaffected when treated with a mixture of hydrochloric, nitric, and sulfuric acids generally used for decomposition of the sample. During some investigations on the microstructure of aluminium-silicon alloys undertaken in this laboratory, certain lack of coördination between the structure of metal as seen under a microscope and the results of analytical determinations led to a closer study of the properties of silicon, especially its graphitic variety, and resulted in two statements, the accuracy of which was proved:

1—Graphitic silicon is oxidized to silicic acid when heated with a mixture of hydrochloric, nitric, and sulfuric acids.

2—Graphitic silicon rapidly oxidizes when subjected to the temperature and for the length of time necessary for dehydration of silica. The amount of oxidation is closely related to the temperature and time of ignition.

In other words, the amount of graphitic silicon in a certain alloy is not a definite quantity, but a function of the composition and amount of acid mixture used for solution of the sample, temperature, and time of ignition. With a considerable degree of certainty the theory may be advanced that in an alloy silicon is present in a state which, after proper treatment, will yield 100 per cent of its graphitic variety. The fact that some silicon dioxide is always present finds its explanation in the oxidizing power of the factors entering a routine analysis, which is sufficiently intense to convert particles of silicon that are very minutely divided—as, for example, in solid solution—into silicic acid during the comparatively short time used in an ordinary analytical determination.

If, being powerless to increase materially the concentration of the acids employed, we intensify other variables affecting oxidization, such as time and temperature of ignition, we shall observe in a given sample a gradual transformation of the ratio of silica to graphitic silicon. The percentage of silica will be continuously increasing and, under proper conditions, no graphitic silicon will be present. The intensity of the necessary conditions is in close relation to the silicon content of the sample, comparatively little depending on the heat treatment to which the alloy is subjected.

It is quite impossible to consider the amount of silicon in a given sample present in the graphitic state as an absolute value. If no standardization of analytical procedure is made, the results obtained will be in inadmissible discord. If all details are carefully standardized and closely adhered to, one may be sure of the amount of graphitic silicon, but for a different set of conditions, a different value will result.

Microscopic examinations and study of cooling curves support the theory that silicon is present in alloys in one modification, graphitic silicon, which as such, instead of being an ingredient the presence of which may indicate certain properties of the alloy, becomes just an undesirable complication in analytical work.

A method was devised which eliminates from consideration graphitic silicon and, without being long or elaborate, gives dependable data for routine determinations:

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[1] Received March 3, 1924.

Place a 0.5-gram sample of well-mixed borings in a 50-cc. iron crucible and add 2 grams of solid sodium hydroxide. Cover with a watch glass and moisten with 1 cc. of water. When the violent action ceases, add 9 cc. of water, place on a hot plate, and heat for 30 minutes. At the beginning the liquid boils rapidly, but later, when most of the water has been expelled, no ebullition is observed. Without cooling, transfer the contents of the crucible into a porcelain evaporating dish. Rinse the crucible carefully with water, 35 cc. of acid mixture, and then with water again. Collect the washings in the evaporating dish into which the melt was transferred. Evaporate to dryness and fume strongly for 5 minutes. Cool, take up with 50 cc. of sulfuric acid (1 : 10) and boil until the solution is complete. Filter on ashless filter paper. Wash at least six times with water. Ignite in a platinum crucible and weigh. Add a few drops of sulfuric acid, about 20 drops of hydrofluoric acid, evaporate carefully on edge of a hot plate, and ignite. The difference in weight will give the amount of silicon present expressed as SiO_2.

To prepare acid mixture, mix in the order given, 300 cc. sulfuric acid (specific gravity 1.84), 300 cc. water, 300 cc. hydrochloric acid (specific gravity 1.19), and 100 cc. nitric acid (specific gravity 1.42).

Blanks for deduction should be run on reagents used.

Effect of Iron Oxide Pigments on Rate of Oxidation of Linseed Oils[1]

By F. H. Rhodes, C. R. Burr, and P. A. Webster

Cornell University, Ithaca, N. Y.

The red iron oxide pigments tend first to retard and then to accelerate the oxidation of linseed oil in paint films. Partially hydrated iron oxide is more active than is the anhydrous oxide, while the presence of calcium carbonate in the pigment renders it less active in accelerating the oxidation. Black iron oxide is a relatively inert pigment, although it retards slightly the oxidation of the oil.

THE effect of certain paint pigments on the rate of drying of linseed oil has been studied by Rhodes and Van Wirt.[2] This investigation, however, was confined to the study of the effects of various white paint pigments, and no attention was paid to the iron oxides or to any of the other colored pigments. In view of the great importance and the extensive use of the iron oxide pigments, it was thought advisable to make the study of the effect of these pigments the subject of a separate investigation. The present article describes the results obtained with various typical iron oxide reds and with black oxide. The work on the yellow and brown iron pigments is as yet incomplete.

Materials

The materials used in this work were pure, refined linseed oil from North American seed, lead linoleate paste drier, and representative iron oxide pigments obtained from various manufacturers. The linseed oil showed the following analysis:

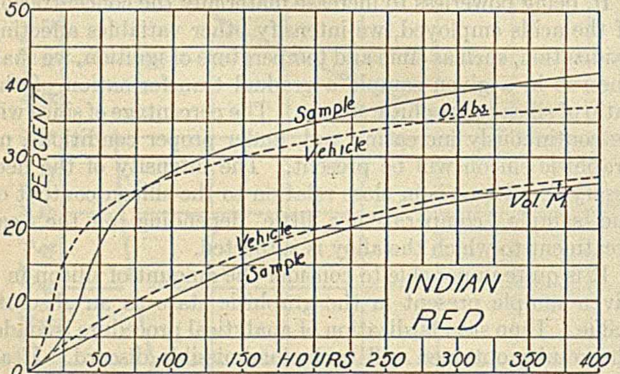

Fig. 1

Specific gravity at 15.5° C.	0.934
Refractive index at 25° C.	1.4803
Acid number	0.473
Saponification number	193.3
Iodine number	173.

The analyses of the various pigments employed are shown in Table I.

Procedure

The apparatus used and the procedure followed in determining the rate of oxidation of the oil in the presence of the pigments were essentially similar to those described by Rhodes and Van Wirt.[2] Paints were prepared by grinding together two parts by weight of the pigment to be studied and three parts by weight of the vehicle. In each case the vehicle was prepared by dissolving in the linseed oil a sufficient quantity of lead linoleate paste (17 per cent lead) to contain an amount of lead equivalent to 0.2 per cent by weight of the oil. The paints were allowed to stand in sealed containers for at least 2 weeks before use. Weighed samples were then spread on cloth and exposed to an atmosphere of pure oxygen at 30° C., and the rate of absorption of oxygen and the rate of evolution of volatile matter were measured. The rate of oxidation of the vehicle alone (linseed oil with 0.2 per cent lead) was determined in a similar manner. In each case at least two determinations were made with each paint. The individual determinations gave results which agree with each other within the limits of experimental error.

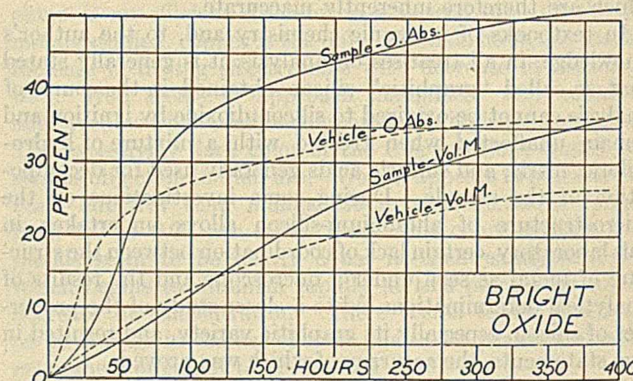

Fig. 2

Results

The results are shown graphically by the accompanying curves, in which the amounts of oxygen absorbed and the amounts of volatile matter evolved (each expressed in terms of percentage by weight of the oil in the paint) are plotted

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[1] Received June 17, 1924.

[2] This Journal, 15, 1135 (1923).

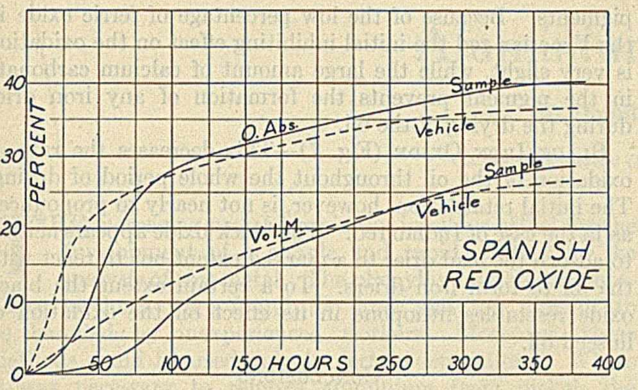

Fig. 3

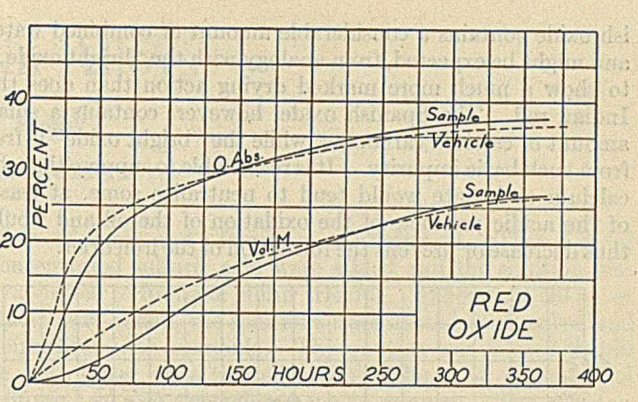

Fig. 4

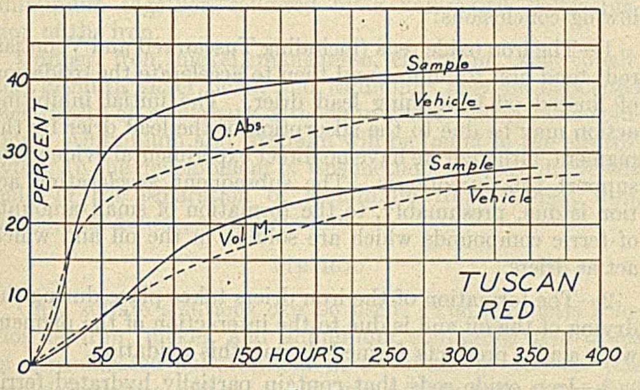

Fig. 5

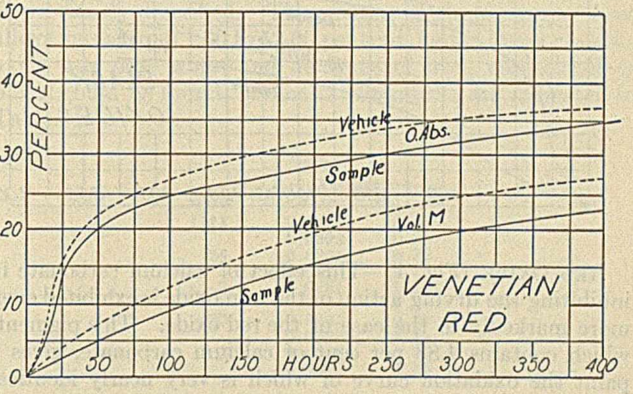

Fig. 6

against the lengths of time of exposure. For each pigment there is plotted only one curve, depicting the average results of the two or more check determinations. On each diagram the graphs for the rate of absorption of oxygen by the vehicle alone and for the rate of evolution of volatile matter from the vehicle alone are shown for purposes of comparison. These graphs are drawn as dotted lines.

Indian Red (Fig. 1)—This pigment first retards and then increases the rate of absorption of oxygen by the vehicle. The initial retardation does not seem to be due to the mere physical effect of the pigment in increasing the thickness of the film and preventing rapid diffusion of oxygen into the mass, but to a specific effect of the iron oxide in accentuating the initial period of induction of the oxidation reaction. One hypothesis which may explain this effect is that the finely divided ferric oxide absorbs some of the lead drier and thereby lowers the concentration of this catalyst in the oil. The subsequent acceleration of the oxidation is probably due to the reaction of the iron oxide with some component of the vehicle or with some oxidation product of the oil, with the resulting formation of a salt or soap of iron which acts as a drier. In this respect Indian red appears to behave somewhat like Carter white lead.[2]

Table I

Pigment	Fe_2O_3 Per cent	SiO_2 Per cent	$BaSO_4$ Per cent	Al_2O_3 Per cent	MnO Per cent	$CaCO_3$ Per cent	$MgCO_3$ Per cent	$CaSO_4$ Per cent	Free H_2O[a] Per cent	Combined H_2O[b] Per cent
Indian red	98.77	0.83	..	..	0.15	..	..	..	0.46	0.10
Bright oxide	93.30	1.10	..	..	0.75	..	..	0.52	0.77	3.84
Spanish red oxide	87.92	6.93	..	1.55	0.21	1.01	..	..	0.39	1.38
Red oxide	86.52	6.57	..	0.70	0.31	5.88	..	..	0.50	0.31
Tuscan red[c]	14.75	0.13	6.55	3.27	0.11	..	..	6.46	2.85	3.65
Venetian red	9.24	1.22	..	0.22	0.43	85.93	1.01	..	0.79	1.27
Black oxide[d]	96.96	1.10	..	..	0.75	..	..	0.52	0.77	3.84

[a] Loss on drying 3 hours at 105° C.
[b] Includes organic matter.
[c] Contains a considerable amount of a red organic coloring matter.
[d] Calculated as Fe_3O_4.

If compounds of iron which act as driers in the oxidation of linseed oil were formed by the direct action of the ferric oxide on the oil itself, we should expect these compounds to be produced during the 2 weeks' period of aging to which the paints were subjected before being exposed. That such was not the case is apparent from the form of the oxidation curve; the driers are formed *after* the oxidation starts. Apparently, therefore, the iron oxide reacts with certain acidic oxidation products formed during the drying of the oil. Of course it is possible that in a highly acid, unrefined oil iron driers may be formed in the paint before it is exposed to air.

Bright Oxide (Fig. 2)—In general form this oxidation curve resembles that obtained with Indian red, but the effect of the pigment in promoting the oxidation of the oil is much more pronounced than in the case of the Indian red. The "bright oxide" also more markedly increases the rate of evolution of volatile matter. The differences in the amounts of iron oxide or in the amounts of impurities in the two reds are, at first glance, hardly sufficient to explain the difference in their effects on the oxidation. It will be observed, however, that the "bright oxide" contains a relatively large amount of combined water, while the Indian red contains but very little moisture. Apparently, the partially hydrated ferric oxide of the "bright oxide" is much more reactive and forms iron driers much more readily than does the more nearly anhydrous ferric oxide of the Indian red.

Spanish Red Oxide (Fig. 3)—This gives results quite similar to those obtained with Indian red, although the initial inhibitory effect is somewhat more pronounced. The Spanish oxide contains a considerable amount of combined water and might be expected, from analogy with the "bright oxide," to show a much more marked drying action than does the Indian red. The Spanish oxide, however, contains a small amount of calcium carbonate, while the "bright oxide" is free from such basic impurity. It is reasonable to suppose that the calcium carbonate would tend to neutralize some, at least, of the acidic products of the oxidation of the oil and would thus decrease or prevent the formation of the iron drier.

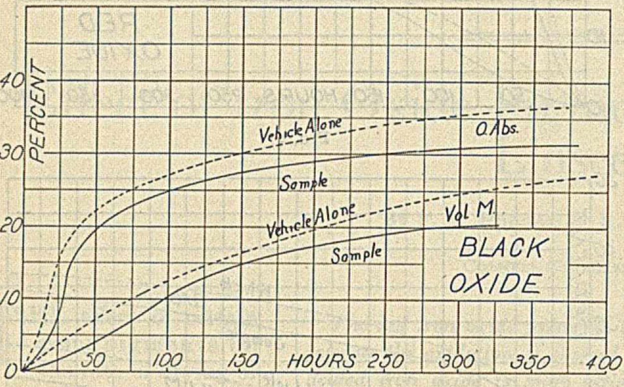

Fig. 7

Red Oxide (Fig. 4)—This effect of calcium carbonate in inhibiting the drying action of the iron oxide is exhibited even more markedly in the case of the red oxide. This pigment, which contains 4.88 per cent of calcium carbonate, gives a paint the oxidation curve of which is very nearly identical with the curve for the oxidation of the vehicle alone.

Tuscan Red (Fig. 5)—With the Tuscan red the effect of the pigment in decreasing the initial rate of oxidation of the oil is very slight. This might be expected, for this pigment contains only a relatively small amount of ferric oxide. The ferric oxide present, however, is in a rather highly hydrated and very active form, so that the iron driers are formed readily and the pigment shows a very pronounced accelerating effect shortly after the beginning of the period of exposure.

Venetian Red (Fig. 6)—This pigment gives results that are quite consistent with those obtained with the preceding pigments. Because of the low percentage of ferric oxide in the Venetian red the initial inhibiting effect on the oxidation is very slight, while the large amount of calcium carbonate in the pigment prevents the formation of any iron drier during the drying of the oil.

Black Iron Oxide (Fig. 7)—This decreases the rate of oxidation of the oil throughout the whole period of drying. The initial retardation, however, is not nearly so pronounced as in the case of Indian red. The black oxide appears neither to adsorb the lead drier to a marked extent nor to react with the oil to form iron driers. To a certain extent the black oxide resembles lithopone in its effect on the oxidation of linseed oil.

Conclusions

The results obtained in this investigation justify the following conclusions:

1—The iron oxide reds (including Tuscan red and Venetian red) tend first to inhibit and then to accelerate the oxidation of linseed oil containing lead drier. The initial inhibiting action may be due to the adsorption of the lead drier by the pigment, although we have no direct experimental evidence to support this hypothesis. The subsequent accelerating action is due, presumably, to the formation of small amounts of ferric compounds which are soluble in the oil and which act as driers.

2—The formation of the iron driers takes place during the drying of the oil and is due to the interaction of the pigment with acidic products formed during this oxidation.

3—Iron oxide reds that contain partially hydrated ferric oxide are much more active in accelerating the oxidation of the oil than are the more nearly anhydrous oxides.

4—The presence of basic substances—as, for example, calcium carbonate—tends to prevent the formation of iron driers during the drying of paints containing iron reds, and thus prevents the pigments from exhibiting their normal effect in accelerating the reaction.

5—Black oxide shows only a slight effect in inhibiting the initial oxidation of the oil, and displays no tendency to react with the oil to form iron driers.

Things Not Known about Rubber

The souvenir number of the *India Rubber Journal*, which commemorates its fortieth anniversary and which was issued August 2, 1924, contains the following among "More Things Not Known about Rubber."

What happens when raw rubber "freezes?"

Why is frozen rubber opaque and thawed rubber transparent?

Why do basic substances have an accelerating and acidic substances a retarding effect in vulcanization? (A simple rubber-sulfur mixture is here in mind.)

Can rubber particles in latex be subdivided—i. e., further dispersed?

Can vulcanized rubber, or crude rubber, or both, be stabilized to such an extent that deterioration or "perishing" shall be no greater than in the case with metals, such as gold or aluminium, or with organic substances, such as horn, leather, wood, and the like?

Why is rubber that is kept in use—i. e., mechanically worked—less liable to deterioration than rubber that remains quiescent?

Does rubber possess coarse—i. e., nonmolecular—structure, and, if so, how does this structure bear on the mechanical properties?

Or are the properties of rubber explainable solely by virtue of its molecular constitution and the grouping of the molecules to form definite aggregates?

Why do finely divided, insoluble compounding ingredients reinforce rubber?

Why have the two forms of finely divided carbon—viz., lamp black and gas black—such widely different effects on rubber in which they are compounded?

To what extent does flocculation really occur among the particles of the compounding ingredients in rubber after vulcanization?

Why does synthetic rubber age more rapidly than natural rubber?

What are the effects of (*a*) air, (*b*) light, and (*c*) temperature in the natural aging of vulcanized rubber?

Why does vulcanized rubber age less rapidly in moist air than in very dry air?

How many other factors affect the aging qualities of manufactured rubber?

Why do the soluble serum substances of latex offer such great resistance to removal in washing latex rubber?

What alteration in the molecular or colloidal structure of rubber occurs in the softening of rubber by milling or by heating?

To what extent is the effect of softening rubber by heat comparable with that of softening by milling?

To what extent is the action of atmospheric oxygen an important factor in the softening of rubber by milling?

Are the great differences observable between the resistance of milling of various natural rubbers caused by differences in the rubber hydrocarbon or by differences in the noncaoutchouc—e. g., pro tem—substances present?

What is the exact nature of the physical alteration in rubber on vulcanization?

When will it be possible to produce "raw" rubber from vulcanized scrap by total removal of the free and uncombined sulfur and the fillers?

Exactly what happens when rubber swells or "dissolves" in a liquid?

Aluminium in Alloys[1]

By Dorothy H. Brophy

GENERAL ELECTRIC CO., SCHENECTADY, N. Y.

THE increasing use of aluminium in alloys called for the development of a simple and rapid method for the analysis of this metal. The phenylhydrazine and phosphate methods were found too long and too difficult to be handled by inexperienced workers. Moreover, these methods could be used only in certain separations. Where it was necessary to remove aluminium from nickel, the basic acetate method had to be used, separating the iron and aluminium together, followed by a volumetric determination of the iron.

Copper, iron, nickel, manganese, chromium, zinc cobalt, tin, bismuth silver, lead, and cadmium[2] may be deposited electrically on a mercury cathode in dilute sulfuric acid solution. Aluminium and titanium will be found in the electrolyte. In the development of this method, we were interested only in the separation of aluminium from copper, iron, nickel, manganese, and chromium.

METHOD

Only sulfate solutions can be used. The synthetic solution of iron, nickel, and aluminium containing five drops of concentrated sulfuric acid in a volume of 100 cc. was transferred to a 150-cc. electrolysis beaker with about 0.63 cm. of mercury at the bottom. A current density of 1 ampere 6.25 sq. cm. was found to be the most satisfactory for the rapid removal of the metals without heating the solution too much. A constant stirring at the rate of 600 r. p. m. was maintained. In 45 minutes no trace of iron or nickel was found in the electrolyte. The clear liquid was siphoned off, using a suction flask and washing the mercury with 150 cc. of distilled water while the current was still on.

The aluminium was then precipitated as aluminium hydroxide in a volume of 100 cc. Methyl red was used as an indicator. The neutralization with the ammonia must be done very carefully, since aluminium hydroxide is soluble in ammonium hydroxide.[3] The precipitate was filtered while hot, washed several times with hot water, dried, and ignited in a weighed platinum crucible to Al_2O_3.

Samples were analyzed, using the procedure just described. About 1.5 hours were required for a complete analysis. Fourteen-hundredths gram of iron and 0.14 gram of nickel were added to each sample.

TABLE I

Aluminium		
Taken Grams	Found Grams	Error Mg.
0.1095	0.1095	0.0
0.1107	0.1111	+0.4
1.0583	0.0581	−0.2
0.0620	0.0604	+0.2
0.0804	0.0804	0.0
0.0735	0.0736	+0.1
0.0719	0.0719	0.0
0.0962	0.0966	+0.4
0.0300	0.0299	−0.1
0.0213	0.0213	0.0
0.0220	0.0215	−0.5

ANALYSIS OF ALLOYS

Twenty-five hundredths to 0.3 gram samples of the alloys containing iron, nickel, chromium, manganese, and aluminium were dissolved in 5 cc. of concentrated hydrochloric acid, 10 cc. of water, and a few drops of nitric acid. Then 5 cc. of concentrated sulfuric acid were added and the solution was evaporated to fumes of sulfur trioxide. When cool, 20 cc. of water were added, the solutions were heated to dissolve and neutralized with ammonia. The solution was diluted to 100 cc. with water, then treated with five drops of concentrated sulfuric acid and electrolyzed for 45 minutes. The colorless electrolyte was siphoned off and the aluminium precipitated as previously described. The amount of aluminium in these alloys varied from 1.00 to 12.00 per cent, and in every case the oxide was pure white and no trace of iron, chromium, or nickel could be found. Some of the results are indicated in Table II.

TABLE II

	Aluminium	
Alloy	Grams	Per cent
1114	0.0111	0.93
	0.0092	0.89
24	0.0264	9.50
	0.0195	9.53
9	0.0231	11.13
	0.0234	11.21
30	0.0321	10.98
	0.0328	11.11
1	0.0348	5.42
	0.0282	5.30

If the alloys contain silicon, SiO_2 separates upon sulfuric acid dehydration and must be filtered before the electrolysis is made. Titanium, if present, remains with aluminium and must be determined colorimetrically in the ignited oxides. The mercury used for the cathode may be replaced after each electrolysis or may be used until it has absorbed approximately 0.6 gram of iron and 0.6 gram of nickel. When used too long, it becomes stiff and blistered on the surface and will not absorb any more metal.

The procedure for the separation of aluminium in alloys containing copper, iron, manganese, nickel, and aluminium differs only in the solution of the sample. About 0.3-gram samples were dissolved in 10 cc. of (1:1) nitric acid and 0.5 cc. of hydrochloric acid, then evaporated with 5 cc. of concentrated sulfuric acid. In electrolysis copper separates at once on the mercury, but with alloys containing 65 per cent nickel in 0.25 to 0.3-gram samples it may take 1.5 hours to remove the last traces of nickel. In every case the Al_2O_3 is obtained pure white, free from the other metals. Some of the results are indicated in Table III.

TABLE III

	Aluminium	
Alloy	Grams	Per cent
1	0.0085	0.81
	0.0026	0.85
2	0.0059	1.95
	0.0058	1.91
3	0.0072	2.84
	0.0073	2.88
19	0.0072	2.80
	0.0071	2.81
16	0.0089	3.52
	0.0089	3.51
23	0.0065	2.93
	0.0077	3.02

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[1] Received May 10, 1924.

[2] Smith, "Electro-Analysis," P. Blakiston's Son & Co., **1907**.

[3] Blum, *J. Am. Chem. Soc.*, **38**, 1282 (1916).

Chemical Society Formed in India

The Indian Chemical Society has been formed with headquarters at Calcutta. Sir P. C. Ray is the president; J. L. Simonsen and G. J. Fowler, vice presidents; P. C. Nutter, treasurer; E. R. Watson, editor.

The first issue of the *Journal of the Indian Chemical Society* was scheduled to appear in August.

Vitamin Potency of Cod-Liver Oils[1]

IX—Oil Produced by the Rotting Process

By Arthur D. Holmes

The E. L. Patch Co., Boston, Mass.

Three liver oils were prepared from the same lot of livers, one from freshly rendered livers, the second from livers rotted 4 months, and the third from livers rotted 8 months. The chemical and physical characteristics of the three oils were determined and compared. The vitamin potency of the oils was studied under comparable experimental conditions, and it was found that the vitamin potency of the oils decreased as decomposition progressed.

DURING practically the entire Christian era, fish-liver oils have been used for medicinal purposes. Until very recently, these liver oils were manufactured by the so-called "sun-dried" or "rotting" process. In brief, this process consists of allowing fish livers to decompose until the liver tissues have been weakened sufficiently to release the liver oil. Owing to its lower specific gravity, the oil rapidly rises to the top of the mass, where it is bailed off.

This method of separating oil from the livers of cod, hake, haddock, pollock, or other fish producing fat-rich livers has certain commercial advantages. It requires no attention and no equipment other than a barrel, which possibly explains its use even up to the present time.

The average fish-liver oil produced by the rotting process is high in free fatty acids and contains fat-soluble decomposition products which possess undesirable odors and flavors. The quality of the best grade oil, the light brown oil, produced by the short-time rotting process, may be greatly improved by chemical treatment.

The fatty acids can be removed, and the objectionable color, flavor, and odor materially decreased by decolorizing, deodorizing, and alkali-washing processes. Considered from the standpoint of energy value, renovated oils would be as valuable as oils rendered from fresh livers. Since at the present time medicinal cod-liver oils are administered principally as a source of fat-soluble vitamins, the question naturally arises as to whether liver oils produced by the rotting process have a potency equal to that of oils produced from fresh livers. It was for the purpose of securing information in this connection that the experiments discussed herein were undertaken.

Experimental

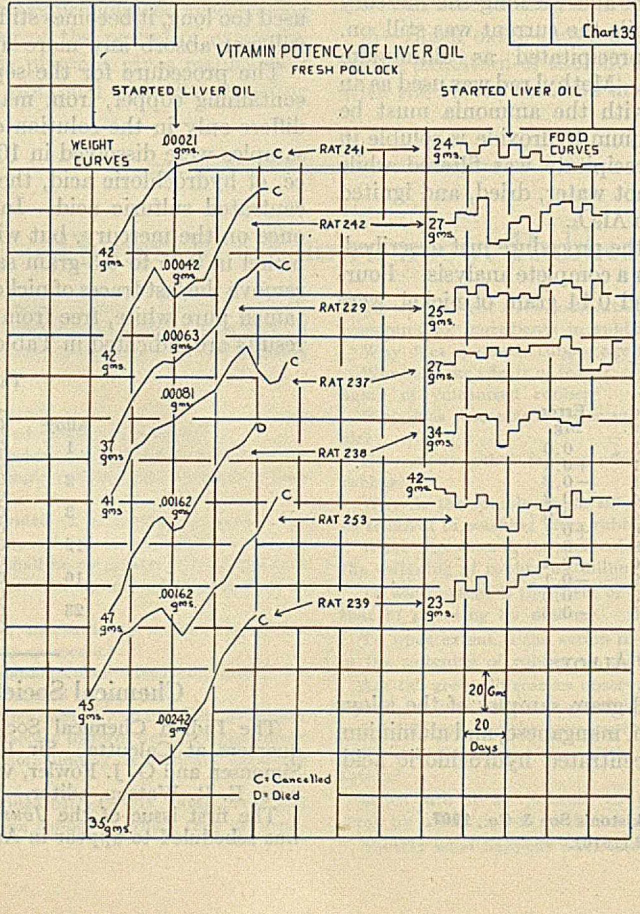
To provide freshly rendered and rotted oils from a common source the author obtained a supply of pollock livers from fish that had been out of the water only a few hours. These livers were cut into two parts and divided into two lots so that each lot contained a lobe from each liver. One lot of livers was rendered promptly under laboratory conditions. The second lot was put in an earthen crock and placed on the roof of a four-story building exposed to sunshine, storms, and fluctuating temperature.

When the livers had rotted 4 months, a sample of oil was removed for experiment purposes. After the livers had been exposed to the weather for another 4 months, a third sample of oil was obtained. The samples of freshly rendered oil, the oil from livers rotted 4 months and from livers rotted 8 months were analyzed by the usual laboratory methods. The results are reported in the table.

Chemical and Physical Characteristics of Pollock-Liver Oils

	Fresh oil	Rotted 4 months	 8 months
Specific gravity	0.9210	0.9296	0.9548
Refractive index	1.4775	1.4787	1.4795
Saponification value	187.3	186.4	206.8
Iodine value	151.4	142.3	112.9
Free fatty acid	1.3%	14.9%	23.3%

The figures for specific gravity, refractive index, and saponification value of the three oils under test increased as the rotting process proceeded. The iodine number was materially lowered as decomposition progressed. The effect of the rotting process was particularly noticeable in the formation of free fatty acids, for the free fatty acid content of the oils from livers rotted 4 and 8 months was 14.9 and 23.3 per cent, respectively, as compared with 1.3 per cent for the freshly rendered oil.



To secure information concerning the vitamin potency of these oils, three comparable series of tests were made with laboratory animals. All the animals were produced by the same breeding colony. Their diet during the experimental period was identical with that described in earlier papers,[2] and consisted of purified casein 18 per cent,

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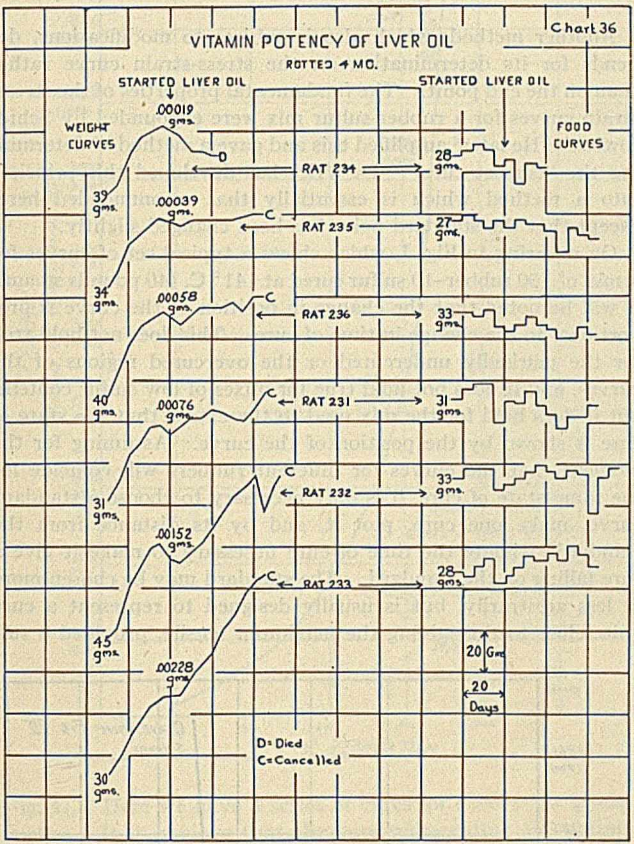
[1] Presented before the Division of Chemistry of Medicinal Products at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] *J. Metabolic Research*, **2**, 131 (1922); **3**, 585 (1923).

peanut oil 22 per cent, cornstarch 28 per cent, milk sugar 28 per cent, and salt mixture 4 per cent, supplemented by a 0.2-gram tablet of dried brewer's yeast daily.

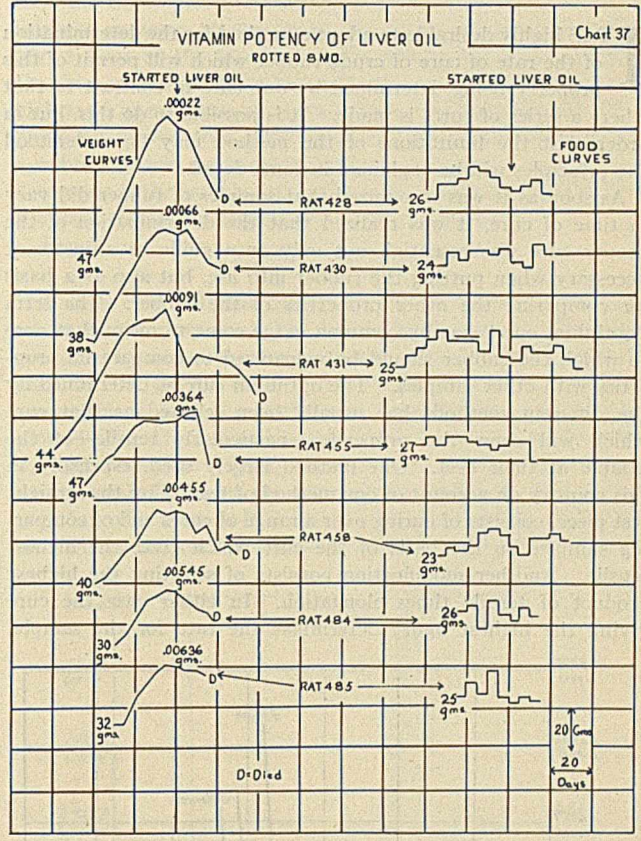
When the physical condition of the experimental animals indicated that their body reserve of vitamin A had been exhausted, they were divided into three groups and their diet was supplemented with varying amounts of the freshly rendered oil, oil from livers rotted 4 months, and oil from livers rotted 8 months. The accompanying charts supply detailed data concerning the change in body weight and the food intake of the experimental animals.



In the tests of the vitamin potency of the freshly rendered oil (Chart 35), seven animals were fed amounts of oil varying from 0.21 to 2.42 mg. daily. One rat (No. 241) was able to do slightly more than maintain his body weight on as little as 0.21 mg. of the oil daily. The remainder of the animals receiving from 0.42 to 2.42 mg. of oil daily grew rapidly.

Six animals were used to determine the vitamin potency of the oils from livers rotted 4 months. Comparing the results of these tests (Chart 36) with those obtained with the freshly rendered oil, it is found that approximately three times as much of the oil from the livers rotted 4 months were required to produce the same growth as with freshly rendered oil.

Of the seven animals fed the oil from livers rotted 8 months (Chart 37), not a single animal was able to complete the 45-day experimental period, even though the amount of oil that they were fed in one instance exceeded 6 mg. daily. Comparing these results with those obtained with the freshly rendered oil, it is evident that this oil contained less than one-twelfth of the vitamin potency possessed by the freshly rendered oil.



Conclusion

From these results it is evident that fish-liver oils produced by the rotting process do not have as high vitamin A potency as oils produced from fresh livers. This conclusion is in accordance with the generally accepted belief of cod-liver oil manufacturers that the highest grade of cod-liver oil is obtained when strictly fresh livers are promptly rendered under carefully controlled rendering conditions.

Calendar of Meetings

American Chemical Society—68th Meeting, Ithaca, N. Y., September 8 to 13, 1924.

The Franklin Institute—Centenary Celebration, Philadelphia, Pa., September 17 to 19, 1924.

American Mining Congress—Sacramento, Calif., September 29 to October 4, 1924.

American Electrochemical Society—Detroit, Mich., October 2 to 4, 1924.

American Ceramic Society—Los Angeles, Calif., October 6 and 7, 1924.

American Institute of Chemical Engineers—Pittsburgh, Pa., December 3 to 6, 1924.

Third Pan-American Scientific Congress—Lima, Peru, December 20, 1924.

American Association for the Advancement of Science—Washington, D. C., December 29, 1924, to January 3, 1925.

National Chemical Equipment Exposition and American Institute of Chemical Engineers—Providence, R. I., June 22 to 27, 1925.

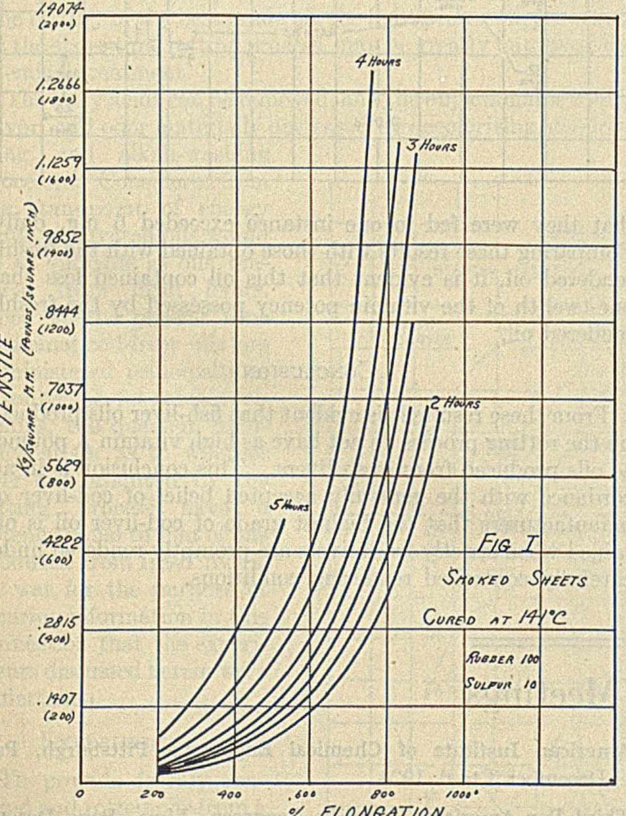
Crude Rubber Testing—Rate of Cure[1]

By C. W. Sanderson

The Fisk Rubber Co., Chicopee Falls, Mass.

It is highly desirable to adopt a method for the determination of the rate of cure of crude rubber which will permit of this property being determined by one cure in contrast to that where a series of cures is made. It is possible to do this, but in order that the limitations of the method may be understood the principles will be explained in some detail.

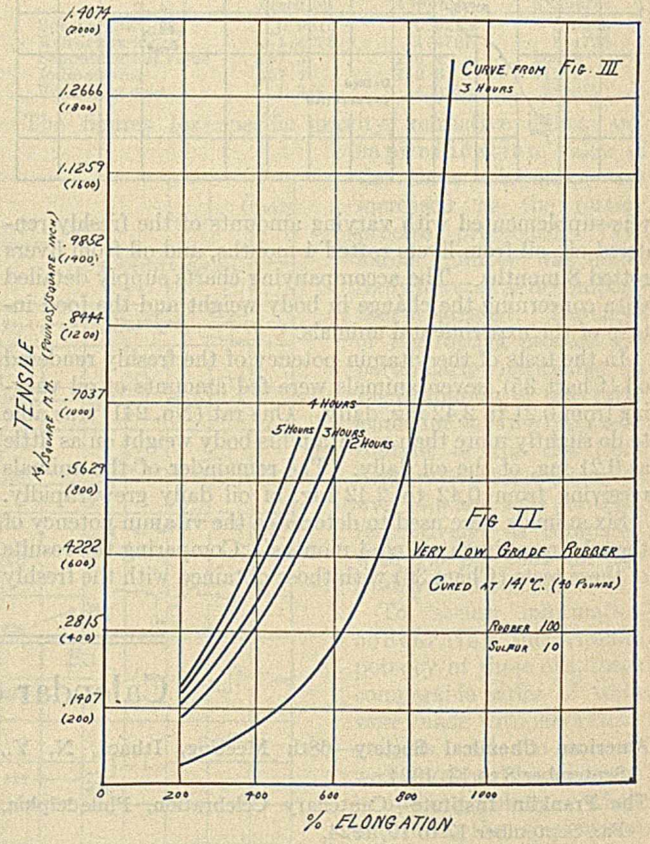
As soon as it was recognized that samples of rubber did vary in time of cure, it was realized that the determination of the proper cure was essential, not only as a guide to adjustment necessary when putting the rubber into use, but also as a basis for comparing the other properties of the rubber. The term "optimum cure" has by common usage come to mean that cure to which the rubber should be vulcanized to compare its properties with other samples. The optimum cure as determined by the different methods has usually been selected as that cure which will show the properties—particularly tensile—of the sample at their best. One method largely used, especially in this country on account of our method of testing by the straight test piece, consists of curing over a range of cures and of comparing samples on the basis of the cure which gives the highest tensile. Another modification consists of selecting the highest product of tensile times elongation. In either case the cure giving the highest figure determines the rate for the sample.



This method has the disadvantage of requiring several cures, and also the greater objection due to the fact that the determination depends on the breaking figures, the uncertainty of which is well recognized.

Another method, which also is subject to modifications, depends for its determination on the stress-strain curve rather than on the end point. The fundamental properties of the stress-strain curves for a rubber-sulfur mix were expounded by Schidrowitz.[2] He later[3] amplified this and gave a method of determining the "correct cure." De Vries has developed this principle into a method which is essentially that recommended here, except that the standard point has been changed slightly.

On referring to Fig. I, which shows a typical set of curves for a mix of 100 rubber–10 sulfur cured at 141° C. (40 pounds steam), it will be noted that the change in position of the curve is proportional to the change in time of cure. This does not hold true for the markedly undercured or the overcured regions of the curves, and it does not hold true for mixes of low sulfur content, but it does hold for the mix used to the extent that the state of cure is shown by the position of the curve. Assuming for the moment that the curves for different rubbers will coincide for the same state of cure, it is only necessary to choose a standard curve, make one cure, plot it, and by its distance from the standard estimate the time of cure necessary to make it give a cure falling on the standard. The standard may be chosen more or less arbitrarily, but is usually designed to represent a cure quite close to that giving the maximum tensile, provided a sufficiently large number of tests are made to determine this tensile accurately.



The problem is not quite so simple as outlined, however. Schidrowitz showed that different grades of rubber did not give

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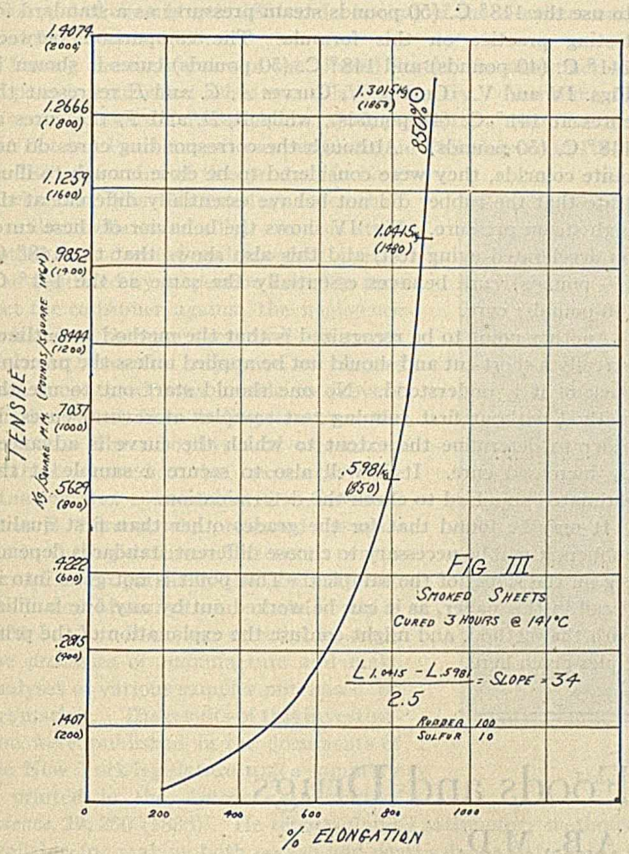
[1] Part of report of the Crude Rubber Committee presented before the Division of Rubber Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

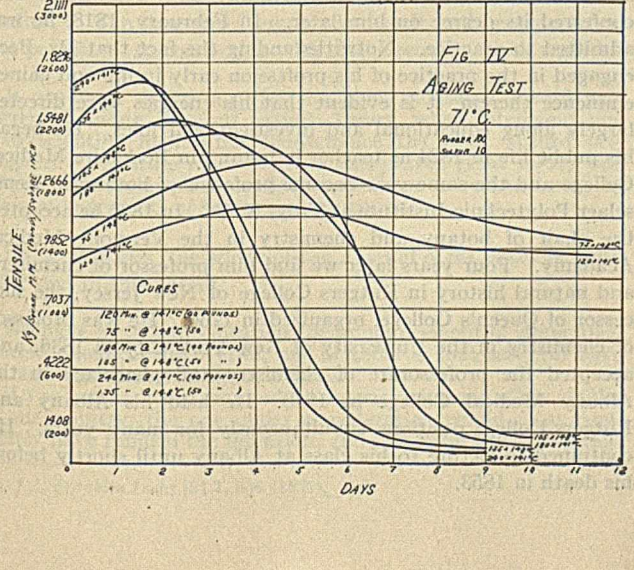
[2] *Rubber Ind.*, **1914**, 212.

[3] *J. Soc. Chem. Ind.*, **38**, 347 (1919).

parallel curves (in the upper portions) at equivalent cures, and that at equivalent cures the elongation at a given load for one sample might be lower than for another. This is illustrated in Fig. II. Here we have a series of cures for a very low grade of rubber. It is obvious that the cure representing the optimum for the low-grade rubber will go through a point of very much lower elongation for a given load than will the optimum cure for a high-grade rubber, and it would be necessary, therefore, to have a different standard point for such a rubber. Theoretically, it would be necessary to have a different standard point for each different slope. In actual practice, however, De Vries, for example, considers it unnecessary to work to such accuracy, particularly because variation of slope large enough to be considered in this connection occurs quite rarely and only in very low-grade rubber.

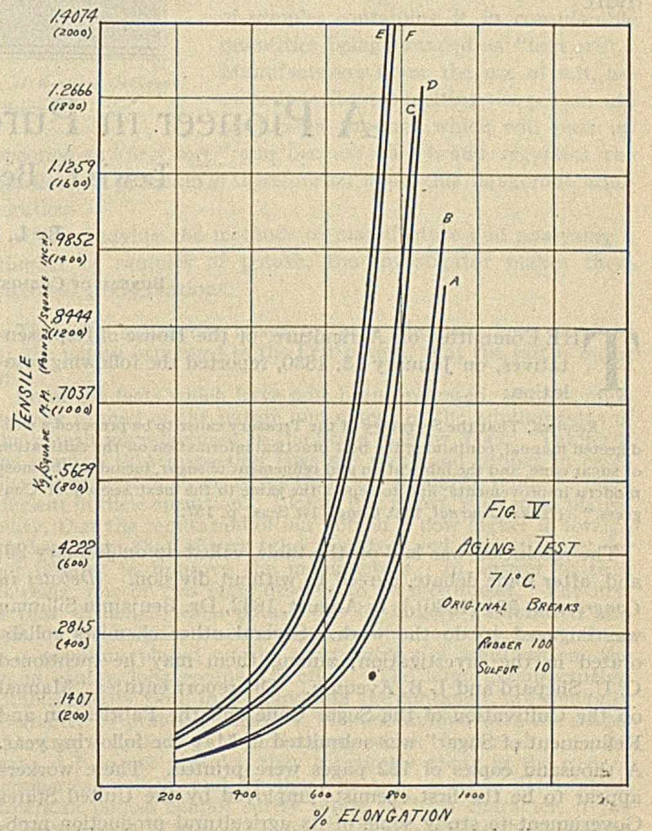


The slope is determined conventionally by Schidrowitz by taking the elongation at a load of 1.04 kg. per sq. mm. minus the elongation at 0.60 kg. and dividing by 2.5. This, of course, is purely conventional, but is much simpler than the actual determination of the slope. The figure should be determined on all samples, for reasons which will be shown, even though one is not working to the accuracy of allowing for different standard curves or points for different slopes. While it is true that the slope does vary slightly for different cures, it is sufficiently accurate to determine the figure on any test within, say, 1 hour of the standard. The figures for slope found by De Vries vary from 35 to 38 on the first grades and run up to as high as 50 in rare cases on lower grades. As stated by De Vries,[4] "high figures for slope, such as 42 and more, generally indicate a rubber which on keeping becomes tackey." Therefore, to determine if the sample falls within the grade represented by the standard, the slope should always be obtained.[5]



Recommended Method

A single cure of 3 hours at 141° C. (Fig. IV) is run on the sample mixed in the proportion 100 rubber to 10 sulfur. The pieces are tested by any of the usual methods to get the full stress-strain data, so that the full curve may be drawn. Usually, four pieces are sufficient, and the results are averaged and one curve is plotted (Fig. III). The slope is then determined in this curve by subtracting the per cent elongation at 386 kg. (850 pounds), which equals 785, from the per cent elongation at 672 kg. (1480 pounds), which equals 870, and dividing by 2.5, the result being 34. (These figures are chosen to compare with those of Schidrowitz.) The distance from the standard point is then determined. For the standard point an elongation of 850 per cent at a load of 840 kg. (1850 pounds) has been taken. (This compares with De Vries' figures of 890 per cent at 1.30 kg., or 1850 pounds per square inch.) The distance of the 3-hour cure from this point is found to be 4.5 units on the per cent elongation



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[4] "Estate Rubber," p. 470.

[5] For further details in regard to the methods indicated above see Schidrowitz, footnote 3; Whitby, "Plantation Rubber," p. 340; De Vries, "Estate Rubber," chapters 17 and 18.

scale. By taking results from a large number of tests, it has been found that a difference of cure of 60 minutes produces a movement of 13.5 units. Therefore, by proportion, since the 3-hour curve is 4.5 units from the standard, the difference of cure necessary to bring this rubber to the standard is 20 minutes. For important tests and for a check it is well to cure another sample at the estimated cure and see how closely it agrees with the standard.

In applying this method it should be borne in mind that the test is suggested simply as a means of determining the time of cure. It is not intended to discuss other qualities in this paper. It should also be recognized that in using this method it is necessary to choose certain arbitrary points, and in these there may be some difference of opinion. For example, curing a rubber to an elongation of 850 per cent at a load of 840 kg. (1850 pounds) represents a technically overcured rubber. The argument for a lower cure is that it will better correspond with technical practice, while the argument for the cure as used in this paper is that the rubber is cured to a state where the full properties are shown to best advantage. Looking at it in this way we are only interested in its properties for test purposes, and its deterioration with age may be determined in a separate test if desired.[6]

When this work was started by the Crude Rubber Committee, it was thought advisable to cure the tests at 141° C. (40 pounds steam pressure), and the foregoing explanation is carried out on that basis. After the first preliminary work, however, it was recognized that there was no essential difference in the character of the curve, whether cured at 141° C. (40 pounds) or 148° C. (50 pounds), and, therefore, in order to save time it was decided to use the 148° C. (50 pounds steam pressure) as a standard for testing practice on this formula. The comparison between 141° C. (40 pounds) and 148° C. (50 pounds) cures is shown in Figs. IV and V. On Fig. V, Curves *A*, *C*, and *E* represent the cures at 141° C. (40 pounds), while *B*, *D*, and *F*, the cures at 148° C. (50 pounds). Although the corresponding cures do not quite coincide, they were considered to be close enough to illustrate that the rubber did not behave essentially different at the high steam pressure. Fig. IV shows the behavior of these cures on accelerated aging test, and this also shows that the 148° C. (50 pounds) cure behaves essentially the same as the 141° C. (40 pounds) cure.

Another point to be recognized is that the method as outlined is really a short cut and should not be applied unless the principle back of it is understood. No one should start out to use the method without first running test samples at several cures, in order to determine the extent to which the curve is advanced by increased cure. It is well also to secure a sample at the estimated standard to check the determination.

It may be found that for the grades other than first quality rubbers it will be necessary to choose different standards depending on the slopes of the samples. This point is not gone into in detail in this paper, as it can be worked out by any one familiar with the method, and might confuse the explanation of the principles given here.

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[6] Comments on this point are given by De Vries, *India Rubber J.*, **61**, 87 (1921).

A Pioneer in Pure Foods and Drugs[1]

Lewis C. Beck, A.B., M.D.

By L. F. Kebler

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

THE Committee on Agriculture, of the House of Representatives, on January 13, 1830, reported the following resolution:

> *Resolved*, That the Secretary of the Treasury cause to be prepared a well-digested manual, containing the best practical information on the cultivation of sugar cane, and the fabrication and refinement of sugar, including the most modern improvements; and to report the same to the next session of Congress." (*House Journal*, 21st Cong., 1st Sess., p. 157.)

The resolution was laid on the table, called up on January 25, and, after some debate, agreed to without division. [*Debates in Congress*, **6**, 554 (1830).] In August, 1832, Dr. Benjamin Silliman was engaged to do the work. Several other chemists collaborated in the investigation; among them may be mentioned C. U. Shepard and J. B. Avequin. The report entitled "Manual on the Cultivation of the Sugar Cane and the Fabrication and Refinement of Sugar" was submitted in May the following year. A thousand copies of 122 pages were printed. These workers appear to be the first chemists employed by the United States Government to study some of its agricultural production problems.

The first chemist to be engaged under a specific appropriation by Congress to make chemical analyses and study the adulteration and deterioration of food products was Dr. Lewis C. Beck, a man of unusual attainments. Energy, enthusiasm, integrity, thoroughness, and love of science dominated his life. He was a physician by education and engaged in the practice of medicine at the age of nineteen. In this profession Dr. Beck and two of his brothers became eminent. Biographies of these three brothers appear in Dr. Samuel D. Gross's "Lives of Eminent American Physicians and Surgeons of the 19th Century," 1861. Another biography of Lewis C. Beck appears in the Annals of the Medical Society of Albany, New York, 1864. In these biographies his work in connection with pure foods, drugs, and other commodities is only briefly mentioned.

Dr. Beck received his A.B. degree from Union College in 1817, and the College of Physicians and Surgeons of New York City conferred its degree on him later. In February, 1818, he was admitted to practice. Notwithstanding the fact that Dr. Beck engaged in the practice of his profession early in life and gained eminence therein, it is evident that his energies were directed largely along educational and investigational lines. He began his public life in 1824 as teacher in botany in Berkshire Medical College and the same year became professor of botany in Rensselaer Polytechnic Institute at Troy, N. Y. In 1826 he accepted the chair of botany and chemistry in the Vermont Medical Academy. Four years later we find him professor of chemistry and natural history in Rutgers College of New Jersey, the successor of Queen's College, organized in 1766. He was professor of chemistry in the University of New York City in 1836, and accepted the professorate of chemistry and pharmacy in the Albany Medical College in 1840. He held his Albany and Rutgers College positions simultaneously for many years. He continued to lecture to his class at Albany until shortly before his death in 1853.

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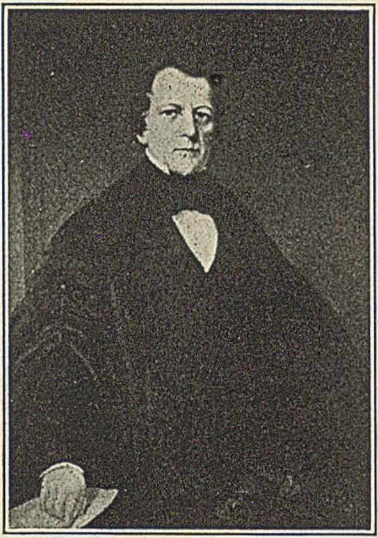
[1] Presented under the title "Lewis C. Beck, M.D., a Pioneer in the Food and Drug Adulteration Movement in America" before the Section of History of Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

In addition to the teaching positions held by Dr. Beck he contributed many articles on various subjects, a list of which will be found in Dr. Gross's autobiography. He also published a manual of chemistry in 1831 and a botany of the Northern and Middle States in 1833.

During the early years of the United States, the manufacture of potash from wood ashes was a large industry. According to Watson's Annals of Philadelphia, 1830, page 218, a manufactory of "Pot and Pearl Ashes" was established in Philadelphia in 1772. In 1832 the value of this product in New York State was estimated at more than a million dollars annually. In this state potash was deemed so important that it was regulated by inspection laws "to protect the consumer against the negligence or frauds of the manufacturer." It seems, however, that the inspection service, as then constituted, was unable to prevent inferior potash from finding its way to the market. The adoption of chemical methods seemed to be necessary. The situation was communicated to Governor Enos B. Throop, who presented the matter to the legislature. The result was a formal investigation by the Committee on Trade and Manufacturers of that body in 1832–3. Dr. Beck was selected to study the processes of manufacture and make analyses of various samples purchased on the market. The results of this investigation were published in the documents of the New York legislature, and a summary is printed in the *American Journal of Science*, 29, 260 (1836). He reports finding satisfactory methods available for making both potash and pearl ash of good quality:



Courtesy of Rutgers College

LOUIS C. BECK

> But instead of following them, various substances are frequently added, either previous to or during the boiling, ostensibly for the sole purpose of facilitating the manufacture, but which really have the effect of increasing the weight of the resulting mass at the expense of its purity.

One of the disturbing factors he discovered was a United States patent, granted February 2, 1831, to Thomas H. Sherman, of New York, for what is termed "an improvement in the manufacture of potash." According to this patent about one-half bushel of salt and two bushels of slaked lime are added to a sufficient quantity of potash to make a barrel of the finished potash. Towards the end of the operation one-half pint of "lamp oil" is added to "create a blaze to consume"—whatever that may mean. The salt is added to create heat, to purify the potash "to burn up and add nothing to the quantity but the quality." The lime was "supposed to melt and become a first rate potash." In connection with this patent Dr. Beck remarks:

> It need not excite surprise that such nonsense should gain currency among ignorant manufacturers, when intelligent and even scientific men often countenance the most absurd pretensions. Scientific men often do themselves great injury and subject those who place confidence in them to serious losses by their endorsements of such valueless paper.

Dr. T. P. Jones, the editor of the *Journal of the Franklin Institute*,[2] says of this patent:

> We have in this specification the announcement of some magnificent chemical discoveries; one of them is that salt will burn up, and that lime will become potash. * * *
>
> If a patent had been required for deteriorating one of the staples of our country, the one under consideration would most completely have fulfilled the intention; and it is earnestly hoped that its validity may in some way be tested in our courts of law, where we apprehend it would not be esteemed to be a "useful invention," according to the intention of the patent law, as its inevitable result if acted upon must be to injure the reputation of American potash in foreign countries; the material would be entirely spoilt as regards its use in many manufactures.

It is difficult to see what value would accrue to anyone contesting the validity of such a debasing patent. It ought never to have been granted.

Dr. Beck found that the addition of quicklime in the process of leaching increased and improved the potash, but of its addition to the lixivium without a second filtration he says:

> * * * becomes then a fraudulent operation, * *. And in the law regulating the inspection of Pot and Pearl ashes, it is made the duty of every inspector to condemn every cask thus adulterated.

Dr. Beck says:

> The addition of common salt is a most unwarrantable practice, as it injures the quality of the potash * * *.
>
> It was not until I had proceeded in this investigation, that I ascertained how general this mode of adulteration had become.

He calls attention to the danger of potash so adulterated escaping detection by the ordinary mode of inspection, and of samples containing it in considerable quantities being branded as "first sort." Manufacturers favor the use of salt, because it facilitates melting the potash and produces a product which will pass inspection as "first sort," and because this brand regulates the market. A premium is therefore set upon this dangerous adulteration.

After studying the methods of manufacture and analyzing a number of samples of potash, the investigator makes these interesting observations:

> This is an instructive lesson to those who have been deceived by the notion expressed in the first patent, that the salt is burnt up.
>
> From the facts which have now been presented, some opinion may be formed of the nature and extent of the adulterations of the potash manufactured in the State of New York. Taking it for granted that inspection laws are right and proper in cases like the present, it seems to me that they should be rendered more efficient in their operation. I know it is urged, with some plausibility, that the reputation of our potash is now higher in foreign markets than that of any other country, and that it is not for our interest to improve the manufacture. In answer to this, however, one or two facts deserve to be mentioned. The first is that, although when potash can be largely adulterated and still, by the ordinary inspection, pass as first or second sort, there is a premium placed on the most successful adulteration, the fraud cannot long escape detection. The large manufacturing establishments, both in England and the continent, are generally conducted by practical chemists, who are familiar with the modes of testing the purity of the substances which they employ. Such tests, if I do not mistake, they constantly apply in the case of commercial potash, and by them its true value is determined. American potash cannot surely retain its high character, if the consumer finds it to contain one-third or one-fourth its weight of soda salts.
>
> It is therefore plainly our interest by all means to prevent the adulteration of our potash and to encourage the adoption of those chemical principles which should regulate the manufacture.

The standard prescribed for potash designated as "pure" or "first sorts," as the result of the foregoing study, was that it should contain at least 85 per cent of potassium carbonate, be free from lime and sodium chloride, and contain not in excess of 3 per cent of insoluble matter.

This report represents one of the best investigations making

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[2] *J. Franklin Inst.*, [2] 7, 366 (1831).

for pure products that was ever made. It is deserving of study by anyone engaged in regulatory work. The investigation covered patents, manufacturing operation, injury to trade caused by adulteration products, analytical data, a standard for pure potash, and necessary legislation.

John A. Dix, New York Secretary of State in 1836, United States Senator 1845–49, called attention to the importance of making a geological survey of the State of New York. One hundred and five thousand dollars were appropriated for the purpose. Dr. Beck was employed as mineralogist. He spent nearly seven years in this work, and his report covers 536 pages, with many plates and cuts. His aim was to make the work useful to the people of the state.

By this time, 1843, considerable sentiment existed against the importation of low-grade drugs and chemicals. A goodly number of books had been published abroad dealing, either in whole or in part, with food and drug adulteration. F. C. Accum's celebrated "Treatise on Adulterations of Food" was reprinted in Philadelphia in 1820, the same year that it appeared in England. J. Cutbush, a contemporary of Dr. Beck, published his "Lectures on the Adulteration of Food and Culinary Poisons" in 1823. Dr. Beck was thoroughly familiar with some of these works, as is clearly shown by the references in his book appearing in 1846 entitled, "Adulterations of Various Substances Used in Medicine and the Arts." Among the publications cited may be mentioned "The Domestic Chemist," 1831; Dumas' "Traite de Chimie," 1843; Burnett's "Outlines of Botany," 1835; J. Garnier et Ch. Harel's "Des falsifications des substances alimentaires," 1844. Dr. Beck's book includes not only medicines, but many foods and some articles used in the arts, together with methods of detecting the various sophistications. It may be interesting to point out a few debasements to which he calls attention:

> Aconitine, mixed with calcareous matter; asafetida, variously adulterated, but about one-fifth of its weight should be insoluble in spirits of wine; beer, mixed with narcotics to increase its intoxicating effects; cayenne pepper, mixed with red lead to prevent loss of color due to light; chicory, cheap as it is, adulterated with roasted barley, spent charcoal, and dregs of coffee; cider, lead salts used to neutralize an excess of acetic acid; confectioner's colored sugars, colored with red lead, vermilion, the copper arsenates, lead chromate and gamboge; copaiba, artificial copaiba a common substitute (the instance is cited of an insurance company refusing to indemnify a proprietor for loss by fire resulting from the manufacture of spurious copaiba); milk, manipulated by extracting the cream, adding water, various gums, eggs, chalk, etc.; orpiment, a mixture of charcoal, sulfur and arsenious acid; soda water, contaminated with lead and imitated by adding a few drops of sulfuric acid to a solution of sodium bicarbonate and quickly corking; sweet spirit of niter, of various grades to suit the price.

The first appropriation by Congress for making chemical analyses of agricultural products was made by the 30th Congress in the following language:[3]

> For defraying the expenses of chemical analyses of vegetable substances produced and used for the food of man and animals in the United States, to be expended under the direction of the Commissioner of Patents, one thousand dollars.

The Commissioner of Patents, in commenting on the investigation says:[4]

> At the last session of Congress an appropriation of $1000 was made for the institution of a system of analyses of the different grains produced in this country, and of flour manufactured here and exported abroad. The two most important problems which it was deemed desirable to have solved in reference to this matter were the effect of soil and climate upon the different varieties of grain produced in this country, and the effect of a sea voyage and storage upon the flour and meal manufactured from grain produced here and sent abroad.
>
> For this important work I engaged the services of Professor Beck, of New Brunswick, New Jersey, an experienced analytical chemist, who has been occupied during the past season in the execution of the investigation confided to his charge, and who has submitted to me a most interesting and valuable report.

The report is entitled "Report on the Breadstuffs of the United States—Their Relative Value, and the Injury Which They Sustain by Transport, Warehousing, etc.," by Lewis C. Beck, M.D., Appendix No. 1, page 245. In the introduction the investigator refers to the object of the work as follows:

> My object has been to show in the simplest manner, and with as few technicalities as possible, how the value of the various breadstuffs may be determined, their injury guarded against, and their adulterations detected.

He discourses on the relations of chemical studies to agriculture, the use of chemical examinations to determine the real value of wheat and other flours, to detect adulterants of flour, such as alum, copper sulfate, the carbonates, pipe clay, plaster of Paris, used to conceal damage or inferiority, and to increase weight. The methods of analysis used are set forth and the data obtained by numerous analyses of flour are given, showing the amounts of water, gluten, starch, and sugar. Attention is called to a few extracts from the report:

> * * the rapid and improper mode of grinding, regrinding the middlings, and mixing therewith the portion first ground, and also the still more objectionable practice, perhaps still followed, of mixing old and spoiled flour with newly ground wheat. * * *
>
> A gentleman residing in the city of Albany, N. Y., informed me that during the past season he witnessed an operation which, if generally performed, will sufficiently account for all the losses sustained in the shipment of the cereal grains. Several persons were engaged in transferring wheat from a canal boat to a river barge; and, while this was going on, it was the business of one of them to sprinkle the grain quite freely with water containing in solution a portion of common salt. As soon as one pailful was exhausted, another was prepared; and the effusion was continued until the work was completed. The addition of the salt to the water was a mere cover for a really fraudulent and most reprehensible operation. * * *
>
> The alkaline carbonates, the carbonate of magnesia, chalk, pipe clay, and plaster of Paris, have all been used, either to correct the acidity of damaged flour, to preserve the moisture, or to increase the weight and whiteness of the bread.
>
> Other frauds which have been resorted to are more difficult of detection; but these are, happily, less prejudicial to health, although not always perfectly harmless. Among these may be mentioned the adulteration of wheat flour with potato starch, the flour of leguminous plants, buckwheat, rice, linseed, etc.

The second report of Dr. Beck appeared in 1849.[5] It is largely an extension of the earlier work. Regarding certain practices, he says:

> It is a matter of deep regret that circumstances have occurred which must have a most injurious influence upon the trade in breadstuffs between this country and Great Britain. I refer to the mixtures of damaged, inferior, and good kinds of flour, which it appears on authentic testimony have been largely exported during the past year. Whether this fraudulent operation, which is said to have been principally confined to New York, is the result of the change in the inspection laws, as some assert, I am unable to say. But it requires no great foresight to predict that, if continued, it will create a distrust of our breadstuffs in foreign ports which it will be very difficult to remove. It cannot but excite the indignation of the many honorable dealers, that the unworthy cupidity of a few individuals should lead to such disastrous consequences.
>
> The frauds which are occasionally practiced should be promptly exposed, and those who are engaged in them held up to merited reproach.

This report, in addition, shows that a large proportion of the flour exported was more or less injured during the voyage. Reference is also made to the controversy then running in Europe and the United States regarding the nutritive value of whole-wheat flour as compared with white flour.

Dr. Beck's investigations are the beginnings of a work that in subsequent years played such a prominent role in the Department of Agriculture activities.

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[3] U. S. Stat. at Large, 30th Cong., 1st Sess., **9**, 285 (1848).

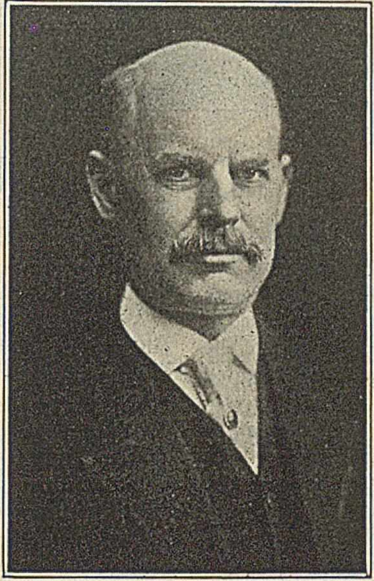
[4] *Pat. Office Rept. Agr.*, **1848**, p. 11.

[5] *Pat. Office Rept. Agr.*, **1849**, p. 49.

AMERICAN CONTEMPORARIES

Edward Goodrich Acheson

IN A lecture delivered many years ago Dr. Edward G. Acheson specified what his experience had taught him were eight important qualities required by a successful discoverer and inventor, which, in somewhat condensed form, are as follows: (1) optimism, (2) imagination, (3) observation, (4) appreciation of the possible value of the new, (5) knowledge of the existing art, (6) self-reliance, (7) determination, and (8) perseverance.



Edward Goodrich Acheson

This list of qualities is worthy of the study which should be given to what is doubtless a self-analysis of one whose discoveries and inventions during a third of a century have had a marked effect, both directly and indirectly, on a number of manufacturing processes. From the time when he was a boy Dr. Acheson has been a keen experimenter, and his talent in that field was early recognized by Edison, who gave him some extremely difficult problems to work out in the construction of the incandescent electric lamp. Not only was his ability as an experimenter recognized, but also his skill as a construction engineer, for Edison engaged him to put in some of his electric light plants in various places in Europe.

After leaving Mr. Edison's employ, Dr. Acheson turned again to his experimental work, and the commercial development of his important discovery of carborundum called for the exhibition of all the eight qualities which he specifies as necessary for ultimate success. It was imagination that led to his experiments; keen observation and appreciation of the value of the new thing that made him follow up the results he obtained; a knowledge of the art which directed the manufacturing processes he developed; and an extraordinary combination of optimism, self-reliance, determination, and perseverance which overcame the innumerable difficulties facing the creation of the new industry of artificial abrasives which have so profoundly modified a great number of manufacturing methods.

It was during the building-up of the carborundum industry that Dr. Acheson carried on experimental work in the manufacture of artificial graphite, although his discovery of the method subsequently used in its production was made almost simultaneously with the discovery of carborundum. This experimental work led to the creation of the artificial graphite industry and its development illustrates Berthelot's aphorism, "La chimie crée l'objet de ses études," for problems which arose and observations made in the course of this work led to further experiments in the manufacture of a new refractory which he called "Siloxicon," and in the artificial production of plastic clays. It was during research work on the latter that, acting on a hint contained in Exodus, chapter 5, verses 7 to 19, he invented "Egyptianized clay," which established certain principles that a few years later he applied to the production of a new form of lubricating graphite.

In a lecture delivered several years ago describing his method of manufacturing graphite, Dr. Acheson gave reason for objecting to the description of his product as "artificial" graphite, his idea being that the adjective "artificial" gave an impression that the material qualified by it must be inferior to the natural product. This perhaps is true; but it is interesting to note that all Dr. Acheson's work had for its object the production of materials having qualities that are not to be found in the substances obtained from natural sources. His creation of the carborundum industry represented pioneer work in the field of artificial materials which have revolutionized the abrasive industry; his experiments on siloxicon were for the purpose of producing an artificial refractory superior to natural products; his "Egyptianizing" process was developed for the purpose of artificially producing in refractory clays a higher plasticity than was found in the natural product; his inventions in the manufacture of graphite led to a successful industry because he could produce artificially a substance having qualities superior for many purposes to the natural product. In short, his success is largely due to an intuitive realization of the possibility of improving on natural products which people had been content to use for years.

The extension of the use of graphite as produced in the electric furnace and manufactured by processes he has invented is still his principal interest, and there can be no doubt that his gratification in these developments is great—as, for example, in the recent war, when the use of his graphite in small arms so greatly increased the efficiency of the rifles with which the soldiers of the American Expeditionary Force were armed.

One of Dr. Acheson's most cherished possessions is a "grandfather's clock," which formerly belonged to Michael Faraday and which he obtained under peculiar circumstances. In 1883, after completing his work for Edison, installing electric light plants in Europe, he was taken seriously ill in London, but fortunately happened to meet there a Mr. James Holloway, formerly a machinist in Edison's employ at Menlo Park, who took good care of him till he could return to America. Eleven years later, when he went to Europe to dispose of some of his European patents for carborundum, he went to London and after a long search found Halloway in poor health and straitened circumstances and was able to give him some assistance. It was while visiting Mr. Halloway on this occasion that he saw in his house the Faraday clock which belonged to Mrs. Halloway and which she afterwards presented to him.

Perhaps something in the early history of Faraday's career excited Dr. Acheson's sympathy, for he also is an interesting example of one who has made a name for himself in technical achievements without the advantages of that formal education which is usually considered a requisite. At the age of sixteen, with but three years' schooling in Belfonte Academy in Pennsylvania, he was thrown altogether on his own resources and thereafter had to earn his own living and incidentally to undertake his own technical education. Possibly his belief that this was actually one of the causes of his success is sound; but the doctrine would be a dangerous one to inculcate generally.

F. A. J. Fitzgerald

Toronto Meeting of the British Association

THE British Association for the Advancement of Science held its Toronto meeting from August 6 to 13, this being the ninety-fourth year of the association. Approximately 3000 were registered, with 582 of that number from overseas, and included in that group were representatives from the farthest corners of the British Empire. There were several who have been knighted in recognition of their services to their country and to science.

Among the outstanding impressions were the manner in which the people of Toronto prepared for, received, and supported the association during its meeting, and the substantial grants of money made by the Dominion Government and the Governments of Ontario, Alberta, and Saskatchewan, which made it possible to secure the attendance upon the meeting of world authorities in various branches of science. Many even returned from vacation resorts in order to do their part in showing appreciation for this the fourth meeting held by the association in the Dominion.

Civic organizations took advantage of the presence of men of international reputations to have them address them, and a demonstration was given of the association's success in reaching citizens and the children through a specially arranged series of lectures. These lectures were given by some of the best men of which the association can boast, and any one who heard Sir William Bragg discuss "Diamond and Black Lead" before an audience of children and then give his presidential address before the Physics Section on "The Analysis of Crystal Structure by X-rays" could not help but be impressed with the success of this great physicist in adapting himself to a particular audience.

The lack of interest sometimes shown by the American public in failing to attend popular lectures on chemical subjects is quite in contrast with the attendance of the Toronto public upon the eight lectures arranged for their benefit. The speakers were received with enthusiasm, their remarks carefully attended, and their efforts applauded. No less enthusiastic was the reception accorded those presenting papers before the thirteen sections of the association. The English custom of extending a vote of thanks to the speaker seemed a pleasant one, while the discussion of papers indicated a familiarity with the subject and a willingness to speak frankly regarding the points made by the author.

All such gatherings require an immense amount of labor and preparation, and the efforts made to abstract papers in advance, to publish these abstracts in the journal available at the meeting, and the large number of section presidential addresses preprinted were especially appreciated. Not only was the journal new to most Americans attending the meeting, but the daily time-table was even more unusual. This booklet gave the actual hours when the addresses, discussions, and papers were given before the sections, and one could decide just which of several meetings he might care to attend at ten o'clock, at ten-thirty, or at any hour.

As was to be expected, so notable a gathering produced several outstanding addresses: Sir Ernest Rutherford on "Atomic Disintegration," the address of Sir William Bragg to which reference has been made, the lectures by A. S. Eddington on "Einstein's Theory," and the "Theory of the Outflow of Radiation from a Star," by Sir Richard Paget on "Voice Production," and the encouraging presidential address of Sir David Bruce on the "Prevention of Disease" are typical examples.

Section B, Chemistry, was well attended at all sessions, though many of the chemists found it difficult to choose between a particular program in their own section and the concurrent one in Physics. Sir Robert Robertson, president of the section, gave his address on "Chemistry and the State," following which W. A. Bone discussed the "Activation of Nitrogen in the Explosion of Carbon Monoxide–Air Mixtures at High Initial Pressures;" James Kendall described a "New Method of the Separation of Elements of the Rare Earths;" F. W. Atack, "Isomerism of Oximes;" J. F. Snell, "Malic Acid and Maple Sugar Sand." One session was devoted to a discussion of Canadian electrochemical industries, and the section joined with Physics in discussing crystal structure, with Physiology in a symposium on vitamins, with Physics in a joint discussion on colloids, and with Geology on liquid and powdered fuels. An excursion was made to plants in the Niagara Falls district. One evening a group of chemists discussed informally the mechanism of explosions and of radiation, and exchanged views on many other topics.

Following the Toronto meeting, two special trains took a limited number of visitors to Vancouver, Victoria, and return, with meetings at Saskatoon, at the University of Saskatchewan, at Edmonton, Victoria, and elsewhere, thus continuing the spread of scientific information to the western portions of the Dominion.

As in all meetings, no small part of the benefit was derived from informal conferences and discussions, which were encouraged, not only by the delightful surroundings of Toronto University, but especially by Hart House, a university social center, which cannot be surpassed anywhere upon the North American continent.

The British Association advances science through grants for the support of research, by the presentation of papers at its sessions, by summing up, from time to time, the actual advance of science in various directions, and partly by bringing to the locality of its meetings a better appreciation for scientific work and education generally. The consensus of opinion is that in the 1924 meeting at Toronto the British Association accomplished its purpose. What more need be said?

NOTES AND CORRESPONDENCE

International Union Meetings

Editor of Industrial and Engineering Chemistry:

It has been my privilege to attend two of the five meetings of the International Union—the third, held at Lyon in 1922, and the fifth, which has just closed at Copenhagen. I have been impressed by several things which may be of interest to members of the American Chemical Society.

These meetings are not intended for the presentation of papers by those in attendance, as is the case with the semiannual meetings of our Society, but only for the discussion, in small committees, of such topics as are of international interest to chemists. These questions embrace such matters as nomenclature, compiling and abstracting chemical literature, preparation and distribution of pure compounds for analysis and standardization tests, the purity of chemical reagents, food preservation, solid and liquid fuels, industrial hygiene, etc.

At the Copenhagen meeting there were 93 delegates from 16 countries. Except for Denmark, whose delegation comprised 21 names, the number from the other countries varied from 1 each in the case of Japan and Argentina, to 15 for France. There were 2 each from Spain, Norway, and Sweden; 3 each from Belgium and Switzerland; 4 each from Poland and Roumania; 5 each from Czechoslovakia, England, and the United States; 9 from Italy; and 11 from Holland. It is therefore a comparatively small gathering, but is composed of some of the most distinguished chemists of the several countries represented.

At the opening meeting the general secretary, M. Gérard, of France, outlines the order of business and requests each delegation to assign its members to the committees on which they are best qualified to serve. At Copenhagen there were thirteen committees and each of the five American delegates served on two or more committees.

The committees consist usually of about ten members, and the discussions are quite informal. The chairman presents the report for the current year and outlines the recommendations for which it is considered desirable to obtain general agreement. The results of the deliberations are embodied in new resolutions, which are usually adopted with unanimity by the committee and presented to the general meeting of the congress for final adoption.

The point which strikes one most is that the delegates usually are prepared to present the authoritative views of their fellow countrymen whom they represent, owing, in many instances, to conferences at home since the preceding meeting. This, however, sad to relate, is not the case with the American delegates, and those of us who are supposed to represent the United States are able to express only our personal views, which may not be in accord with those of our fellow chemists at home. Thus, as happened last year when the new decisions in regard to the nomenclature for biological chemistry were announced in the United States, a great deal of criticism was aroused and our country placed itself in the position of refusing to uphold the engagements of the men who were considered to represent us at the meeting.

This state of affairs should certainly be remedied, and we, as American chemists, should not allow the same criticisms to be applied to our science as is justly applied to our international politics. Our National Research Council, or some other organization, should arrange for a proper discussion among our own men of the questions that are on the agenda for the international meetings, and the delegates representing the United States should be adequately instructed in advance as to the wishes of the majority of our chemists. In this connection, however, we should remember that, even though we are a large and important center of chemical activity, we are only one member of a much larger group, and it should not be our aim to impose our wishes on the others, but to coöperate by making such concessions as will result in the greatest good to the largest number.

This point is especially noticeable at the international meetings. There appears to be a somewhat limited spirit of concession. Each of the larger countries represented considers that its usage is the best and should be followed by the others. This attitude results in misunderstandings and retards progress. I was particularly impressed by this in the discussions of the revised nomenclature for biological chemistry. It has been pointed out very clearly by M. Bertrand, however, that in selecting new names the requirements of a large number of languages must be satisfied if possible. New names must be such as may be written and pronounced in more or less the same manner in such different languages as those of Latin, English, Germanic, Slavonic, and possibly Asiatic origin. Hence the names which a particular country has used for many years and desires to preserve may be extremely difficult of adoption by another country, and certain concessions to the general good may sometimes be required of all.

In regard to the language of intercourse at the meetings, there is no doubt but that French can be used by a larger number of the delegates than can English. Aside from most of the Americans and a few of the English, all the delegates are able to understand and speak French. We must, therefore, recognize the necessity of making some effort to acquaint ourselves with the spoken French language, if we are to contribute our share towards the improvement of matters of international chemical interest.

It is expected that the 1926 meeting of the International Union of Pure and Applied Chemistry will be held in the United States. Here is an opportunity for us to perfect our coöperation in the work of this very important international organization organized for the advancement of chemistry.

Atherton Seidell

Paris, France
July 14, 1924

When Silence Is Golden

Editor of Industrial and Engineering Chemistry:

I have read with interest the various communications of W. A. Noyes, who evidently has set himself to the task of reconciling the recent belligerents. While this is a commendable work, it seems to me that the methods chosen are unlikely to be successful; they are, in fact, more likely to prolong the irritation. All the belligerents are still suffering, and anything that calls attention to the questions at issue only irritates the boils and rouses the fighting spirit. It would be very easy for a northern man to arouse southern sectional feeling by a few poorly chosen sentences after all these years have passed since the Civil War. Silence is therefore the better choice. I think this applies equally to the present situation. If we do the possible things and pass over the impossible ones without notice, we shall be likely to have real peace the sooner. The desirability of peace is apparent to every thinker, the unthinking will not be convinced by any amount of discussion.

Edward Hart

Easton, Pa.
July 8, 1924

The Rennin Coagulation of Milk

Editor of Industrial and Engineering Chemistry:

On page 633 of the June, 1924, issue of THIS JOURNAL, Leroy S. Palmer, in speaking of the views of Alexander, and of Schryver, on the rennin coagulation of milk, says:

> Both these purely colloidal theories of the rennin coagulation are shown to be impossible by the observation of the writer that perfectly stable suspensions of calcium caseinate can be prepared without the presence of other protective colloids. Moreover, these calcium caseinate milks, in the proper concentration and when brought to the proper Sörenson value of 6 to 6.5 in the presence of a trace of calcium ions, show a normal rennin clot which exhibits all the properties of syneresis, etc. These gels, however, lack the firmness of normal rennin gels, showing that this property is contributed in part by the other constituents of the milk.
>
> The chemical properties of calcium paracaseinate, as the product resulting from the action of rennin on calcium caseinate is called, indicate that the rennin coagulation is both chemical and colloidal.

The view advanced by Alexander as to the rennin coagulation of milk[1] is that the enzyme splits the lactalbumin, converting it probably into products that exert a coagulative rather than a protective action, the coagulation being aided by calcium ions released from adsorption. This view is supported by the fact that the highly protected mother's milk is coagulated slowly, if at all, by rennin, whereas the cow's milk, having a low protective ratio, is readily coagulated. Furthermore, lactalbumin, a protector to silver chloride, becomes a coagulator when acted on by pepsin.

While casein is generally considered a definite chemical substance, any substance supposed to be such a chemical individual as "sodium caseinate" should have the closest scrutiny. Even granting that perfectly stable suspensions of "sodium caseinate" of unquestioned purity can be prepared, how does that prove the impossibility of the view that protective action is a factor in the behavior of milk (which it is)? If impurities in the "sodium caseinate" will not account for its behavior, there is the question of autoprotection, a phenomenon of wider occurrence than is generally recognized. Dr. Palmer's argument recalls that of the Irishman who, to rebut the testimony of witnesses who swore they saw him steal the pig, offered to bring in ten times as many witnesses who would swear that they never saw him steal it.

It is not out of place to quote a few of the opening sentences from Herbert Spencer's "First Principles:"

> We too often forget that not only is there a soul of goodness in things evil, but very generally, also, a soul of truth in things erroneous. While many admit the abstract probability that a falsity has usually a nucleus of verity, few bear this abstract probability in mind, when passing judgment on the opinions of others.

Even granting that the Alexander-Schryver view does not take into consideration *all* the factors involved, the nucleus of verity should be supplemented, not discarded.

JEROME ALEXANDER

50 EAST 41ST ST., NEW YORK, N. Y.
June 12, 1924

[1] *8th Intern. Cong. Appl. Chem.*, **6**, 12 (1912).

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Editor of Industrial and Engineering Chemistry:

Dr. Alexander apparently takes exception to my criticism of his rennin coagulation theory because I did not permit a "nucleus of verity" in his opinion regarding the explanation of this phenomenon. He also inquires how the behavior of "sodium caseinate" solutions disproves the possibility "that protective action is a factor in the behavior of milk."

Replying first to his question, I may say that the behavior of sodium caseinates throws no light on the rennin coagulation of milk, because (1) rennin will not clot such a caseinate, (2) casein exists in cow's milk, not as a sodium compound, but as a calcium compound. No doubt Dr. Alexander would call the behavior of sodium caseinate towards rennin a case of autoprotection, but I confess I do not quite understand the mechanism by which a colloidal dispersion protects itself.

It is the behavior of dispersions of calcium caseinate, not sodium caseinate, towards rennin which renders Dr. Alexander's theory untenable. The fact that such dispersions will clot with rennin at the proper pH and in the presence of salts of the divalent cations seems to me to be an experimental demonstration of rennin coagulation which throws out of court the circumstantial evidence which Dr. Alexander has cited in support of his lactalbumin-protection theory.

As to whether there is a nucleus of verity in Dr. Alexander's theory, I am of the opinion that there is none at all and that it constitutes one of the exceptions in Herbert Spencer's philosophy which caused him to insert the words "generally" and "usually" in the quotation which Dr. Alexander gives. It was obviously impossible in my paper to review in detail the evidence which Dr. Alexander brought forth in his paper.[1] He cites four points in support of his theory, all of which fall to the ground on close examination:

(1) The failure of mother's milk to clot like cow's milk is not due to a high protective ratio between casein and albumin, as Dr. Alexander believes, but to the very low concentration of casein in mother's milk and to its higher pH. If cow's milk is diluted with water so that it contains only 0.2 to 0.3 per cent casein[2] and the pH value raised to that of mother's milk[3] it will clot like mother's milk without having its casein-albumin ratio changed.

(2) It is undoubtedly true that lactalbumin will protect colloidal dispersions of silver chloride, whereas the peptic digestion products will not do so, but this does not prove that it is the lactalbumin in milk which stabilizes the calcium caseinates. Calcium caseinates are stable without the presence of lactalbumin.

(3) Dr. Alexander states that the products of peptic digestion of lactalbumin "coagulate" the silver chloride in the reaction (pepsin $+$ lactalbumin) $+$ NaCl $+$ $AgNO_3$. This is obviously as much an error as to assume that the coagulation of calcium paracaseinate is caused by albumoses and peptones formed by rennin from lactalbumin. This assumption involves the further one that rennin digests lactalbumin at a sufficiently rapid rate to account for the instantaneous coagulation which it is possible to secure with rennin. Dr. Alexander must admit that he has not demonstrated the correctness of either of these assumptions, but has merely drawn his conclusions from the lactalbumin–silver chloride experiments. Analogies sometimes lead to false conclusions.

(4) Dr. Alexander is correct in stating that "casein" prepared by the method described in his paper requires a smaller quantity of acid for coagulation than a like quantity of milk. This is not due, however, to the absence of lactalbumin, but rather to the absence of buffer salts in which milk abounds. According to Dr. Alexander's reasoning his casein preparation should also be more sensitive to rennin. He apparently failed to try this experiment. Had he done so he would have found that his casein preparation was less sensitive to rennin and very probably would have failed to coagulate. As a matter of fact, there is no analogy between the acid and rennin coagulation. The former is a decalcification resulting in a curd of more or less isoelectric casein (depending on the experimental conditions), while the latter is a gelation of calcium containing protein (paracasein) due apparently to chemical and physico-chemical changes not yet clearly understood. One thing is clear, however—namely, that neither lactalbumin nor its digestion products have ever been demonstrated to play any part, either directly or indirectly, in the actual coagulation process.

L. S. PALMER

UNIVERSITY OF MINNESOTA
UNIVERSITY FARM, ST. PAUL, MINN.
June 24, 1924

[1] *8th Intern. Cong. Appl. Chem.*, **6**, 12 (1912).

[2] Bosworth, New York Agr. Expt. Sta., *Tech. Bull.* **43** (1915).

[3] Clark, *J. Med. Res.*, **31**, 431 (1914–15).

E. F. Armstrong, the immediate past president of the Society of Chemical Industry, expects to sail for the United States on September 13 and to address the New York Section of the Society of Chemical Industry on October 17. His address while in the United States will be in care of Leber Brothers Co., Cambridge, Mass.

Does the *zn/p* Function Fit the Facts?

Editor of Industrial and Engineering Chemistry:

In his article under this title [This Journal, **16**, 856 (1924)] Becker used the classical data of Tower to dispute the validity of the hydrodynamic theory of perfect lubrication [This Journal, **16**, 347 (1924)]. In doing so, he has made the serious mistake of assuming that the temperature rise in a bearing is the same, regardless of the speed or load under which it is operating. Such an assumption is far from correct.

Tower's experiments were performed on four oils—olive, lard, sperm, and rapeseed. Reynolds calculated the temperature rise in the oil film for the experiments on olive oil, and found very good agreement between calculated and experimental friction values. In his calculations Reynolds made allowance for the heat carried away by the oil, by metallic conduction, and for the effect of thermal expansion of journal and brass. He neglected the somewhat minor effect of load on the amount of heat generated, basing his calculations entirely on rubbing speed and oil viscosity. If the effect of load were also considered, the agreement would have been still better. The present writer has applied the same method of correction to the data on lard oil given in Becker's article, with the results given in Fig. A.

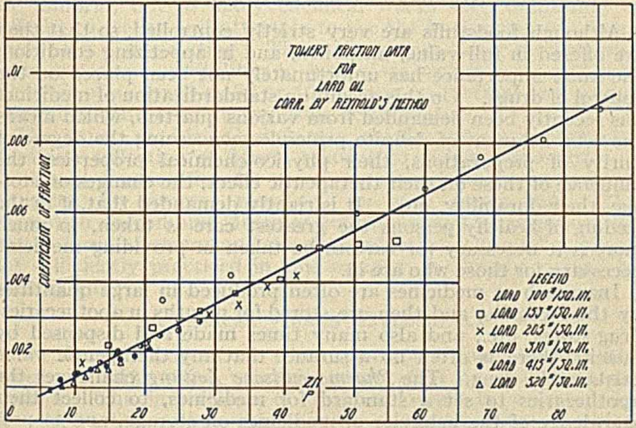

Fig. A

It is interesting to note that the agreement becomes better at low values of *zn/p*—i. e., at small film thicknesses—which is exactly contrary to the effect which would be produced by boundary disturbances. No significance can be attached to the lack of concordance between the results on different oils, as Tower did not record their viscosities. The differences are well within the error involved in estimating viscosities from present-day data.

The present writer has been convinced by careful experimentation that viscosity is the only property of the lubricant involved in fluid film lubrication. That this is not always observed in practice is due to the fact that all machinery, in starting and stopping at least, must pass through the region of adsorbed film lubrication where the chemical characteristics of the lubricant are all-important. Neither is the question of stability of the lubricant involved in the foregoing statement.

The *zn/p* function will fit the facts provided the two régimes of lubrication are not confused.

D. P. Barnard

Massachusetts Institute of Technology
Cambridge, Mass.
June 12, 1924

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Editor of Industrial and Engineering Chemistry:

Mr. Barnard has replotted the data of Fig. 1 in my article after correcting the film temperatures. The plotted points of his Fig. A show that he must have assumed film temperatures of approximately 140° F. for the data at 450 r. p. m., which is a correction of 50° F. Reynolds concluded that the maximum probable rise in the temperature of the film above that of the bath was only about 15° F. in the case of Tower's olive oil experiments.[1] These corrections were found necessary to make his calculated curve correspond to Tower's experimental curve. Reynolds, therefore, concluded that the temperature of the oil film was about that amount above that of the bath. It is hardly justifiable to make a correction of as much as 50° F.

A correction of 50° F. has apparently been made by Barnard for both the 100-pound and the 520-pound loads at 450 r. p. m. A correction of approximately 40° F. has been applied for the same loads at 150 r. p. m. From Fig. 1 it obviously follows that such corrections can only result in a shifting of the entire curves, since the corrections are constant for any given speed.

The real reason that all the points lie close to the curve prepared by Barnard is that he has reduced his scales far below that permitted by the data. This is easily demonstrated by merely replotting the data of Fig. 1 on a scale similar to that used by him. It will be noted that such a curve, Fig. B, fits the observed data as well as that prepared by Barnard. It does not bring out all the facts, however, since the accuracy of Tower's data is such that even larger scale drawings than those used in Figs. 1, 2, and 3 are permissible, as shown by the accuracy with which the various curves of these figures fit the observed data.

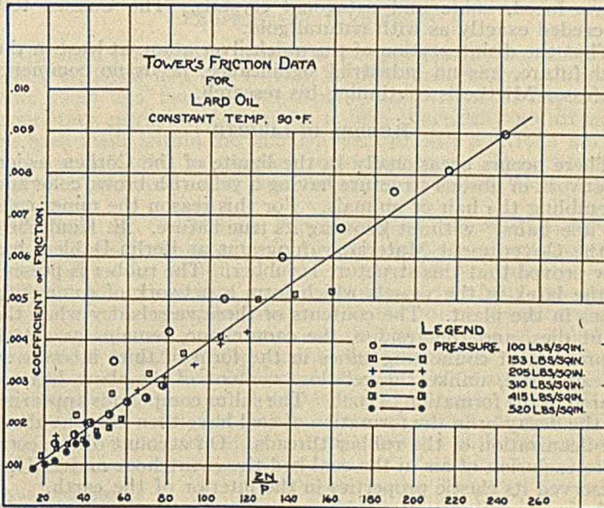

Fig. B

Furthermore, what about the curves of Figs. 2 and 3, where those at the higher loads lie above some of those for lighter loads? For such cases temperature corrections similar to those made for Fig. 1 would tend to separate the curves rather than bring them closer together.

Even though the scales were diminished to the point where a single curve can be used to represent the data of each figure, the curves so obtained for the three oils would by no means coincide with each other. Yet Table I shows that the coefficients for corresponding points for sperm and lard oils are not very far apart. Accordingly, Reynolds' method of calculation should give approximately the same temperature corrections in the two cases. Such being the case, the two *zn/p* curves cannot correspond, as demanded by the theory, since Figs. 1 and 2 show that for identical coefficients and loads the values of *zn/p* are almost in a ratio of 2 to 1. Corrections sufficient to account for discrepancies of this magnitude are hardly justifiable.

A. E. Becker

Elizabeth, N. J.
July 16, 1924

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[1] Archbutt and Deeley, "Lubrication and Lubricants," p. 78.

WORLD-WIDE CHEMISTRY

German Letter

By Walter Roth

Cöthen, Germany

Gold from Quicksilver

As a result of recent investigations of Professor Miethe and his assistants the dream of the alchemist of turning quicksilver into gold seems to have been fulfilled. According to preliminary information in *Die Naturwissenschaften*, Professor Miethe, during research on the coloring of transparent minerals and pastes under the action of the ultra-violet rays, obtained this quicksilver transformation. Jaenicke's new mercury lamp quickly formed a black coating on the inside. To great surprise, investigation showed a gold content, although the mercury of the lamp was entirely free from gold before the experiment. The presence of gold was quite readily proved. The metal that remained after dissolving the last trace of quicksilver in saltpeter was golden yellow and consisted of an agglomerate of beautifully shaped, mirror-faced, cubic and octagonal crystals. The Cassius test proceeded exactly as with natural gold.

That the disintegration of the quicksilver atom, at least in the near future, has no industrial significance, needs no comment. Professor Miethe is continuing his research.

Rubber in Lignite

There occurs occasionally in the lignite of the Cöthen region a network of fibrous structure having a yellowish brown color and resembling the hair of animals. For this reason the miner calls it "ape hairs," without knowing its true nature. E. Kindscher, in the Government Materialprüfungsamt at Berlin-Dahlen, has now proved that this structure is rubber. The rubber is present in the latex in the vessels which form a network of connecting tubes in the plant. The contents of these vessels dry when the plant dies, and the residue, the caoutchouc, remains as a true impression of connecting tubes in the form of thin, interwoven threads, and, unlike the cellulose content of the plant, has not shared in the formation of coal. The sulfur compounds appearing by the decay or in the formation of coal have then brought about a vulcanization of the rubber threads. On account of the complete exclusion of air in the coal bed the caoutchouc material has preserved its elastic properties in the interior of the earth.

A similar occurrence of rubber was found in the lignite deposits of the Geiseltal at Merseburg. Here also it is a case of vulcanized rubber, and the Cöthen occurrence can be spoken of as "soft gum," and that at Merseburg as "hard gum."

Pollopas, a New Synthetic Colloid

The synthetic resin chemist and discoverer of "Juvelite," Fritz Pollak, by the condensation of carbamide and thiocarbamide with formaldehyde under quite definite conditions, has obtained a product, "Pollopas," which in many cases will supplant glass and similar materials. Pollopas can be rolled, bored, fraised, polished, and cut. It can be used for optical apparatus instead of flint glass, and also of making ornaments, and smoking, traveling, and similar articles. For example, fountain pen reservoirs, which could not be made of glass, can be made from the less frangible, very light, and still transparent Pollopas. This substance can be colored and darkened as desired. Opalescent glass and imitation porcelain of all kinds have been made of Pollopas, by using luminous, fluorescent colors, which give a beautiful effect. Pollopas can be etched with hydrofluoric acid or concentrated sulfuric acid in a way similar to which glass is etched. Because of this, door signs and illuminated advertising signs can be made. It is also recommended combined with glass panes for automobiles, as Pollopas does not splinter.

A Little-Known Source of Lead Poisoning

Herr Beintker, industrial health adviser, has recently described lead poisonings that have occurred in the tempering rooms of a large wire mill.

For the purpose of tempering, the steel wire is heated in a furnace to about 700° to 800° C. and then cooled by immersion in a lead bath at about 500° C. In this way changes take place in the structure of the wire so that it can be drawn like other wire. Two processes are used, immersion and drawing. By the second process, in which alone lead poisoning was observed, the wire is first placed in the rotary stand, or "crown," then drawn through the furnace and a lead bath and is wound up on the mechanically moving "disks." When the wire comes out of the furnace it is covered with a layer of ferrous oxide. This layer is very porous and in going through the lead bath is saturated with lead. To get rid of the superfluous lead the wire is passed through a sand bath, which retains a part of it. Upon coming out the oxide layer loosens, and in the oxide falling to the floor is a large amount of lead.

Even when severe lead poisoning did not occur, lead colic was often observed. Owing to the nature of the industry, especially the continuous running of the wires, which must not be stopped, it was necessary for the workers to eat their meals at the work room. This must under all circumstances be prevented, and the other directions for industries where danger of lead poisoning exists must be observed. Attempts to substitute baths of molten metal salts for the lead baths, as in the tempering of files and tools, met with no success in wire tempering.

Standardization of Medicines

Although foodstuffs are very strictly controlled, so that they are offered in full value, unspoiled, and in appetizing condition, the same importance has unfortunately not been placed on the control of drugs. On this account a standardization of medicines has recently been demanded from various quarters, which means the establishment of definite principles concerning the degree of purity of preparations, their physico-chemical properties, the influence of these on their therapeutic effect, the changes on storage, their durability, etc. It is rightly demanded that, if in the feeding of healthy persons the greatest care is taken, so much more is it necessary for care to be taken in providing medicine necessary for those who are ill.

Inasmuch as medicines are often produced in large quantities by the factories, and then are stored for months in apothecaries, drug stores, etc., and also many times made and dispensed by quacks, there is often no assurance that any therapeutic value exists in the drug. The *Pharmazeutische Zeitung* challenges the apothecaries to set a standard for medicines, to collect their knowledge of the behavior of medicines on storage, and to provide a central place at which the material delivered to pharmaceutical institutes shall be scientifically examined.

Lime in Pearl Form

After experimenting for a year the joint stock company of H. Scheidemandel, of Berlin, has succeeded in producing lime and gelatin in the form of beads or pearls, called for short "lime pearls" and "gelatin pearls." These pearls are produced by passing lime or gelatin through fine openings into a fluid or gaseous medium. In falling the drops form, as a result of the surface tension, as pearl-like, spherical bodies. Through appropriate cooling of this medium the pearls gelatinize in less than a minute. An ingenious apparatus makes it possible, by absolute prevention of premature decomposition due to heat, for the pearls to possess the same qualities as the liquid lime or gelatin before being made into pearls. In this way a great saving in time and space is accomplished—the pouring of the liquor on lime tables, the cutting of the dried jelly, the week-long drying, the tearing of the slabs, the difficult packing, are all avoided and instead of the troublesome lime slabs one obtains the lime pearls.

According to the new process it will be possible in the future to produce lime and gelatin in hot countries, which has heretofore been impossible.

July 15, 1924

Decreased Use of Phosphoric Acid in Germany—The current agricultural year will show a 65 per cent decrease in the use of phosphoric acid fertilizers in Germany, as compared with the previous year, according to the *Deutsche Bergwerkszeitung*. From May 1 to December 31, 1923, only 82,000 tons were used, as compared with 336,000 tons in the same period of 1913. The amount of phosphoric acid fertilizer used in Germany has never quite reached 50 per cent of pre-war years. Prices are said to be one and a half times as high as during war times.

London Letter

By Hugh Griffiths

15 New Bridge St., London, E. C. 4

The World Power Conference

The World Power Conference, organized by the British Electrical and Allied Manufacturing Association, opened at Wembley on June 30. A very large number of papers has been presented, many of which are of great interest to the chemical industry. In connection with this conference a committee has been formed to standardize the methods of boiler testing. The proposals made have been the subject of a certain amount of criticism in the technical press.

The most interesting papers presented at the conference, from the point of view of those engaged in chemical manufacture, were one on steam accumulation by J. Ruths, and one by B. M. Gerbel entitled "The Reciprocal Utilization of Waste Energy." It will be realized that the steam-raising problem in a chemical works is a very real one, partly on account of the enormous fluctuations in demand placed upon the steam-raising plant, and partly because the ratio of process steam to power steam is generally unusually high. In several large works in this country the back pressure system is used; namely, the exhaust steam from the power plant is used at a low pressure for heating purposes. It has frequently been pointed out that this system is not difficult to apply as long as the demands for power and steam are uniform, but in many chemical works such uniformity is difficult to realize and attempts to use the back pressure system have been disappointing. The steam accumulator method presents important possibilities in such cases, and it is claimed that increases of as much as 30 or 40 per cent in thermal and output efficiencies can be secured by using accumulators.

The paper of Mr. Gerbel was chiefly interesting because it gave a collection of figures relating to different industries of the steam consumption for power purposes, and the steam consumption for process purposes, for unit productions. The suggestion to combine different industries in the same locality on the basis of steam and power production, although perhaps not sufficiently practiced in this country, is already applied to some extent.

Chemical Works Explosions

The annual report of the chief inspector of factories, recently issued, contains some valuable information on industrial explosions. The importance of dust explosions is indicated by the circumstance that twelve such explosions were reported during the year 1923 as being due to carbonaceous dusts from such varied materials as coal, malt, meals, dyes, cork, pitch, naphthalene, and ebonite. Four explosions occurred in sulfur-grinding plants.

While most of these explosions were unquestionably due to lack of proper precautions, a very noteworthy suggestion in connection with sulfur grinding is made—i. e., that the grinding be done in an atmosphere containing carbon dioxide. A similar method has been found satisfactory in preventing explosions due to solvent vapor given off from rubber-spreading machines, in which case the supply of gas was drawn from a boiler flue. These methods are reminiscent of the proposal made some years ago by Harger for the prevention of coal dust explosions in mines.

The risks involved in grinding azo dyes in disintegrators are indicated by the circumstance that two such explosions occurred during the year, one of which was fatal. The exact causes of these explosions do not seem to have been fully ascertained, and it is therefore recommended that such plants be so arranged that no workmen are present in the grinding room while the grinding is in progress.

Explosions in gas-compressing plants due to the use of unsuitable lubricating materials in the compressors are dealt with in the report, two serious explosions having occurred in oxygen works. The inspector of factories urges that oxygen compressors be lubricated with pure distilled water only, and maintains that the view held in many quarters that soap solution may safely be used as a lubricant is incorrect, one of the explosions having been definitely traced to the use of less than 0.1 per cent of soap in the lubricating water.

Theory of Grinding

The underlying principles of size reduction processes have always been the subject of controversy. In some cases this has been due to the weakness which most research workers possess for attempting to derive too much from their experimental data. The British Portland Cement Research Association has recently made an exhaustive study of the grinding of a standard sand. The research is perhaps not so interesting in its results as in its methods. The investigation is an attempt to derive a law of size reduction, and the lines upon which the investigation has been pursued are purely statistical. Each product obtained was subjected to microscopic measurement, and the frequency distribution of the sizes plotted and studied. This frequency distribution method of examining the grinding problem looks promising, and while up to the present the research has been merely of a preliminary character, the association has certainly not erred on the side of drawing conclusions from insufficient data, and if the subsequent researches are on the same lines they will no doubt form a valuable contribution to a difficult subject.

Institution of Chemical Engineers

At the last meeting of the Institution of Chemical Engineers E. A. Alliott read a paper on self-balancing centrifugals. It was maintained that the most important factor in the design of a flexibly supported machine is the critical speed of rotation. This paper is essentially a study of the self-balancing centrifugal from the point of view of the theory of whirling shafts, and it was maintained that the simple gyrostatic theory is illusory and inadequate as a basis for centrifugal design.

A preliminary paper by G. W. Himus and J. W. Hinchley on the evaporation of water in currents of air was also presented, and a new formula given for the rate of evaporation of water per unit area at different air velocities, this new formula giving results considerably different from that of Carrier.

Proprietary Medicines

Although proprietary medicines are periodically subjected to strong criticism and the British Medical Association published some years ago two volumes dealing with the most important proprietary medicines before the public, practically no attempt has been made within the last ten years to raise a serious movement against the proprietary manufacturers. The chemical analyst is as a rule rather chary about undertaking work of this kind.

Not long ago Sir William Pope published in a daily paper an article on one of the most widely advertised proprietary preparations, known as "Yadil." This preparation has been so extensively advertised that recently a special company was promoted with a large capital, simply with the object of undertaking the printing work. Inasmuch as the proprietors of "Yadil" have issued a writ for libel against the proprietors of the newspaper and against Sir William Pope and Professor Dixon, no expression of opinion can be given at the present time. It is not often that eminent chemists become involved in matters of this kind and the developments are awaited with the greatest possible interest in chemical circles.

August 5, 1924

Apparatus for Testing Colors—A new German apparatus for testing the resistance of colors has been constructed at Hanau in the form of a mercury vapor lamp, according to Consul General Dument.

The fading of color being chiefly due to the influence of ultra-violet rays, which are not numerous in the ordinary daylight at low altitudes, the lamp accelerates the process in emanating these rays in considerable quantities. The effect on textiles, for instance, of one hour's exposure to this source of light is greater than that of many hours' exposure to the ordinary sunlight.

The lamp has a quartz glass burner similar to those used for medicinal purposes and is said to be more powerful than any other model. Mercury vapor, which at high temperature emanates the desired chemically active rays, is contained in an airtight, transparent tube of quartz glass and heated by means of electric current. Contrary to ordinary glass, the fused quartz allows the ultra-violet rays to pass freely. It remains firm at a temperature at which glass liquefies. The apparatus consists of a quartz burner and a suspension and tilting mechanism, the latter used in igniting the lamp. It is possible to direct the rays in any direction.

Germany Proposes Increase in Duties on Leather-Refining Materials—The German Government is contemplating increased import duties on chemicals and other raw materials used by the leather-refining industry. The Central Union of the German Leather Industry is making vigorous protest against the proposed duty on the ground that if production costs are to be lowered so that Germany can again compete on the world market, the Government has to assist by removing all restrictions against the import of such necessary materials as oils and fats, coloring materials, chromium salts, olein and stearin, etc.

Paris Letter

By Charles Lormand

4 Avenue de l'Observatoire, Paris, France

Congrès de Chimie Industrielle

The Congrès de la Société de Chimie Industrielle, which was held at Bordeaux in June, has already been reported in several communications. We would like to give special mention to some of the important decisions which were given out after the congress, especially the obligation of sellers of fish oil to indicate from what fish the oil put on sale comes. The congress has also requested the revision of the specifications for supplies to the Government of construction materials such as cement. The present conditions of reception date from 1887 and are no longer in accord with the standards now used.

The delegates visited the Institut du Pin and certain works in the Landes region. At the request of a special committee of the Société des Experts-chimistes de France, the definition of the essence of turpentine has been discussed and the decisions of the Paris congress of 1909 have been modified as follows:

> Essence of turpentine is the product of the distillation, at a temperature below 180° C., of oleoresinous sugars coming from various kinds of pines. The extra essence of turpentine can only answer to this name if it corresponds to certain definite chemical characteristics. The ordinary essence of turpentine, without any qualification, is also defined, as well as the products known under the names of essence of pine, essence of wood, oil of pine, essence of resin, and oil of resin.

These specifications make possible the distinction between the true essence of turpentine and the essence produced by the distillation of dead wood, this last product being the essence of pine or Swedish turpentine.

Moreover, an American mission is now visiting the exploitations of Landes as well as the Institut du Pin. According to a member of this mission, the methods employed in the United States are inferior to those used in France by reason of the large consumption of wood which brings about the destruction of trees that might furnish more resin.

Other Meetings

The large industrial chemical companies are holding their general assemblies at this season and the reports of their councils of administration contain information as to the development of these societies.

The Société Kuhlmann, meeting with the Compagnie Nationale des Matières Colorantes, explained to its stockholders that it has this year perfected the manufacture of synthetic acetic acid with a view to the manufacture of artificial silk. This society has also perfected a new method of manufacture of nitric acid by the decomposition of ammonia, the ammonia being supplied by the coke ovens of the Société des Mines d'Anzin, which are controlled by the "Ammonia" society, mentioned in the July letter. The question of the agreement with the I. G. has also been considered at the general assembly. The president, M. Donat-Agache, stated that the Kuhlmann establishments had not taken up the agreements entered into by the Compagnie Nationale des Matières Colorantes with the I. G., but that certain understandings were being considered. At present there is absolutely no agreement. Moreover, the delivery of dyestuffs by virtue of the reparations has been stopped by reason of the uncertainty of present political conditions. In a meeting held a few days later, the Société Kuhlmann absorbed the Société Commerciale Lambert Riviere, special selling agents for the Kuhlmann establishment in the fertilizer market.

The Société Alsacienne de Produits Chimiques has undertaken the manufacture of synthetic camphor and has constructed in Brittany a factory for the extraction of iodine from algae, and also a factory for the production of plastic materials with phenol or cresol base.

The Société de l'Air Liquide has also held its meeting, at which M. Claude described his researches on the extraction of hydrogen by compression. He has also separated ethylene to be used for the synthesis of alcohol.

Separation processes other than compression have been studied by MM. Lebeau and Damiens. The synthesis of alcohol by means of ethylene by the process indicated by Lebeau and Damiens, catalyzing the hydration of the ethylene by sulfovanadic acid, has been studied on an industrial scale at the Mines de Lens. The process is the same as that of Damiens just mentioned for the separation of hydrogen by copper sulfate. M. Lebeau has contributed a modification of this process by adding to copper sulfate a little beta-naphthol; the compounds thus formed with carbon monoxide have absolutely no vapor tension; the separation of the hydrogen is complete.

Catalysts of Dehydration

M. Mailhe is studying the catalysts of dehydration. He uses either zinc or magnesium chloride, which he heats directly with the products such as the waxes, the fats, or even chlorophyll extracts—that is, the crude chlorophyll extracted from the leaves by washing with water, an extract which, besides the chlorophyll, contains greasy, resinous, and waxy matter. Under the action of heat, mixing gives condensable products formed by methyl and ethyl carbides analogous to petroleum. A slight residue of coke impregnated with magnesium chloride remains. The yield of hydrocarbons permits consideration of industrial use of the process.

New Process for Production of Oxalic Acid

M. Matignon has described a new process for the production of oxalic acid. He uses carbon monoxide and potassium carbonate as in the processes now employed, but he works at a temperature of 470° C., and under a pressure of 250 atmospheres. Under these conditions the reaction is complete.

Sulfuric Acid for Destruction of Weeds

M. Brioux has studied the saturation in the soil of sulfuric acid which is used for the destruction of weeds. This use of sulfuric acid is becoming more and more general in France.

M. Brioux has studied the concentration of hydrogen ions and has ascertained the important role played by heat in the saturation of the soil. In soil very weak in calcium carbonate, the sulfuric acid becomes saturated very rapidly, but in the delimed soil the concentration of hydrogen ions increases very sensibly and renders impossible the cultivation of plants that are sensitive to the reaction of the soil. The marling and the liming are, then, indispensable in the decalcified land where it is desired to destroy the weeds by the spraying of sulfuric acid.

Copper Cooking Utensils Harmless

Since the work of Galippe, in France, copper has no longer been considered a toxic material in nutrition. M. Effront has resumed the study of this problem and has ascertained very carefully the amount of poisoning by copper salts. He has shown by many experiments that vegetables adsorb copper salts, so that vegetable foods, such as salads or legumes and cooked herbs (spinach), prepared in copper vessels, become impregnated with copper salts, but these salts remain fixed to the vegetable fiber in such a way that, even in the stomach and intestine, they do not pass into the organism. There is therefore no poisoning. When the action of the stomach is too acid, however, there is a partial liberation of these salts and poisoning may result.

These experiments are all the more interesting as they tend to make more general in France the use of aluminium bronze, which is more or less rich in copper, as cooking vessels.

August 1, 1924

To Study Liquid Oxygen Explosives in Mexico—G. St. J. Perrott, of the Bureau of Mines, has gone to Pachuca, Mexico, where he will spend approximately two months observing methods employed in the use of liquid oxygen explosives in a silver-lead mine of the Compania de Real del Monte Y Pachuca. Mr. Perrott has spent considerable time in the explosives laboratory of the Bureau of Mines at Pittsburgh, Pa., in research relative to the use of lampblack, kieselguhr, and various other materials suggested as suitable cartridge ingredients for liquid oxygen explosives.

While at Pachuca Mr. Perrott will study the possibilities of developing a successful cartridge ingredient for the absorption of liquid oxygen which may be cheaper to manufacture than materials now used. Other experimental work under consideration comprises the use of cartridges so sensitized as to detonate with fuse alone and requiring no fulminate cap, the study of the effect of rate of detonation on size and amount of ore brought down, firing with electric delay-action detonators protected with fiber tube, and the obtaining of gas samples of mine air immediately after blasts.

Decrease in Our Chemical Exports—During the second quarter of the current year the exports of chemicals and allied products recorded a 7 per cent advance over the first quarter of this year, but a 15 per cent decline from the high figure of a year ago. The exports during the month of June were lower than in the preceding June, and also less than in the previous month of the current year, although above the other months.

Scandinavian Letter

By C. H. A. Robak

Horten, Norway

The Nitrogen Industry

The Norwegian production of synthetic nitrates is likely to be considerably increased in the near future. At present negotiations are in progress between the Royal Department for Public Works and the Norsk Hydro-Elektrisk Kvaelstofaktieselskap, the latter on certain conditions offering to buy the power of a Government water-power plant at Glomfjord with a capacity of 100,000 horsepower, for the purpose of manufacturing calcium nitrate by the Birkeland-Eyde process. Notwithstanding the competition of the German synthetic ammonia industry, the nitrate market is now rather favorable. If this new plant is built, the production will be increased by approximately 40,000 tons nitrate a year, being now about 100,000 tons.

New Possibilities for the Production of Pyrites

At present the production of pyrites in Scandinavia is very low. Not a single mine can be worked with profit. The cause is not so much the competition of the Spanish pyrites as the new methods employed in the sulfur mines of Texas, making the sulfur quite as cheap as pyrites for use in the sulfuric acid industry. In a recent article in *Teknisk Ukeblad* a mining engineer, Kirsebom, points to the new possibility appearing through the development of the so-called Eustis process, which aims to produce electrolytic iron from the pyrites, from which an eventual copper content is separated by a new efficient flotation process, and sulfur is obtained as a by-product. With a possible production of 1,000,000 tons a year of pyrites, nearly 300,000 tons of iron and 400,000 tons of sulfur can be produced in this way.

Reëstablishment of Arsenic Ore Production

The world's demand for arsenic has been increasing for some time owing to the extensive use of arsenic trioxide in agriculture, and so the prices on arsenic ores have shown a rising tendency. In northern Norway there are several large deposits of arsenopyrites containing 25 to 35 per cent of arsenic. After the war it was not possible to work the mines with a profit, but recent higher prices caused a change in this situation, and the owners will start working some of the mines in the near future. It has not been decided, however, whether the ore is to be exported as such or in the form of manufactured arsenic.

Oil from Bituminous Coals of Spitzbergen

On the Arctic isles of Spitzbergen, which recently have become a Norwegian dominion, are located a great many rich coal deposits. The coals appear in various qualities, one of which, the coals from the Kings Bay mines, has turned out to be typical cannel coal with a rather high content of ashes and sulfur, but nevertheless very promising as a material for obtaining oil as a by-product by burning in producers. Technical experiments are now going on at the power plant of the Sydvaranger mining company at Kirkenes in Finmarken, particularly aiming to produce an oil which can replace the solar oil used as a motor fuel by the fleet of fishing vessels.

American Investment in the Aluminium Industry

Recently a reorganization has been accomplished within a great aluminium company in Norway, the Hoyangfaldene. The company's factories were built during the war and got too expensive. Then the raw material had to be imported from France, and during the war it was impossible to get a license for exportation of aluminium oxide from that country. So the company could make no profit from the high prices, and when peace time arrived and raw materials could be had the capital was lost and the prices dropped. The company has striven against the economical difficulties till this year, when some American money was invested in the enterprise, buying half of the aluminium factories whereas the original company still owns the other half as well as the appurtenant water-power plant. The production is now about 6000 tons of aluminium a year and can be increased to 10,000 tons.

Evaluation of Whale Oil

Each year huge quantities of whale oil are carried to Norway from various places on the globe by the Norwegian whalers. The finest qualities of this oil can be refined to a high-grade solid fat by hydrogenation and can then be used as a human food—in margarine and pastry. During the fat emergency of the war practically all the margarine consumed in Norway was manufactured from hydrogenated whale oil, and although most people in those days would turn up their noses at the "whale taste," the refining processes have now reached such a degree of perfection that I find myself wondering if we do not now eat more whale fat in our margarine and pastry than we should like to know. One of the large hydrogenation factories which for a couple of years has been out of work owing to economic troubles, recently has been started again with fresh capital invested by the whaling companies.

"Titan White," a New White Paint

Two Norwegian chemists have developed a process by which the black material ilenite can be transformed into an intensively white powder consisting of titanium dioxide. A large factory has been built and the new paint is now conquering the world market because of its superiority in covering value and durability, although it costs a little more than lead and zinc white. In the United States a similar process has been worked out independently by American chemists, who have started the production in the States. The Norwegian and American companies have agreed to divide the market between them, the latter covering the two American continents while the former takes care of the rest of the world market.

July 31, 1924

Tokyo Letter

By K. Kashima

792, Ikebukuro, near Tokyo, Japan

Limitation of Dyestuffs Imports

Since the Great War the dyestuff industry of Japan has made great progress. About twenty important dyes of good quality are being supplied by the domestic dye companies. She therefore needs to import only about 2,500,000 pounds of special dyes from foreign countries. The dye industry plays an important role in the organic chemical industry and also in the national defense of every country. It is therefore natural that every country is striving to develop this industry. Europe was a central market for the dyes, but now the balance is changed. The oriental market is being disturbed by the dumping of the foreign dyes. Therefore, the Japanese Government has wisely taken the policy to protect her dye industry. An ordinance was issued from the Agricultural and Commercial Department requiring merchants who wish to import coal-tar dyes and chemicals derived from fractionally distilled compounds from coal tar, except medicines and phenol, to get permission from the minister of the department. The substances limited are as follows (the numbers correspond to those given in the table of the Japanese Customs Tariff Law): No. 135, artificial musk; No. 1507, salicylic acid; No. 203, saccharin; No. 215, chemical compounds derived from fractionally distilled compounds from coal tar, among which are perfumes, with the exception of benzaldehyde, nitrobenzene and nitrotoluene, phenol, salicylic acid, Bakelite, and medicines; No. 221, β-naphthol, methyl and ethyl ethers, cinnamic acid, benzyl and salicylic esters, etc.; No. 237, artificial indigo; and No. 243, other coal-tar dyes.

Japan's Paper Industry

Since olden times Japan has been manufacturing her own special papers. Among these we can mention "Torinoko," which because of its durability was used for printing the Versailles Treaty. This paper is considered to be an art production like British esparto paper. Its manufacture needs special material and technic and the amount of production is therefore limited.

Japan is consuming a large amount of papers manufactured by her own and by foreign methods. The former production is called "washi" (Japanese paper), while the latter, "yôshi" (foreign paper). There is a tendency for the production of "yôshi" to exceed that of "washi," since "pen and ink" is taking the place of "hair pencil and India ink," and the modern printing is almost limited to "yôshi." The amount of match paper and colored paper is decreasing. Perhaps in the near future almost all papers will be manufactured by modern mechanical methods.

Since the war Japan's paper exports have greatly increased as is shown in the following table:

	Export	Import
	(Unit 1000 pounds)	
1912	13,334	56,241
1913	16,282	59,270
1914	18,193	41,308
1915	30,910	19,957
1916	62,744	28,533
1917	65,321	13,163
1918	70,819	28,306
1919	59,086	46,603
1920	54,446	45,810
1921	57,731	37,063
1922	56,306	92,627

About 45 per cent of "yôshi" manufactured is used for newspaper and a considerable proportion is used for printing paper and high-quality printing paper. The classified production of "yôshi" in 1923 is as follows:

	1000 Pounds
Paper for news	330,149
Printing paper	108,443
High-quality printing paper	100,915
Imitated "Torinoko"	51,798
Wrapping paper	39,029
Roll paper	13,796
"Renshi-Tôshi"	10,403
Match paper	9,125
Colored paper	8,872
Miscellaneous	57,974

Printing paper was imported from the following countries in 1921:

	1000 Pounds
Sweden	4296
United States	4162
Germany	3778
Great Britain	2417
Norway	99
Canada	14
Others	936

Although some special papers are manufactured from the paper mulberry and *Edgeworthia chrysantha*, the material for manufacturing these papers is mainly pulp made from fir and larch, etc., produced in Hokkaido, Kabafuto, the foot of the Mt. Fuji, etc. A large amount of pulp is being imported from Canada. At present the method of manufacturing paper in Japan is greatly improved, and almost all papers except heavy paper such as is used to cover books are manufactured. Recently a company was started for making Kraft paper, which will be put on the market this year. A corporation has been formed by twelve paper-making companies, and is manufacturing about 90 per cent of the total production.

Japan's Coal Problem

Electric power is gradually taking the place of coal in every direction. Japan may be mentioned as one of the countries rich in hydroelectricity. The hydroelectricity utilized at present is about 1,000,000 kilowatt-hours, which corresponds to 6,000,000 tons of coal. The annual consumption of coal is as follows:

	Tons
Railroads	3,200,000
Ships	5,000,000
Manufacturing iron	2,200,000
Salt industry	800,000
Miscellaneous industries	12,000,000
Total	23,200,000

In addition, coal is used for manufacturing coal gas, dyes, paints, medicines, and as domestic fuels, etc. There are also heat-engine power stations in small towns, whose power is about 490,000 kilowatt-hours and corresponds to 2,940,000 tons of coal, and whose chief source of power is coal. The total production of coal in recent years is as follows:

	Production	Import	Export	Consumption
		(Unit 1000 tons)		
1897	5,230	77	2123	4,091
1907	13,840	36	2972	10,858
1916	22,902	556	3017	18,579
1917	26,361	713	2813	20,707
1918	28,029	768	2197	23,026
1919	31,271	700	2001	24,801
1920	29,245	797	2130	25,665
1921	26,221	777	2388	24,610
1922	27,702	1169	1691	27,180
1923	28,675	1651	1574	28,752

As shown above, the annual production of coal is gradually increasing, and it will be seen that the production is doubling every ten years, comparing those of 1897, 1907, and 1917. Its maximum amount of production, according to an economist, will be about 35,000,000 tons. On the other hand, the consumption is also increasing and it is expected that the amount will reach 50,000,000 tons within ten years.

According to the report of the Agricultural and Commercial Department, the amount of coal buried is about 8,700,000,000 tons, among which the utilizable amount will be about 3,700,000,000 tons. Up to 1923, about 300,000,000 tons had been mined. In Manchuria, the South Manchurian Railway Company is mining in Bujun about 5,500,000 tons annually, but this amount will be increased to 7,000,000 tons in near future. The Santô Mining Company has opened their works in the District of Santô, and their production is expected to be about 800,000 tons. A part of the coal from these mines will be imported to Japan for controlling her production.

July 28, 1924

Washington Letter

Mills Appointed Chief Chemist for C. W. S.

The Chemical Warfare Service is to be congratulated upon its selection of John E. Mills as chief chemist. He received his chemical education in the South, but soon after the war broke out he resigned his professorship in a southern university, and early in the fall of 1917 entered the Chemical Warfare Service, being one of the very first officers in the First Gas Regiment. He was designated as engineer officer for the regiment. In that capacity he served throughout the war. He went to France with the Headquarters in January, 1918, and as a consequence into training with the British at their headquarters for training gas troops at Helfaut in northern France. Within a month Captain Mills was in the front-line trenches with the British.

After the war closed he returned to his position as professor of chemistry in the University of South Carolina, where he remained until July, 1923, when he accepted the position of technical adviser or chief of the Technical Division at Edgewood Arsenal. In May, 1924, he was sent to Europe, where he spent three months visiting England, France, and Germany.

At one time, Dr. Mills owned and managed a small cotton plantation. This knowledge is of particular value at this time when the Chemical Warfare Service is charged with experiments looking to the further control or elimination of the cotton boll weevil.

Dr. Mills brings to the Chemical Warfare Service a knowledge that no other man possesses. Starting out as a highly trained research chemist and teacher, he had the good fortune to go through the entire war with the Gas Regiment on duty at Headquarters. That duty brought him in contact with every battle and phase of training. He thus learned at first hand an extremely practical use of gas in the field. His work of the past three years in the technical direction and coördination of chemical research at Edgewood has given him the deepest and broadest possible knowledge of the work now being carried on at Edgewood.

Dr. Mills was not only the first choice of the chief of the Chemical Warfare Service for the position of chief chemist, recently made vacant, but was the unanimous choice of the Committee of the American Chemical Society Advisory to the War Department.

Part IV of the Nitrogen Survey

This report, prepared by Harry A. Curtis, of the Bureau of Foreign and Domestic Commerce, will be issued in the near future as a Trade Information Bulletin. It discusses the principal features of the nitrogen situation in a number of European countries. The rapid growth of the air-nitrogen industry in Europe is making fundamental changes in the position of the United States in the nitrogen market.

Chile has long been the chief exporter of fixed nitrogen. Within recent years, however, because of the development of the air-nitrogen industry, and the relatively small domestic demand, Norway's exports of fixed nitrogen have exceeded her imports. Great Britain likewise exports more fixed nitrogen than she imports, having but a moderate agricultural demand and a relatively large production of by-product nitrogen from the coal and gas industry. Since the war, Germany has been practically self-sustaining with regard to fixed nitrogen, although under stable economic conditions she would probably become an exporter of nitrogen. Most of the more thickly populated countries of the world are buyers of fixed nitrogen in the world market, and even where domestic sources of supply have been developed, the increasing domestic demands of agriculture and industry have usually more than absorbed the supply. The nitrogen situation in any one country of the world is necessarily linked more or less closely with that in every other country, for fixed nitrogen is an article of international commerce and it follows that any country which can more than meet the domestic demands finds a ready world market with many purchasers.

NEW DYE CENSUS

As we go to press the Dye Census for 1923, on which the Tariff Commission has been engaged for many months, is in page proof and the detailed report should be ready for distribution by the time THIS JOURNAL issues. The report shows the largest output of dyes in the domestic industry, a reduction in prices, the addition of many new dyes to our manufacturing program, reduced imports, and increased exports on account of the reduced production of the German dye factories following the Ruhr Occupation. It discusses the dye industries of the chief producing countries, including Germany, Switzerland, Great Britain, France, Japan, and Italy, gives production data, and considers readjustment of international dye trade following the establishment of industries in the above-mentioned countries. The report indicates a large increase in capacity to produce dyes since the war—in fact, in excess of normal requirements in many instances.

Increases are also noted in the production of other coal-tar dye products, including color lakes, medicinals, flavors, synthetic resins, tanning materials, and rubber accelerators, also a large increase in the output of synthetic organic chemicals not derived from coal tar.

COMMITTEE ON STANDARDS MEETS

The Joint Committee on Definitions and Standards held its twenty-sixth meeting in the Bureau of Chemistry, August 18 to 22, inclusive. Proposed standards for ice cream, meat and meat products, wheat flour, and jams and jellies were discussed.

The Joint Committee is composed of nine members, three representing the Association of Official Agricultural Chemists, three appointed by the Association of American Dairy, Food and Drug Officials, and three from the United States Department of Agriculture. This committee recommends definitions and standards for food products for the guidance of federal and state officials in the enforcement of food laws.

THE BOLL WEEVIL PROBLEM

The appropriation for the Chemical Warfare Service for this fiscal year carries the proviso that not to exceed $25,000 may be spent in experiments looking to the extermination of the boll weevil. The Chemical Warfare Service lost no time in attacking this problem and already has mapped out a systematic, direct, and energetic plan of attack.

Some more efficient poison must be found for the boll weevil. Work has accordingly been planned along the following lines: A list of poisonous chemicals has been prepared, which the Chemical Warfare Service has reason to believe should poison the boll weevil more or less effectively. This list will be expanded as a result of further studies which the Chemical Warfare Service will conduct, and finally by suggestions from the whole chemical profession. In connection with the compilation of this list, small quantities of the chemicals themselves will be manufactured. These quantities will be sent to the Georgia Experimental Station at Griffin, Ga., about forty-two miles southeast of Atlanta, in the heart of the cotton belt. There employees of the Chemical Warfare Service, familiar with the poisons, will carry out the actual work of poisoning the boll weevil. In these tests no attention will be paid to whether the poison will injure the plant.

USE OF TEXAS KAOLIN IN WHITEWARE BODIES

The Bureau of Standards recently conducted a short investigation on a sample of kaolin taken from a large deposit in Texas. The material was practically pure white, very uniform and, as received, was comparatively coarse-grained and without plasticity.

Six whiteware bodies, varying in ball clay content from 0 to 14 per cent, and in which the English china clay was replaced in increasing amounts by Texas kaolin, were prepared and made up in the form of test bars, circular disks, and 5-inch plates. These were fired to cones 8 and 10. The test bars were used in determining shrinkage, transverse strength, and absorption, and the disks were used in determining relative resistance to impact. In addition, several shapes were made by the casting process, using slips containing Texas kaolin. The bodies obtained were very high in transverse strength when dried. The fired bodies were exceptionally white, but had a high absorption, and were correspondingly low in transverse strength and resistance to impact. The glaze specimens were very good as regards resistance to crazing. The results as a whole indicated that Texas kaolin could be used satisfactorily in whiteware bodies, but because of the relative coarseness of grains and its high refractoriness, it would require more preliminary grinding than the English clays as well as the use of a larger percentage of ball clay to produce the desired dried and burned structure in the body.

LARGE CLAY POTS MADE BY CASTING PROCESS

The drying of several clay pots of unusually large size has recently been finished by the Bureau of Standards. The pots were made by the casting process developed at the Bureau of Standards and are intended for use in making optical glass. Each one is 3 feet 6 inches high and has an outside diameter of 4 feet 9 inches. The walls have a maximum thickness of 5 inches, and each pot requires 1.5 tons of material.

In making pots by this process the clay slip is poured into a plaster mold and allowed to "set" or harden. To make the mold for these large pots 10 tons of plaster were required, and a number of difficulties were encountered in handling so much of this material. For example, in making the largest section it was necessary to mix the plaster in eight batches. Retarder was added to each batch in such proportions that all parts of the mold became hard at about the same time. Otherwise the bottom of the casting would have become too hard for turning before the top was hard enough to permit removal of the forms.

INDUSTRIAL ALCOHOL COMMITTEE MEETS

The Alcohol Trades Advisory Committee met in Washington on August 14 to consider several important questions submitted by the Commissioner of Internal Revenue. The committee, being advisory, issues no statements as to its recommendations and reports, and as we go to press no announcements have been made by the Commissioner of Internal Revenue or the Prohibition Unit indicating the decisions on the questions that were discussed at length at the meeting.

RESUMÉ OF MOLASSES PATENTS

Belief that the future of the American beet sugar industry is to a great extent dependent on the profitable utilization of the molasses produced, has led the Bureau of Standards to prepare a resumé of the patents relating to the utilization of the nonsugars contained in this product. Molasses contains many valuable substances which have never been successfully recovered except in Germany. For many years that country has seen fit to veil its developments and discoveries and to maintain the strictest secrecy regarding the operation of its molasses plants. So far as actual results achieved in Germany are concerned, the scientific literature on the subject is practically barren.

In order to carry out the necessary experimental work for the American industry every possible source of information has been investigated. After a few clues were obtained the United States Patent Office literature was searched and eventually over a thousand German patents on molasses utilization and associated subjects were uncovered.

The difficulty in locating these patents was because they are not listed under sugar or molasses, or other subjects known to the investigators. The value of the information contained in many of them was so apparent, and the necessity for knowledge of their contents was so obvious that it was thought worth while to compile a resumé of the more important ones, dealing with the recovery of the nonsugars.

This resumé is given in *Circular* **145** of the Bureau of Standards, copies of which can be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C. The price is 15 cents, cash.

WEATHER TESTS OF WIRE SCREENS

Tests to determine the relative resistance to atmospheric corrosion of wire screens of different metals are planned by the Bureau of Standards in coöperation with the American Society for Testing Materials. The metals to be included in the test are copper, commercial bronze, low brass, aluminium bronze, silicon bronze, and Ambrac metal. All materials will be tested in the form of standard No. 16 mesh screens.

The screens will be exposed to the weather in four locations: an inland location, an industrial center, a seacoast, and a tropical seacoast. The cloth of each material will be exposed on a painted frame that will withstand the weather. Three types of frame will be used: 12 × 12 inch wooden frames, 30 × 36 inch wooden frames, and 30 × 36 inch metal frames. The tests will be made in coöperation with the manufacturers of the materials. The Bureau of Mines, the Bureau of Lighthouses, and the Panama Canal will coöperate with the Bureau of Standards in making the exposure tests.

August 22, 1924

BOOK REVIEWS

Colour Index. Edited by F. M. Rowe. 371 pages. Published by the Society of Dyers and Colourists, England, 1924. Price, £ 5 15 s.

This index is truly a welcome contribution to manufacturers and users of dyestuffs of every kind. The announced purpose of the work—"to produce in the English language as accurate and comprehensive a work of reference as possible—one that would meet the requirements alike of Intermediate and Colour Makers on the one hand, and Colour Users and Students on the other"—has been carried out with painstaking care. After the disappointing 1923 edition of Schultz's "Farbstofftabellen," which was essentially a reprint of the 1914 edition, the Colour Index stands out conspicuously. It is naturally similar to the Farbstofftabellen in general arrangement, but outclasses it in completeness and up-to-dateness. It lists 1316 coloring matters, of which 1230 are synthetic organic dyes, 20 are natural organic dyestuffs, 5 are color lakes of the natural organic dyestuffs, and 62 are mineral pigments.

The information given on each dye is arranged in five columns, which give the Commercial Name; the Scientific Name-Components-Formula; Preparation; Discoverer-Literature; Description-Properties-Mode of Application. Another column is left blank for manuscript notes by the owner. The number of the dyestuffs in Schultz's 1914 edition is given in parenthesis and lighter faced type below the new Colour Index number. The synthetic organic dyes are grouped together in 26 classes, which are further subdivided as necessary.

A very convenient feature is the series of General Indices at the back of the volume, which include a cross index of the Schultz and the Colour Index numbers, indexed references to Schultz-Heumann's "Die Anilinfarben," indexed references to patents arranged chronologically by countries, an index of intermediates giving their formulas and the dyestuffs for which they are used, and an index of the synthetic organic coloring matters used for purposes other than dyeing textile fibers.

The whole work is so complete and well arranged that no manufacturer or large user of dyes can afford to be without it. It can easily displace Schultz's "Farbstofftabellen," not only in English-speaking countries, but even in Germany itself.

Joseph A. Ambler

Textbook of Cellulose Chemistry. By Emil Heuser. A translation from the 2nd German edition by Clarence J. West and Gustavus J. Esselen. 203 pages. McGraw-Hill Book Co., Inc., New York, 1924. Price, $2.50.

The appearance of a textbook on cellulose chemistry indicates that this important field is beginning to receive the attention due it. The present volume treats the subject from the point of view that cellulose is an aliphatic alcohol and that the cellulose molecule is made up of anhydrocellobiose building units held together by partial valences and that these in turn are combined through crystal valences to give the cellulose fiber. The chapter headings are Alcoholates, Esters, Ethers, Oxidation of Cellulose, Degradation of Cellulose, and Constitution of Cellulose.

Cotton cellulose is used as a basis for discussion, and the postulate is made that there is only one type of cellulose and that this is the same chemical individual in all plants. The term "cellulose" is accordingly limited by definition to a single chemical individual, $(C_6H_{10}O_5)_n$, for which the name "orthoglucosan" [This Journal, **16**, 141 (1924)] has recently been proposed, since the term "glucosan," which would be even more appropriate, has long been used to designate a simple anhydride of glucose. Whether the term "cellulose" is to be limited thus or whether it is to be generic in the sense that sugar and alcohol are generic is a matter that depends upon usage as well as further development in the subject.

The author appears somewhat provincial in his treatment of the literature on the subject. This is apparent also to the translators, who have considered it necessary to extend the discussion of the work of one American contributor on cellulose chemistry. The book must therefore be regarded as presenting the particular point of view and hypothesis of the author, rather than as a comprehensive survey of the subject.

The assumption of "partial valences" in the make-up of the cellulose molecule is one that has scant support from an experimental point of view. One could expect these valences to be of the same order of magnitude and to be indicated by some definite line of cleavage in the cellulose molecule, but as yet no such evidence is available.

The book is to be commended for its simplified presentation of the subject, and it should prove a stimulus to further investigative work. The translators have rendered a service to the cause of cellulose chemistry in making this volume available in English.

S. A. Mahood

Lime and Magnesia. By N. V. S. Knibbs. 306 pages. Ernest Benn, Ltd., London, 1924. Price, 30 s.

Although the burning of limestone is one of the oldest chemical operations, the literature is quite scattered, and this volume represents the first attempt at a collection of the mass of information, data, and practical experience into a single authoritative treatise. The subject is handled under three main headings. Part I deals with the origin and occurrence of limestone and magnesite and the physical and chemical properties of lime and magnesia; Part II discusses their manufacture; and Part III, their uses in the arts and industries. A rather extensive appendix includes tables of physical and chemical properties (including hitherto unpublished data from the National (U. S.) Lime Association, methods of analysis, and other valuable data.

The first part is wholly scientific and records in excellent manner and with creditable selectivity the existing information and data regarding lime. The treatment of magnesia and its compounds is not so thorough. Especial emphasis is directed to the very great lack of existing experimental data on most of the subjects discussed. This section contains facts of great value to lime manufacturers if they will have the patience to read it in the technical form in which it is presented, but this portion of the book will appeal more to the technical man than to the lime burner.

The section on lime manufacture is woefully incomplete, and the subject is not accorded the space it deserves. It is unfortunate, for example, that only six pages, including curves, etc., are devoted to the theory of the extremely important and scientifically interesting problem of hydration, and only about five pages of text to the practice of hydration. A relatively large amount of space is given over to a description of the pot and mixed feed type of kilns, which, although rather generally used in England, are almost never found in modern American plants outside of the sugar and alkali industries. On the other hand, such recent developments as the application of rotary kilns are dismissed with a reference to texts on Portland cement manufacture, and such equipment as air-swept tube mills and such operations as tunneling and mining of limestone are either barely mentioned or entirely ignored. In discussing the very low efficiencies of kilns, the causes are treated at relatively great length, but no hints are given as to how the losses may be avoided in the actual operation of a plant, and unfortunately the lime burner is not so much interested in a diagnosis of his troubles as he is in a cure. In fact, the impression is gained that this portion of the book is not the product of practical and first-hand experience in the industry, but is rather a compilation from various contributions. In this compilation, however, a compliment is paid to Yankee progress in that the major portion of the latter types of operation and equipment described and most of the illustrations are of American plants.

The uses are briefly but very well treated in the last section.

In these days of modern handbook authorship there seems to have developed a tendency toward failure to give proper credit, and it is quite refreshing to find in this text such a complete bibliography at the end of each chapter. In such a reference book for an industry no one subject can be thoroughly discussed, and the bibliography is particularly valuable to those wishing to obtain further information on any question.

As might be expected in a first edition of the first treatise on any subject, a few errors and inaccuracies have escaped attention, but, with the exception of the chapters on manufacture, the book is an excellent and most valuable contribution to the literature of the industry.

G. J. Fink

What Industry Owes to Chemical Science. By Richard B. Pilcher and Frank Butler-Jones, with an introduction by Sir George Beilby. "The Engineer" Series. 146 pages. D. Van Nostrand Co., New York, 1924. Price, $2.00.

No one reading this little book can doubt that the authors have succeeded in showing the dependence of industry on chemistry and on science generally. The contents consist of a series of articles published in the British publication, *The Engineer*, which probably accounts for the reason why it is written in rather technical language and why it seems to presuppose of its readers an extensive knowledge of chemistry. Though many historical and scientific facts are given in an interesting way, it is doubtful if this book could be read with intelligence by the layman, but it might be read with profit by technical men in industry, by teachers of chemistry, or it might help high school students who have had chemistry in deciding their work at college.

Some of the subjects discussed are minerals, metals, heavy chemicals, alkalies, coal, coal gas, dyes, explosives, cellulose, paper, artificial silk, oils, fats, waxes, soap, candles, leather, rubber, mortar, cement, refractory materials, glass, enamels, pottery, porcelain, acids, bases, salts, solvents, fine chemicals, drugs, photographic materials, fertilizers, feeding stuffs, sugar, cold storage, condensed milk, dried milk, alcohols, wines, spirits, tobacco, inks, pencils, and gases.

The chapter on Government Chemistry gives a list of the chemical laboratories maintained by various branches of the Government and shows the value of the work of these laboratories to the Government and public at large, and brings home most effectively to the general reader the value of chemistry to the welfare of the country.

This great amount of material had to be condensed to a point where clearness is sometimes sacrificed and some misunderstanding is introduced. Thus, under Minerals and Metals, in regulating the carbon content of steel, the sentence "while a workman threw in from a shovel sufficient spiegel or ferromanganese to introduce the proper proportions of carbon" is misleading. Some of the subjects, such as oil flotation and photography, are treated at length and in considerable detail, whereas others are dismissed with only a sentence. A chapter on chemical products is in part only a category of a number of chemicals with perhaps one use given, but with no further information. Moreover, the type is too small for comfortable reading.

The book was written for British readers and therefore deals largely with the more common industries of Great Britain. It also makes particular mention of the British who have contributed to the scientific development of the industries.

With fewer subjects considered and written in a more popular style, the book would have a more general appeal to readers interested in science.

C. A. Mann

College Chemistry Companion. By James Kendall. 230 pages. The Century Co., New York and London, 1924. Price, $1.50.

This book of suggestions, questions, and exercises is intended to stand in the same relationship to Smith's "College Chemistry" and Smith's "Laboratory Outline" as the "Revised Catechism" does to the King James Bible and the "Book of Common Prayer." It should prove a real aid to faith for beginners just introduced to Avogadro's number and the ionic theory. Its atmosphere, however, is anything but that of dry theology—is, in fact, so breezy and refreshing that it must have been written while its author was on a trip out West. In Chapter I we see him do a stunt of broncho-busting with density determinations and experimental errors. Note the gleeful yells with which he gallops after the hitherto untamed difficulties of chemical arithmetic, and listen to the shocking language (p. 223) with which he refers to his own book.

Still, closer scrutiny of this exuberant "Companion" reveals evidence of an origin somewhere in the decadent East. For there, we understand, strange new cults are finding converts. We note references to private seances (p. 41) and crystal-gazing (p. 63). Again, Le Chatelier's principle is illustrated by a disgraceful episode, which could have a meaning only to students east of the Hudson. With utter lack of shame the author remarks that crystallized oxalic acid should have a high degree of purity, but implies that the instructor who dispenses it need not (p. 165). Out West personal virtue still seems worth while; for a chemist, testifying on a poison case, was recently asked by the opposing counsel: "Professor, are your *reagents* pure?"

Though addressed to the beginning student, this book is sure to offer new methods of presentation—not to mention snappy stories—with which the instructor using any text may enliven dry lectures. Its graphical charts, to illustrate abstract principles, and its many references to books and recent magazine articles of a popular nature are especially praiseworthy. These features, and especially the remarks concerning what is most worth studying in individual chapters, might well be transferred to future editions of the books it is intended to supplement. So successful should such methods be in holding the student's interest that one might almost wish Professor Kendall had reversed his procedure, by giving us first as sprightly an interpretation of chemical science as this, then supplementing it with a student's manual of problems and exercises, as dull as necessary.

The book has some excellent photographs. The thermodynamic properties of ammonium nitrate are appropriately illustrated by a hole in the ground, at Oppau; adsorption, by a beauty chorus, in gas masks; while at the close is a photograph of two famous scientists examining an unnamed piece of apparatus. From the heading of the page which this faces, the nontechnical reader will probably take it to be an electrical appendix, and remark with Mr. Edison, "What next?"

H. G. Deming

Waterproofing Textile Fabrics. By Herbert P. Pearson. 112 pages. The Chemical Catalog Co., Inc., New York, 1924. Price, $3.50.

This book is well arranged and clearly written, but much of value is omitted. The Bibliography is good, but unfortunately space limitations have prevented patent abstracts which would have been valuable.

The distinction between "waterproof" and "water-resistant" is correct, but the most successful treatments for wagon covers and tarpaulins needing practically effective waterproofing are of the porous, pigmented, blended, soft wax type.

Basic principles are well stated but do not make it clear that the plugging or "Cofferdam" effect of pigments is the chief reason for their use. The fact that some waxes, of high initial water resistance, quickly hydrolyze, saponify, or granulate upon exposure is not emphasized. Blends of metallic soaps and resinates with selected waxes are not considered, though largely used, nor is the effectiveness of different pigments and the danger from oxygen-carrying pigments discussed. The value of pigments for resisting light and for producing agreeable colors might well be emphasized. The difference between destructive mildews and their specific poisons which makes mixed preservatives necessary, is not mentioned. The difficulty of complete fiber impregnation and methods for securing it are not described. The modern, largely produced, and cheap mordanting processes, which make a blend of oxides, metallic soaps, and waxes, and produce practically effective mildew-resisting and rainproof tentages are overlooked. Machinery for waterproofing is sketchily treated and the latest types of regulated roller coating or spreading machines are not described. Awning fabric makers are unjustly criticized. Proofed fabrics have been unsuccessful because awnings are replaced when dull or dirty but still sound.

No mention is made of the successful and convenient liquid waterproofings which benefit the farmer or other user more than the somewhat empirical formulas of uncommon materials, messy and not too safe to mix and apply. These ready-for-use products have greatly increased home and farm treatment of canvas and have been very effective conservators of cotton goods.

William H. Adams

The Resources of the Empire. Chemicals. By A. W. Ashe and H. G. T. Boorman. xxvi + 207 pages. Ernest Benn, Ltd., London, 1924. Price, 21 s. net.

Under the general title, Ernest Benn, Ltd., has published a series of twelve volumes dealing with the principal industries of the British Empire. These are: Food Supplies; Timber and Timber Products; Textile Fibres and Yarns; Fuel, Rubber, Tea, and Cacao; Leather; Chemicals; Ferrous Metals; Non-Ferrous Metals; Oils, Fats, Waxes and Resins; and Communications.

The volume on Chemicals is a stock-taking, with the various chapters giving information regarding chemical raw materials and manufactured products of the various parts of the British Empire, very much as the census issued by the United States Government might deal with similar resources of the various states. The volume therefore brings to the reader concise information otherwise difficult to obtain in such readable form, and in addition there are afforded interesting summaries and arguments on conditions which face the chemical industry of the Empire. The summarized conclusions and argument emphasize the desirability of enabling the Empire to satisfy all its chemical needs for itself and to make itself independent of outside resources. The discussion is expanded to include the question of whether or not it is better from the Empire's viewpoint for each of its parts to produce its own needs with local raw materials or to centralize the manufacturing part of the chemical industry, drawing upon the Empire as a source of raw material. After discussing various phases of this economic problem, in which it is pointed out that "artificial aids are necessary if a chemical industry is to be built up in the newer countries which have not the experience necessary to produce cheaply, and without cheap production they cannot hope to compete in world markets, and lead to the second essential, large production," the conclusion is reached that the United Kingdom should be considered the great chemical manufacturing and distributing organization of the Empire, leaving the dominions to supply the raw material required. In view of the desire of most dominions to establish their own manufacturing centers, it must have required some courage to announce this decision, however sound it may be.

One finds that the same disadvantages which face American manufacturers are to be found in the British problem—namely, competition with countries having debased currencies, low wages, and longer hours, as well as lower taxation. The labor situation is well put in the sentence "if labor would give of its best—and the best British labor is very good—there is nothing whatever to be said against short hours and high wages. The whole matter is simply one of output, and if the output be there the wage can be high and the hours short."

Apparently, Britain also shares the view that "one of the greatest steps that could possibly be taken would be, in our opinion, a greater association of interests in the chemical industry than exists at present." Those of us who look askance at strong organizations will find food for thought in the concluding message of this book, which urges thorough organization of the British Empire industry as the best means of meeting world competition, which is found to be far more severe than ever before, and in the apparent determination of British manufacturers to take such legitimate means as may be necessary to regain and hold their rightful place in the chemical-producing world.

Storage Batteries. By GEORGE WOOD VINAL. 400 pages. John Wiley & Sons, Inc., New York, 1924. Price, $4.50.

Because of his long service at the Bureau of Standards, the author has evidently come in contact with most of the modern storage batteries, and has been assisted in the preparation of this book by competent engineers connected with the industry.

As is to be expected, the book covers quite extensively the different lead cells with pasted plate processes, together with details of mechanical construction, and particularly of testing. The Edison battery is described in about 7 pages, and in the chapter on Theory the theories of all storage and primary batteries are well covered. Sulfuric acid is very carefully discussed in 50 pages, and the treatment of electrical constants and methods of using the diluted acid, as well as the effects of impurities from the viewpoint of good storage batteries, is very thorough.

A great deal of very valuable technical data are given which have evidently been the result of years of collecting, and these data are obtained from the different types of modern practical batteries. Emphasis is laid on the advantages or disadvantages of most of the variations of dimensions and materials for battery uses which would interest a battery maker, and on this account the book gives the impression of being particularly useful to the industry. Details seem judiciously given and explanations of theory are clear.

As nearly 40 pages are devoted to details of charging and discharging batteries, the effects of different rates on life, etc., the practical battery user could learn much from the chapter.

So much is also included on the care and repair of storage batteries that the book ought to be of value to the modern garage men who now handle, or mishandle, the batteries on our millions of automobiles. It is this part of the subject which seems most valuable, and no better excuse for a new book on this old subject is needed than the fact that thousands of new mechanics now want to know more about modern storage batteries. The illustrations are frequent and are particularly well fitted to instruct the man who wants to know about his battery or undertake its test or repair.

The book does not deal with the future of storage batteries or with new principles. It does not open new fields for overcoming the admitted deficiencies of storage batteries in general, and it does not represent new research work on the frontier of the theoretical problems of new electrical storage cells. It does not even emphasize the fact that no fundamentally new steps in our methods of storage of electrical energy have been made in the last quarter century. It helps the user, however, by such practical details as explaining how the automobile may not start well even though its lamps burn well, because corrosion of the battery terminals makes such a difference in available energy rates.

There is a peculiar reason for publishing this kind of a book by this kind of an expert, and Dr. Stratton while director of the bureau evidently recognized it. Bureau experts are presumably competent, well-trained, and industrially neutral men. They are in position to collect great quantities of information on many subjects. Such information is naturally published in bureau reports, but the book type, or the accumulation of years of information covering some one field, which naturally cannot be printed in bulletin form, apparently can and therefore should be made available to the interested public, as is this case of the "Storage Batteries."

W. R. WHITNEY

Eminent American Chemists. A Collection of Portraits of Eminent Americans in the Field of Chemistry from the Earliest Days of the Republic to the Present, together with Short Sketches of the Work of Each. Compiled and edited by D. H. KILLEFFER. 33 pages. Published by D. H. Killeffer, 19 East 24th St., New York, N. Y. Price, $6.00.

The number of requests for a collection of portraits of eminent Americans in the field of chemistry led Mr. Killeffer to undertake the collection and publication of a group of portraits with biographies, including thirty-three of those who have been prominent in chemistry from the earliest days of the republic to the present time. The list was chosen from a much longer list of American chemists by asking many qualified to choose, to indicate their preference. This list represents the result of that vote, the intention being to publish further collections if the present offering meets the approval of the chemist generally.

These portraits, which are suitable for framing, are furnished in a loose-leaf binder with the biographical sketch and statement of work so printed as to be left in the folder or framed with the portrait. The portraits are produced by a new process, which seems very satisfactory.

The collection will be valuable to libraries and indispensable to those teachers who believe in having their students become acquainted with chemists as well as with chemistry.

Schwefel- und Stickstoffstudien. By F. RASCHIG. 310 pages. Verlag Chemie, Leipzig and Berlin, 1924. Price, $2.50.

The studies reported in this book extend over about thirty years. Portions have appeared from time to time in various German journals, but would probably never have been assembled and coördinated if the author, as he states in the preface, had not been forced to leave Ludwigshafen through the prosecution of a case against him by the French occupation troops, and hence had an opportunity, because of the time thus hanging on his hands, to review his laboratory notebooks and prepare the present treatise.

The subjects discussed are: the behavior of nitrous acid toward sulfurous acid; new oxides of nitrogen; the constitution of nitrogen iodide; the nitrogen compounds of gold; monochloramine, the amine of hypochlorous acid; condensation products of chloramine and aldehydes; nitroxyl and dioxyammonia; hyponitrous acid; potassium nitrosylsulfite; the trisulfo acid of hydroxylamine; the isodisulfo acid of hydroxylamine, the disulfo acid of hydroxylamine, the monosulfo acid of hydroxylamine; oxidation of hydroxylamine; oxidation of hydrazine and its sulfo acids; oxidation of triazoic acid; reduction of triazoic acid; combustion of ammonia to hydrazine and diimide; action of sulfite, bisulfite, and sulfurous acid on hydroxylamine; constitution of organic sulfurous acid derivatives; the action of hypochlorite on *p*-cresoldisulfonic acid; action of bisulfite and sulfite on nitro and nitroso compounds; the preparation and properties of polythionic acids; and the constitution of polythionic acids.

This formidable list of subjects, handled in a clear and sure manner, cannot fail to interest a wide circle of workers in as diverse fields as chamber sulfuric acid manufacture and dye manufacture, and since there is much new information sprinkled through the book, it cannot help but start new lines of thought.

The author's tendency to seek a complicated explanation for the course of an apparently simple reaction, one which often involves the assumption of hypothetical or evanescent compounds, is again evident, as it was in some of his earlier papers—for example, in his well-known paper on the chamber process. Wherever such unusual courses of reactions are suggested, however, the author advances experimental evidence which appears to substantiate his conclusions.

While the author was undoubtedly much inconvenienced by the French occupation troops, one cannot but feel grateful to them if they were, even if unintentionally, the cause of the appearance of this valuable book.

FRED C. ZEISBERG

Systematic Organic Chemistry. By WILLIAM M. CUMMING, I. VANCE HOPPER, and T. SHERLOCK WHEELER. xxii + 535 pages. 22 × 15 cm. D. Van Nostrand Co., New York, 1924. Price, $6.00.

"The present work is intended as a complete laboratory guide to the preparations and estimations of organic chemistry for undergraduate and post-graduate students."

The book is very different from any which has previously appeared in English on this subject. Its nearest prototype is the organic part of Vanino's Handbuch. It contains about half as many preparations as that work, but in addition contains excellent sections on apparatus and methods and on organic analysis.

Part I contains 47 pages of hints and suggestions on apparatus and methods which will prove valuable to all organic chemists. Among the very few omissions of important subjects in this part are the use of shower baths in laboratories in case of fire, the poisonous action of the various anilines, the treatment of phenol burns with bromine in glycerol, and the use of the centrifuge in draining crystals. To offset the few omissions there are countless helpful suggestions not ordinarily found in laboratory manuals.

Part II, of 388 pages, contains about five hundred preparations classified under about two hundred types of reactions. The classification of these types of reactions forms the most distinctive feature of the book. They are classified according to the new linkage formed in each reaction. The first of these is naturally the formation of a new carbon-to-carbon linkage. This includes most of the "condensations" classified according to the nature of the compounds which enter the reaction. Then come the linking of hydrogen to carbon, oxygen to carbon, nitrogen to carbon, sulfur to carbon, halogen to carbon, hydrogen to nitrogen, and nitrogen to nitrogen. Then follow chapters that give methods for making important types of dyes, drugs, electrolytic preparations, extraction of products from natural sources, stereochemical reactions, decompositions, and miscellaneous preparations. A valuable feature of this part is the rather full discussions of the various types of reactions before the presentation of specific preparations involving them.

Part III, of 64 pages, considers the analytical side of organic chemistry. After the usual methods of qualitative and quantitative elementary analysis and molecular weight determinations, given somewhat more interestingly than usual, come chapters on estimations of various groups such as amino, hydroxyl, acyl, alkoxyl, etc., estimations of nitro, nitroso, and azo compounds by means of titanous chloride, estimations based on diazotization or coupling, and miscellaneous estimations such as those of thiophene in benzene, enolic compounds, acetone, etc.

Part IV, of 25 pages, contains an inorganic section, which includes the preparation or purification of most of the inorganic reagents used in organic chemistry and a section on tests for common organic acids, alkaloids, and carbohydrates.

The impression produced by the book is favorable from every angle. The material is well chosen and well presented. Moreover, it is thoroughly up to date. Even as recent a work as "Organic Syntheses" has been used as a source of preparations.

While its size and cost will probably prevent any wide use as a laboratory manual, the work is one which should form part of any organic library, however small.

FRANK C. WHITMORE

Kapillarchemie. Eine Darstellung der Chemie der Kolloide und verwandter Gebiete. By HERBERT FREUNDLICH. 3rd edition. xv + 1225 pages, 157 figures, 24 × 15.5 cm. Akademische Verlagsgesellschaft, M. B. H., Leipzig, 1923. Price, 32.50 M.

This third edition of Freundlich's monumental and classic work on colloid chemistry is a reprint of the second edition [for review see *J. Am. Chem. Soc.*, **44**, 2659 (1922)], with the addition of an appendix consisting of 43 pages of notes supplementing the former edition. Each note refers to a definite page number, making reference easy. These supplementary notes serve to bring the book fairly up to date; they are accompanied by 177 references to work mentioned. Among the important additions are discussions of the following: the work of Harkins and Roberts on the relation between surface energy and heat vaporizations of Harkins and Cheng on interfacial tensions of organic liquids against water; a discussion of the theories of Langmuir and Polanyi on adsorption; the experiments of Taylor and Burns on adsorption by finely divided metals; Sulman's paper on flotation; the dependence of adsorbability on solubility for pairs of isomers, as pointed out by Izaguirre; the method of measuring surface areas of powders and thickness of adsorbed films devised by Paneth; the experiments of Adam confirming Langmuir's views concerning orientation of the molecules in oil films on water surfaces; the work of Volmer on the formation of crystals from vapor and from solution; the work of Schuster supporting the view of Weiger that double refraction is due to groups and agglomerations of amicrons; the work of Haber on the crystallinity of colloidal particles and precipitates, showing that these particles are more often crystalline than formerly had been supposed; the view of Fajans concerning the charge on a colloidal particle and the adsorption of ions; the spectrophotometric work of Boutaric and Vuillaume on coagulation speed of As_2S_3 sols, which confirms Smoluchowski's opinion that there is no autocatalytic appearance to the coagulation, but an immediate increase in light absorption; Traube and Klein's observations that many concentrated or saturated solutions of slightly soluble substances contain some of the material in a dispersed condition observable in the ultramicroscope; Loeb's theory of protein behavior and papers of Procter and Procter and Wilson; and the work of Bradford and of Notboom on rhythmic precipitation.

The book is a veritable storehouse of authentic information, and there should be an English translation.

H. J. MATHEWS

NEW BOOKS

Autobiography of John Fritz. 327 pp. Illustrated. John Wiley & Sons, Inc., New York. Price, $2.00.

Carbonisation of Seaweed as a Preliminary to the Extraction of Iodine and Potassium Salts. J. G. KING. *Technical Paper* 9 of the Fuel Research Board. 16 pp. H. M. Stationery Office, London. Price, 6 d. net.

Die Fermente und Ihre Wirkungen. CARL OPPENHEIMER AND RICHARD KUHN. 160 pp. Illustrated. Georg Thieme, Leipzig. Price, $1.50.

Distribution et Réglage de la Chaleur dans les Installations de Chauffage par l'Eau et la Vapeur. A. NESSI AND L. NISOLLE. 40 pp. Illustrated. Dunod, Paris. Price, 8 fr.

Food Products. HENRY C. SHERMAN. 2nd edition, revised and enlarged. 687 pp. The Macmillan Co., New York. Price, $3.00.

Gaz et Cokes. Manuel de la Fabrication et de l'Utilisation des Gaz de Distillation et des Autres Gaz Industriels des Cokes et des Sous-produits de la Houille. A. GREBEL AND H. BOURON. 700 pp. Illustrated. Dunod, Paris. Price, 67 fr. 50.

Handbook of Petroleum, Asphalt and Natural Gas. ROY CROSS. 1924 edition, revised and rewritten. 750 pp. Kansas City Testing Laboratory, Kansas City, Mo. Price, $7.50.

Icarus, or the Future of Science. BERTRAND RUSSELL. 64 pp. E. P. Dutton & Co., New York. Price, $1.00.

James Dewar. H. E. ARMSTRONG. 32 pp. Ernest Benn, Ltd., London. Price, 1 s. 6 d.

Measurement, Compression and Transmission of Natural Gas. LOUIS C. LICHTY. 523 pp. Illustrated. John Wiley & Sons, Inc., New York. Price, $7.50.

New Theories of Matter and the Atom. ALFRED BERTHOUD. 259 pp. Illustrated. The Macmillan Co., New York. Price, $3.50.

Précis de Métallographie Microscopique et de Macrographie. LÉON GUILLET AND ALBERT PORTEVIN. 2nd edition. 337 pp. Illustrated. Dunod, Paris. Price, 65 fr.

Proceedings of the National Wholesale Druggists' Association. 49th Annual Meeting, October 8 to 12, 1923. 688 pp. Illustrated. The National Wholesale Druggists' Association, New York, N. Y.

Pulverised Fuel and Efficient Steam Generation. DAVID BROWNLIE. 470 pp. The Institution of Electrical Engineers, London.

Quantitative Chemical Analysis Adapted for Use in the Laboratories of Colleges, of Technical Institutes, and of Analysts. FRANK CLOWES AND J. BERNARD COLEMAN. 576 pp. P. Blakiston's Son & Co., Philadelphia. Price, $5.75.

Repartition Générale de la Chaleur dans les Immeubles au Moyen de Centrales Thermiques avec ou sans Utilisation de la Force Motrice. A. NESSI. 60 pp. Illustrated. Dunod, Paris. Price, 12 fr.

Technique et Pratique des Moteurs à Huile Lourde à Injection Directe. Y. LE GALLOU. 208 pp. Illustrated. Dunod, Paris. Price, 38 fr. 50.

"Where to Buy" Everything Chemical. 228 pp. 1924 export edition. Editor "Where to Buy," London. Free distribution.

1924 Year Book, American Association of Textile Chemists and Colorists. 210 pp. Howes Publishing Co., Inc., New York, N. Y.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Foreign and Domestic Commerce

French Dyestuffs Industry. F. B. Gorin. *Trade Information Bulletin* 253. Issued August 4, 1924. 21 pp.

New Pharmaceutical Preparations in Germany. W. T. Daugherty. *Special Circular* 44, Chemical Division. 7 pp. Issued July 23, 1924.

Petroleum in Japan. A. T. Coumbe, Jr. *Trade Information Bulletin* 245. 27 pp. Issued June 30, 1924.

Scotland—Dyestuffs Trade. H. A. Johnson. *Chemical Trade Bulletin* 33-B. 1 p. Issued July 11, 1924.

World Survey of the Zinc Industry. J. A. Stader. With a report on United States production and trade by C. E. Siebenthal, geologist, United States Geological Survey. *Trade Information Bulletin* 246. 60 pp. Issued June 30, 1924.

Bureau of Mines

Effects of Extraneous Gas on the Production of Oil Wells in the Lyons-Quinn Field of Oklahoma. M. J. Kirwan. *Reports of Investigations* 2612. 2 pp. Issued June, 1924.

Filter Sand for Municipal Water Supply. W. M. Weigel. *Reports of Investigations* 2622. 6 pp. Issued July, 1924.

Microchemical Analysis and Its Application in the Determination of Low-Grade Ores. E. E. Fairbanks. *Reports of Investigations* 2613. 6 pp. Issued June, 1924.

Saving Gasoline and Increasing Mileage by Proper Carburetor Adjustment. G. W. Jones and A. A. Straub. *Reports of Investigations* 2616. 9 pp. Issued June, 1924.

Size and Character of Grains of Nonmetallic Mineral Fillers. W. M. Weigel. *Technical Paper* 296. 44 pp. Paper, 15 cents.

The Utilization of Dolomite for Refractories. G. A. Bole. *Reports of Investigations* 2627. 11 pp. Issued July 11, 1924.

Bureau of Standards

Physical Properties of Materials. I—Strengths and Related Properties of Metals and Wood. *Circular* 101, 2nd ed. Paper, 40 cents.

Thermal Expansion of Molybdenum. Peter Hidnert and W. B. Gero. *Scientific Paper* 488. 16 pp. Paper, 10 cents.

United States Government Master Specifications for Fire-Extinguishing Liquid (Carbon Tetrachloride Base). *Circular* 134, 2nd ed. 6 pp. Paper, 5 cents.

United States Government Master Specification for Flat Glass for Glazing Purposes. *Circular* 164. 12 pp. Paper, 5 cents.

United States Government Master Specification for Olive Drab Paint (Semipaste and Ready-Mixed). *Circular* 165. 11 pp. Paper, 5 cents.

United States Government Specification for Asphalt for Mineral-Surfaced Roofing. *Circular* 159. Paper, 5 cents.

United States Government Specification for Asphalt for Waterproofing and Damp-Proofing. *Circular* 160. Paper, 5 cents.

United States Government Specification for Asphalt Primer for Roofing and Waterproofing. *Circular* 162. Paper, 5 cents.

United States Government Specification for Asphalt-Saturated Rag Felt for Roofing and Waterproofing. *Circular* 161. Paper, 5 cents.

United States Government Specification for Coal-Tar Pitch for Roofing. *Circular* 157. Paper, 5 cents.

United States Government Specification for Coal-Tar Pitch for Waterproofing and Damp-Proofing. *Circular* 155. Paper, 5 cents.

United States Government Specification for Coal-Tar Saturated Rag Felt for Roofing and Waterproofing. *Circular* 156. Paper, 5 cents.

United States Government Specification for Surfacing Materials for Bituminous Built-Up Roofing. *Circular* 158. Paper, 5 cents.

Congress

Diploma Mills. Hearings before subcommittee pursuant to S. Res. 61, authorizing Committee on Education and Labor to inquire into certain abuses in medical education. January 19 to March 28, 1924. 98 pp. Paper, 5 cents.

Muscle Shoals. Hearings on S. 139, S. 2372, S. 2747, S. 3214, and H. R. 518, bills relative to completion of Muscle Shoals. April 28 to May 20, 1924. Parts 3 to 5. 736 pp. Part 3, 30 cents; Part 4, 10 cents; Part 5, 25 cents.

Water Pollution. Views to accompany H. R. 518 (to provide for manufacture of explosives for use of Army and Navy, to provide for manufacture of fertilizer and other agricultural products, to incorporate Federal Power Corporation, and for other purposes). Submitted by Mr. Ladd, June 3, 1924. *S. Report* 678, Part 2. 20 pp. Paper, 5 cents.

Department of Agriculture

Delinting and Recleaning Cottonseed for Planting Purposes. J. E. Barr. *Department Bulletin* 1219. Paper, 10 cents.

Elemental Composition of the Corn Plant. W. L. Latshaw and E. C. Miller. *Journal of Agricultural Research*, 27 (March 15, 1924), 845–60.

Investigation of Dust Content of Atmosphere. H. H. Kimball and I. F. Hand. Note on Organic Bodies Found in Air of Washington and London. Sir Napier Shaw. Dust Fall of March 29, 1924, Preliminary Note. E. R. Miller. From *Monthly Weather Review*, March, 1924. 8 pp.

Tentative Standard Methods of Sampling and Testing Highway Materials. Adopted by the American Association of State Highway Officials and approved by the Secretary of Agriculture. *Department Bulletin* 1261. Paper, 15 cents.

Tests of Methods of Protecting Woods against Termites or White Ants. Progress Report. T. E. Snyder. *Department Bulletin* 1231. 16 pp Paper, 5 cents. Issued June 26, 1924.

Geological Survey

Bauxite and Aluminium in 1923. J. M. Hill. *Mineral Resources of the United States, 1923.* Part I, pp. 23–24. Published July 21, 1924.

Bibliography of North American Geology for 1921-1922. J. M. Nickles. *Bulletin* 758. 273 pp. Paper, 25 cents.

Fluorspar and Cryolite in 1923. H. W. Davis. *Mineral Resources of the United States, 1923.* Part II, pp. 27–40. Published July 25, 1924.

Gold, Silver, Copper, Lead, and Zinc in the Eastern States in 1923. Mines Report. J. P. Dunlop. *Mineral Resources of the United States, 1923.* Part I, pp. 1–7. Published July 7, 1924.

Ground Water in Musselshell and Golden Valley Counties, Montana. A. J. Ellis and O. E. Meinzer. Prepared in coöperation with the State Engineer; the Department of Chemistry of the Montana State College, Bozeman; and the Water Laboratory of the Montana State Board of Health. *Water-Supply Paper* 518. 92 pp. Paper, 20 cents.

Mineral Resources of the United States in 1923 (Preliminary Summary). Introduction by F. J. Katz. Statistics assembled by M. B. Clark. 130 pp. Published August 6, 1924.

Petroleum in 1922. G. B. Richardson. *Mineral Resources of the United States, 1922.* Part II, pp. 359–438. Published July 15, 1924.

Strontium in 1923. G. W. Stose. *Mineral Resources of the United States, 1923.* Part II, pp. 23–26. Published July 19, 1924.

The Cold Bay-Chignik District, Alaska. W. R. Smith and A. A. Baker. *Mineral Resources of Alaska, 1922-D. Bulletin* 755-D. 218 pp.

The Composition of the Earth's Crust. F. W. Clarke and H. S. Washington. *Professional Paper* 127. 117 pp. Paper, 20 cents.

President of the United States

Barium Dioxide. Proclamation authorizing certain increase in duty on barium dioxide, in order to equalize differences in costs of production in United States and Germany. *Proclamation No.* 1698. 2 pp. May 19, 1924.

Public Health Service

Cancer and Proprietary Cures. *Public Health Reports*, 39 (July 18, 1924), 1746–52.

Effect of Oil Pollution of Coast Waters on the Public Health. F. W. Lane, A. D. Bauer, H. F. Fisher, and P. N. Harding. *Public Health Reports*, 39 (July 11, 1924), 1657–62.

Safeguarding the Sanitary Quality of Drinking and Culinary Water Supplied on Interstate Carriers. E. C. Sullivan. *Public Health Reports*, 39 (July 4, 1924), 1620–34.

Studies on Oxidation Reduction. V—Electrode Potentials of Simple Indophenols, Each in Equilibrium with Its Reduction Product. Barnett Cohen, H. D. Gibbs, and H. M. Clark. Reprint 904 from *Public Health Reports*. 34 pp. Paper, 5 cents.

Same. VI—Preliminary Study of Indophenols; (A) Dibromo Substitution Products of Phenol Indophenol; (B) Substituted Indophenols of Ortho Type; (C) Miscellaneous. Barnett Cohen, H. D. Gibbs, and W. N. Clark. Reprint 915 from *Public Health Reports*. 20 pp. Paper, 5 cents.

The Legal Aspects of Milk Control. J. A. Tobey. *Public Health Reports*, 39 (July 18, 1924), 1739–46.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Notice—*Any publications mentioned under this heading will be sent free, unless otherwise noted, to readers of* This Journal, *on request to the firm issuing the publication. When writing for any of these items kindly mention* Industrial and Engineering Chemistry.

Balances and Weights. Complete catalog and price list of this equipment and accessories for scientific and technical uses. Fully illustrated and indexed. 76 pp. $6^1/_2 \times 9^3/_4$ in. Henry Heil Chemical Co., 210 So. Fourth St., St. Louis, Mo.

Ballard-Sprague Construction Service. Bulletin featuring boiler settings and chimneys in various types of plants. Some typical installations illustrated. 20 pp. $6 \times 9^1/_4$ in. Ballard-Sprague & Co., 200 Fifth Ave., New York, N. Y.

Ball Thrust Bearing Overhung Agitating Devices. *Catalog* C, revised in loose-leaf binder giving illustrations, descriptions, charts, and useful tables on various devices and chemical equipment. 30 pp. $6^1/_2 \times 9$ in. General Machine Co., 398 Market St., Newark, N. J.

Brownell Tubular Boilers. *Bulletin* **B-1,** covering this equipment, with illustrations, diagrams, and technical information. 20 pp. $8^1/_2 \times 10^1/_2$ in. The Brownell Co., Dayton, Ohio.

Cambridge Temperature Measuring Instruments. *Booklet No.* **1.** This handbook carries illustrations with full descriptions of the various thermometers, thermographs, pyrometers, potentiometers, etc., manufactured by this firm. Indexed. 71 pp. $4^1/_4 \times 5^1/_2$ in. Cambridge & Paul Instrument Company of America, Inc., 3512 Grand Central Terminal, New York, N. Y.

Chemical Equipment. *Bulletin* **230.** Descriptions and illustrations of various types of porcelain-lined or plain iron-jacketed kettles, caldrons, storage and mixing tanks, and vacuum and pressure stills, with tabular data covering capacities, sizes, applications, and prices. 16 pp. 6 × 9 in. The Stuart & Peterson Co., Burlington, N. J.

Cleveland Worm Gear Reduction Units. Thoroughly covers worm gearing and speed reduction, together with illustrations, descriptions, and technical data on appropriate equipment. An excellent engineer reference work. 104 pp. $7^1/_2 \times 10^1/_2$ in. The Cleveland Worm & Gear Co., Cleveland, Ohio.

Colorimeters and Nephelometers. Catalog illustrating, describing, and quoting prices on various types of these instruments for biological and industrial chemistry. Directions for use included. 22 pp. $6 \times 8^3/_4$ in. Klett Mfg. Co., Inc., 202 E. 46th St., New York, N. Y.

Conkey Filters. *Folder* A, illustrating and describing the various parts of this continuous and automatic rotary type. Interesting table covering their capacities upon some average materials. 9 × 12 in. Conkey Filter Co., 154 Nassau St., New York, N. Y.

Construction of Large Tanks, Using Acid-Proof Brick and Acid-Proof Cement, for the Lining of Same. A pamphlet with accompanying set of blue prints describing fully how to construct such tanks, vats, towers, etc., and the proper materials and the use thereof. 8 pp. $9^1/_4 \times 11^1/_4$ in. Maurice A. Knight, Kelly Ave., East Akron, Ohio.

Crescent "Roto-Piston" Dry Vacuum Pumps. *Bulletin* **711,** features illustrations, descriptions, and other technical data of these special types. Typical installations and diagrams. 20 pp. 6 × 9 in. Chicago Pneumatic Tool Co., 6 East 44th St., New York, N. Y.

Direct Steam and Oil Separators. *Catalog* **S-24,** featuring and describing this equipment, as well as including facsimile of test reports. 40 pp. 6 × 9 in. The Direct Steam Separator Co., Syracuse, N. Y.

Emerson Conditioning Ovens. Instructive booklet with illustrations, diagrams, and many helpful data on this equipment for determining amount of moisture in textile materials. Instructions for operating. 16 pp. 6 × 9 in. Emerson Apparatus Co., 171 Tremont St., Melrose Highlands, Mass.

Fairbanks Scales. *Catalog* **250.** Appropriate equipment for practically all fields. Indexed. 212 pp. 4 × 7 in. Morse & Co., Inc., Chicago, Ill.

Falk Herringbone Gears. *Bulletin* **31,** illustrating and technically describing various types. 8 pp. $8^1/_2 \times 11$ in. The Falk Corp., Milwaukee, Wis.

Feeders, Sifters, and Mixers. *Catalog* **14,** with illustrations and prices. 40 pp. 6 × 9 in. The Gedge-Gray Co., Lockland, Ohio.

Fitchburg Engines. Brochure giving interesting and instructive information on this equipment. Illustrations, diagrams, and tables. 40 pp. $9^3/_4 \times 7$ in. Fitchburg Steam Engine Co., Fitchburg, Mass.

Hayton Triplex and Centrifugal Pumps. Series of bulletins in loose-leaf binder featuring, with charts, diagrams, illustrations, and complete descriptions, equipment to meet every need. $8^1/_2 \times 11$ in. Hayton Pump & Blower Co., Appleton, Wis.

Homestead Quarter-Turn Valves. *Catalog* **31.** Contains technical data, description, and illustrations of different types. Indexed. 38 pp. 6 × 9 in. Homestead Valve Manufacturing Co., Inc., Homestead, Pa.

"Hy-Speed" Mixer. Illustrated folder giving specifications, prices, and various products on which this type with "Push-Pull" propellers can be used to advantage. Alsop Engineering Co., 47 West 63rd St., New York, N. Y.

Industrial Lubrication. This most interesting booklet contains many valuable lubrication data, tests and other information. Helpful charts. This should be in the hands of every one interested in the lubrication of machinery, etc. 44 pp. $3^3/_4 \times 6^3/_4$ in. Waverly Oil Works Co., 5402 54th St., Pittsburgh, Pa.

Ingersoll-Rand Equipment. Series of bulletins in cloth loose-leaf binder fully illustrating and describing various compressors, pumps, condensers, etc. Diagrams, tables, and other interesting and useful data. Marginal index. $6^3/_4 \times 9^1/_4$ in. Ingersoll-Rand Co., 11 Broadway, New York, N. Y.

Knowles Patent Column Cell. Descriptive pamphlet with illustrations, diagrams, and technical data on this equipment for producing oxygen and hydrogen. Covers some new and interesting features. Tables. 12 pp. $7^1/_2 \times 9^3/_4$ in. International Electrolytic Plant Co., Ltd., New Crane St., Chester, England.

Krogh Pumps. Series of bulletins in loose-leaf binder, featuring with technical information, illustrations, and other interesting data, various types of this equipment. $6 \times 9^1/_4$ in. Krogh Pump & Machinery Co., 147–159 Beale St., San Francisco, Calif.

Leeds & Northrup Specialties. *Catalog* **75,** completely illustrating and describing apparatus for electrometric determinations of hydrogen-ion concentration. Includes prices and interesting technical data. 40 pp. $7^3/_4 \times 10^1/_2$ in. Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia, Pa.

Locomotives for Industrial and Contractors' Service. *Record No.* **86,** fully describing and illustrating steam and internal combustion locomotives. 53 pp. 9 × 6 in. The Baldwin Locomotive Works, Broad and Spring Garden Sts., Philadelphia, Pa.

Monel Metal in the Coal Mine. Pamphlet featuring uses and applications of this product to the coal industry. Illustrates running plates, chutes, various parts of pumps, valves, etc., advantageously employing monel metal. 8 pp. 9 × 12 in. International Nickel Co., 67 Wall St., New York, N. Y.

Murray Steam Power Plants. *Catalog* **85,** containing descriptions and illustrations of engines, air compressors, boilers, etc., for diverse purposes. Indexed. 95 pp. $10^3/_4 \times 7^3/_4$ in. Murray Iron Works Co., Burlington, Ia.

Platinum. A general catalog covering all forms of platinum ware and supplies. 32 pp. $8^3/_4 \times 10^1/_4$ in. Loose-leaf binder. American Platinum Works, New Jersey R. R. Ave. at Oliver St., Newark, N. J.

Roller-Smith Direct Current Portable Instruments. *Bulletin* **110,** containing illustrations and technical data on Type HD ammeters, voltmeters, etc. 8 pp. 6 × 9 in. Roller-Smith Co., 233 Broadway, New York, N. Y.

Spectrometers and Accessories. *Bulletin* **109,** giving complete detailed description and prices. Illustrated. 4 pp. $7^3/_4 \times 10^1/_2$ in. Gaertner Scientific Corp., 1201 Wrightwood Ave., Chicago, Ill.

Tanks. Bulletin on storage tanks, giving detailed drawings and specifications for tanks of from 15,000 to 74,000 gallons. 36 pp. $8^1/_2 \times 11$ in. New edition. Lancaster Iron Works, 101 Hager St., Lancaster, Pa.

Technical and Industrial Platinum. Treatise on platinum with catalog section of illustrations, tables, and other data of value. 70 pp. $5^1/_2 \times 8^1/_2$ in. Bishop & Company Platinum Works, Malvern, Pa.

The Arnold Lining for Limekilns. Booklet giving questions and answers of general and valuable information about lime, its properties and uses. $3^1/_2 \times 6^1/_4$ in. Arnold & Weigel, Woodville, Ohio.

The Gospel of Fresh Air. Brochure containing various illustrations and data covering ventilating equipment. Typical installations. Wide application to many industries. Tables. Indexed. 35 pp. $7^3/_4 \times 10^3/_4$ in. The Swartwout Co., Cleveland, Ohio.

"Waste *vs.* Economy." Illustrated bulletin on automatic refrigeration showing uses and applications of their system, and typical installations. 24 pp. $8^1/_2 \times 11$ in. The Automatic Refrigerating Co., Inc., Hartford, Conn.

York Self-Contained Refrigerating Units. *Bulletin* **70.** Contains illustrations and descriptions of these units and their uses and applications in various fields. 6 pp. $8^1/_2 \times 11$ in. York Manufacturing Co., York, Pa.

MARKET REPORT—AUGUST, 1924

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

JUDGING by the increased volume of business, the firmer prices and better feeling in the trade, the turning point in the depressed chemical market was reached early in August. The downward movement of prices was evidently checked and a firmer undertone has developed. Consuming industries have been showing signs of resuming operations after a long period of idleness. After the hand-to-mouth policy of buying, stocks are believed to be low in all hands, and with any recovery in consumption prices are likely to advance sharply. Buyers thus far have been cautious and are still confining their purchases to moderate quantities, although orders have become more frequent. Price changes during the month show that advances outnumbered the declines.

On September 22 the new and lower tariff rates on coal-tar products will go into effect. All finished and refined products will be cut down from 60 per cent to 45 per cent ad valorem, while crude materials at 55 per cent will drop to 40 per cent. The 7-cent specific duty will remain unchanged. This is in accordance with the terms of the Fordney Tariff Act. The effect on the market is believed to have been almost completely discounted, although some pressure may be brought on prices for high-priced dyes and medicinals. Little effect on low-priced goods is expected.

Caustic soda and soda ash are seasonally quiet, but shipments have already begun to increase. The outlook for next year is for slightly higher prices owing to the continued high cost of production. Bleaching powder and chlorine have been in more or less routine demand, but prices have been steadily maintained during the season when declines are usually expected. Mineral acids have been moving in a quiet way at unchanged prices. Oxalic acid has been a weak item owing to the competition between domestic and foreign material. Sales have been made at $9^{1}/_{4}$ cents a pound but toward the last of the month strengthened slightly. Formic acid has been steady. Tartaric acid was reduced to meet prices of imported acid.

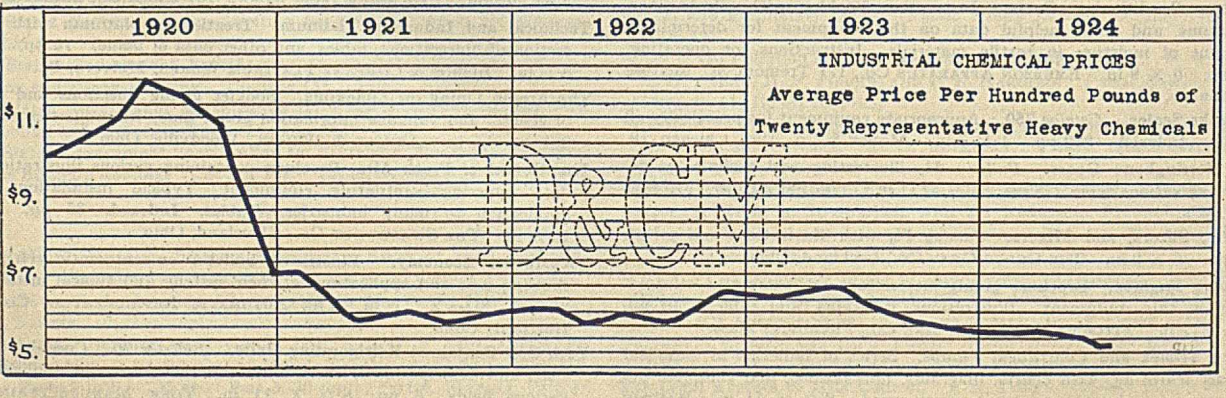
Acetone has started an upward movement as demand began to increase at a time when stocks were low. Ammonium carbonate is higher. Arsenic, usually an active item, has joined the inactive list owing to the lack of demand for calcium arsenate. Prices of both these products have weakened and declined to lowest levels in several years. Antimony products have strengthened with the rise in metal. Owing to the curtailed production in steel plants, ammonium sulfate production in the coking ovens has fallen off and stocks are becoming low. Prices have already strengthened and, with the buying season approaching, are likely to advance rapidly. Ammonium chloride has been weak and sales have been made as low as $5^{3}/_{4}$ cents a pound. Barium chloride has been weak owing to slow demand and prices have declined to $74 per ton for imported material. Barium carbonate has also been weak at $59 per ton.

Copper sulfate has been advanced following the recent rise in the metal. Copperas is under keen competition but prices have held fairly steady. Glauber's salt has firmed up after a period of low prices due to competition. Carbon tetrachloride has been weak, with sellers cutting prices in order to secure orders. Caustic potash has been quiet. Potassium bichromate has been dull and makers have been cutting prices under competition. Potassium permanganate has been subject to shading on good-sized orders though small lots have held at 14 cents a pound. Potassium prussiate has been reduced. Nitrite of soda has strengthened and sales are being made at higher prices. Domestic prussiate of soda has been advanced while the imported product has held at recent levels. Sodium fluoride has advanced. Tin crystals and other tin salts were advanced the first of the month following higher metal prices in July.

Metals have been gaining steadily. Copper advanced to $13^{3}/_{4}$ cents a pound. Tin reached 53 cents. Lead advanced to $8^{1}/_{2}$ cents a pound and zinc to $6^{1}/_{2}$ cents. Fertilizer materials have been moving upward. Ammoniates have been particularly strong. Ammonium sulfate is higher. Acid phosphate was advanced $1 per ton. Nitrate of soda advanced owing to rise in exchange.

Demand for intermediates has shown a marked improvement. Prices are generally steady since the buying has been confined to small quantities. Dyes have been quiet but improved buying is expected. Crude materials have been in small supply but demand has been quiet. Phenol has been reduced to a basis of 25 cents a pound. Benzene and toluene have been firm owing to limited supplies and curtailed production. Naphthalene has been a drug on the market and prices are at low levels. Pyridine has been holding up in price because of the small supplies available. Cresylic acid has been quiet.

Producers of alcohol announced an advance of 2 cents a gallon for all grades of denatured alcohol. Glycerol has strengthened owing to smaller production in soap-making plants. Acetanilide has been advanced to 33 cents a pound. American manufacturers of camphor have announced higher prices. Bismuth compounds have declined owing to sharp decline of the metal. Manufacturers of iodides have advanced prices as a result of higher costs due to rise in exchange.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

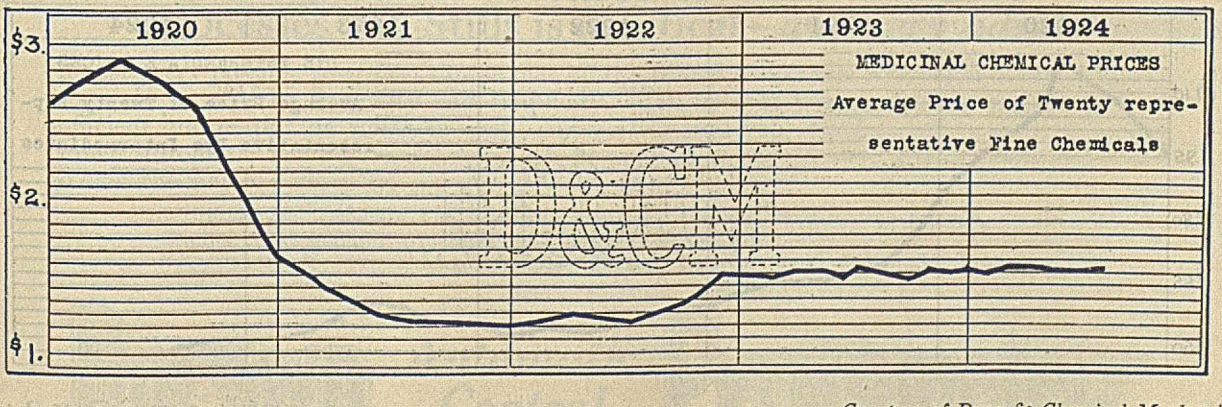
INORGANIC CHEMICALS

	Aug. 1	Aug. 15	Jan. 1924
Acid, Boric, cryst. bbls.........lb.	.09½	.09½	.11
Hydrochloric, comm'l 20°..lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls.....lb.	.07	.07	.07
Hydriodic, 10% U. S. P....lb.	.73	.73	.73
Nitric, 42°, cbys. c/l wks...lb.	.06	.06	.06½
Phosphoric, 50% tech......lb.	.08	.08	.08
Sulfuric, C. P.............lb.	.09	.09	.09
66° tks. wks..........ton	14.00	14.00	15.00
Oleum, 20%.........ton	18.00	18.00	18.00
Alum, Ammonia, lump.........lb.	.03½	.03½	.03½
Potash, lump..............lb.	*.03	*.03	*.03
Chrome.............lb.	.05½	.05½	.05½
Soda, ground.............lb.	.04	.04	.04
Aluminium Sulfate (iron-free)...lb.	.02⅜	.02⅜	.02½
Ammonium Carbonate, pwd....lb.	.09	.09	.10½
Chloride, white gran.......lb.	.07¼	.07¼	.07½
Ammonia, anhydrous..........lb.	.30	.30	.30
Ammonia Water, drums, 26°...lb.	.06¾	.06¾	.07½
Arsenic, white.................lb.	.07¾	.07¾	.13¼
Barium Chloride.............ton	*78.00	*76.00	*85.00
Nitrate..................lb.	*.08½	*.08½	*.08½
Barytes, white...............ton	33.50	33.50	33.50
Bleaching Powd., 35%, works ....100 lbs.	1.90	1.90	1.25
Borax, cryst., bbls.............lb.	.05¾	.05¾	.05¾
Bromine, pure, wks............lb.	.29	.29	.29
Calcium Chloride, fused, f. o. b. N. Y....................ton	24.30	24.30	24.30
Chlorine, liquid, cyl. c/l.......lb.	.05½	.05½	.04½
Copper Sulfate...........100 lbs.	4.50	4.60	4.65
Iodine, resublimed.............lb.	4.40	4.40	4.55
Lead Acetate, white crystals.....lb.	.14½	.14½	.14
Nitrate.................lb.	.12	.12	.12
Red.................100 lbs.	10.50	10.50	11.40
White (Carb.)............lb.	.09¾	.09¾	.09¾
Lime, live and hydrated, bbl....lb.	.01½	.01½	.01½
Oyster shell..............lb.	.03½	.03½	.03½
Lime Acetate............100 lbs.	3.00	3.00	4.00
Magnesium Carbonate, tech....lb.	.08	.08	.08
Magnesite, calcined...........ton	55.00	55.00	55.00
Phosphorus, yellow............lb.	.37½	.37½	.35
Red......................lb.	.—	.—	*.75
Plaster of Paris, tech..........bbl.	3.30	3.30	3.30
Potassium Bichromate.........lb.	.09¼	.09	.09½
Bromide, imported........lb.	.25	*.25	.17
Carbonate, calc., 80-85%..lb.	*.05¼	*.05¼	*.06
Chlorate, cryst............lb.	*.07	*.07	*.07½
Hydroxide, 88-92%.......lb.	*.06¾	*.06¾	*.06¼
Iodide, bulk, U. S. P.......lb.	3.75	3.75	3.75
Nitrate..................lb.	.06¼	.06¼	.06½
Permanganate, U. S. P.....lb.	*.14	*.14	*.14
Prussiate, red............lb.	*.38	*.38	*.42
Yellow...............lb.	*.18	*.18	*.22
Salt Cake, bulk...............ton	20.00	20.00	24.00
Silver Nitrate.................oz.	.45	.45	.44
Soda Ash, 58%, bags......100 lbs.	*1.94	*1.94	*1.94
Caustic, 76%, N. Y...100 lbs.	3.66	3.66	3.66
Sodium Acetate................lb.	.05	.05	.05
Bicarbonate..........100 lbs.	2.25	2.25	2.25
Bichromate..............lb.	.07⅛	.07	.07⅜
Bisulfite, powd............lb.	.04	.04	.04½
Chlorate.................lb.	.06¼	.06¼	.06½
Cyanide, 96-98%.........lb.	.22	.22	.23
Fluoride, tech.............lb.	.08½	.08½	.09
Hyposulfite, bbls......100 lbs.	2.50	2.50	2.75
Nitrate, 95%.........100 lbs.	2.45	2.52	2.52
Nitrite...................lb.	.08¾	.09	.08½
Prussiate, yellow..........lb.	.09½	.10	.11½
Phosphate (di-sod.), tech...lb.	.03½	.03½	.03½
Silicate, 40°..........100 lbs.	.80	.80	.80
Sulfide, 60%, fused........lb.	.03¾	.03¾	.04
Strontium, Nitrate............lb.	.10	.10	*.12
Sulfur, flowers............100 lbs.	3.00	3.00	3.00
Crude, mines.......long ton	14.00	14.00	14.00
Tin Bichloride, 50% soln.......lb.	.14	.14	.13½
Oxide....................lb.	.52	.55	.51
Zinc Chloride, U. S. P..........lb.	.27	.27	.25
Oxide, bbls...............lb.	.08	.08	.08½

ORGANIC CHEMICALS

	Aug. 1	Aug. 15	Jan. 1924
Acetanilide, U. S. P., bbls......lb.	.32	.32	.32
Acid, Acetic, 28 p. c.......100 lbs.	3.12	3.12	3.38
Glacial..........100 lbs.	11.01	11.01	12.78
Benzoic, U. S. P...........lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drums................lb.	.25	.25	.30
50- to 110-lb. tins.........lb.	.27	.27	.32
Citric, crystals, kegs.......lb.	*.47	*.47	*.48
Oxalic, cryst., bbls., wks....lb.	.09¾	.09¾	.12
Pyrogallic, resublimed.....lb.	1.50	1.50	1.55
Salicylic, U. S. P..........lb.	.35	.35	.35
Tannic, U. S. P., bbls......lb.	.83	.83	.83
Tartaric, cryst., U. S. P....lb.	*.27	*.27	*.31
Acetone, drums...............lb.	.17	.17	.25
Alcohol, denatured, complete...gal.	.48	.49	.48
Ethyl, 190 proof, bbls.....gal.	4.85	4.85	4.83
Amyl Acetate.................gal.	3.50	3.50	4.65
Camphor, Jap, refined, cases....lb.	.69	.69	.87
Carbon Bisulfide, c/l..........lb.	.06	.06	.06
Tetrachloride.............lb.	.07	.07	.10½
Chloroform, U. S. P., drums....lb.	.35	.35	.35
Creosote, U. S. P..............lb.	.42	.42	.40
Cresol, U. S. P................lb.	.22	.22	.25
Dextrin, corn............100 lbs.	4.52	4.72	3.64
Imported Potato..........lb.	.07½	.07½	.07½
Ether, U. S. P., 100 lbs.........lb.	.13	.13	.13
Formaldehyde, bbls............lb.	.09¼	.09¼	.10¾
Glycerol, dynamite, drums.....lb.	.17½	.17½	.16½
Methanol, pure, drums........gal.	.77	.77	.92
Methylene Blue, med..........lb.	2.25	2.25	2.25
Petrolatum, light amber.......lb.	.04½	.04½	.04½
Pyridine.....................gal.	4.25	4.00	3.75
Starch, corn, powd.........100 lbs.	3.77	3.97	3.22
Potato, Jap...............lb.	.06	.06	.06
Sago......................lb.	.05	.05	.05

* Resale or Imported (not an American maker's price).



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Aug. 1	Aug. 15	Jan. 1924
Beeswax, pure, white..........lb.	.40	.40	.36
Castor Oil, No. 3..............lb.	.16½	.16½	.14
Ceresin, yellow...............lb.	.09	.09	.08
Corn Oil, crude, tanks, mills....lb.	.11	.12	.10
Cottonseed Oil, crude, f. o. b. mill......................lb.	.11	.12	.09½
Linseed Oil, raw, lc/l..........gal.	1.00	1.02	.90
Menhaden Oil, crude, mills....gal.	.40	.50	.50
Neat's-foot Oil, 20°...........lb.	.19½	.19½	.17½
Paraffin, 128–130 m. p., ref.....lb.	.05½	.05½	.04
Rosin, "F" grade, 280 lbs.....bbl.	5.80	6.15	5.80
Rosin Oil, first run...........gal.	.38	.39	.43
Shellac, T. N..................lb.	.54	.54	.63
Sperm Oil, bleached winter, 38°.....................gal.	.89	.89	.84
Stearic Acid, double pressed....lb.	.11½	.12	.12
Tallow Oil, acidless............lb.	.09½	.10¼	.10
Turpentine, spirits of.........gal.	.84	.92	.94

METALS

	Aug. 1	Aug. 15	Jan. 1924
Aluminium, No. 1, ingots......lb.	.27	.27	.28
Antimony, ordinary.......100 lbs.	8.25	9.00	10.00
Bismuth.......................lb.	2.75	2.20	2.75
Copper, electrolytic...........lb.	.13	.13¾	.13
Lake......................lb.	.12½	.13¾	.13
Lead, N. Y...............100 lbs.	7.50	8.00	8.00
Nickel, electrolytic............lb.	.29	.29	.29
Platinum, refined, soft.........oz.	118.00	118.00	122.00
Quicksilver, flask......75 lbs. ea.	71.00	72.50	60.00
Silver, foreign.................oz.	.67½	.68	.64¾
Tin...........................lb.	.48	.52½	.47
Tungsten Wolframite.....per unit	8.50	8.50	8.50
Zinc, N. Y...............100 lbs.	6.50	6.55	6.70

FERTILIZER MATERIALS

	Aug. 1	Aug. 15	Jan. 1924
Ammonium Sulfate, expt..100 lbs.	2.60	2.75	2.75
Blood, dried, f. o. b. Balt......unit	3.00	3.25	4.30
Bone, 3 and 50, ground, raw...ton	25.00	30.00	25.00
Calcium Cyanamide, unit of ammonia....................	2.00	2.00	2.25
Fish Scrap, dried, wks........unit	3.50	4.25	4.75 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%......ton	2.25	2.25	3.25
Florida, 70%............ton	2.50	2.50	3.55
Florida, 74–75%.........ton	3.75	3.75	4.50
Tennessee, 72%..........ton	5.50	5.50	5.50
Potassium Muriate, 80%......unit	.63	.63	.68
Tankage, high-grade, f. o. b. Chicago................unit	2.75 & .10	3.50 & .10	3.65 & .10

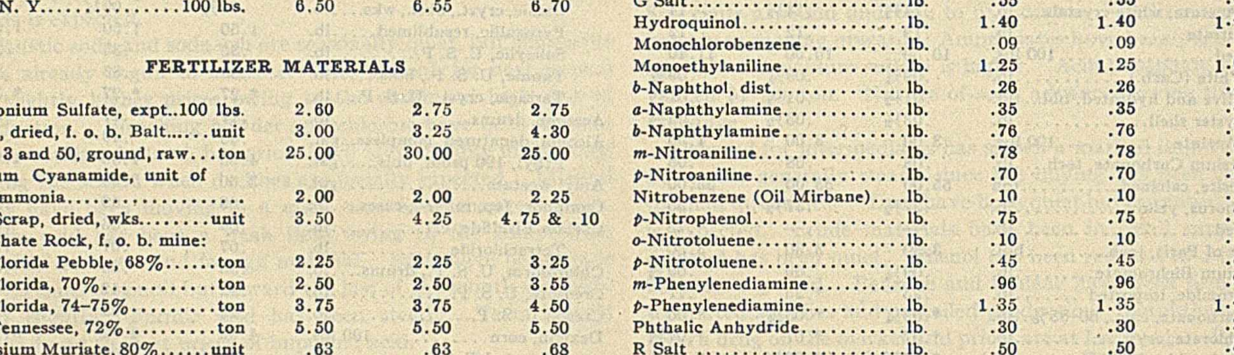
COAL-TAR CHEMICALS

Crudes

	Aug. 1	Aug. 15	Jan. 1924
Anthracene, 80–85%..........lb.	.75	.75	.75
Benzene, pure, tanks.........gal.	25	.25	.20
Naphthalene, flake............lb.	.05	.05	.06½
Phenol, drums................lb.	.25	.25	.30
Toluene, pure, tanks..........gal.	.26	.26	.22
Xylene, 2 deg. dist. range, drums...................gal.	.50	.50	.50

Intermediates

	Aug. 1	Aug. 15	Jan. 1924
Acids:			
Anthranilic...............lb.	.96	.96	.96
Benzoic, tech.............lb.	.70	.70	.70
Cleve's...................lb.	1.00	1.00	1.00
Gamma....................lb.	1.50	1.50	1.65
H.........................lb.	.72	.72	.75
Metanilic.................lb.	.60	.60	.60
Monosulfonic F...........lb.	2.30	2.30	2.30
Naphthionic, crude........lb.	.62	.62	.62
Nevile & Winther's........lb.	1.05	1.05	1.10
Picric....................lb.	.25	.25	.25
Sulfanilic................lb.	.20	.20	.20
Tobias'...................lb.	.90	.90	1.00
Aminoazobenzene.............lb.	1.15	1.15	1.15
Aniline Oil..................lb.	.16½	.16½	.16½
Aniline Salt.................lb.	.21	.21	.24
Anthraquinone (sublimed)......lb.	1.00	1.00	1.00
Benzaldehyde, tech............lb.	.75	.70	.75
U. S. P...................lb.	1.50	1.50	1.50
Benzidine Base...............lb.	.80	.80	.82
Benzidine Sulfate.............lb.	.70	.70	.70
Diaminophenol...............lb.	3.80	3.80	3.80
Dianisidine..................lb.	4.60	4.60	4.60
p-Dichlorobenzene............lb.	.17	.17	.17
Diethylaniline................lb.	.58	.58	.50
Dimethylaniline..............lb.	.35	.35	.39
Dinitrobenzene...............lb.	.18	.18	.19
Dinitrotoluene...............lb.	.19	.19	.19
Diphenylamine...............lb.	.48	.48	.48
G Salt.......................lb.	.55	.55	.55
Hydroquinol..................lb.	1.40	1.40	1.40
Monochlorobenzene...........lb.	.09	.09	.10
Monoethylaniline.............lb.	1.25	1.25	1.00
b-Naphthol, dist..............lb.	.26	.26	.26
a-Naphthylamine.............lb.	.35	.35	.35
b-Naphthylamine.............lb.	.76	.76	.76
m-Nitroaniline...............lb.	.78	.78	.78
p-Nitroaniline...............lb.	.70	.70	.74
Nitrobenzene (Oil Mirbane)....lb.	.10	.10	.10
p-Nitrophenol...............lb.	.75	.75	.75
o-Nitrotoluene...............lb.	.10	.10	.10
p-Nitrotoluene...............lb.	.45	.45	.55
m-Phenylenediamine..........lb.	.96	.96	.96
p-Phenylenediamine..........lb.	1.35	1.35	1.45
Phthalic Anhydride...........lb.	.30	.30	.25
R Salt ....lb.	.50	.50	.55
Resorcinol, tech..............lb	1.40	1.40	1.40
U. S. P...................lb.	2.25	2.25	2.25
Schaeffer's Salt..............lb.	.60	.60	.60
Sodium Naphthionate.........lb.	.62	.62	.62
Thiocarbanilide...............lb.	.30	.30	.30
Tolidine (base)...............lb.	.95	.95	.95
Toluidine, mixed.............lb.	.31	.31	.31
o-Toluidine..................lb.	.13	.14	.14
p-Toluidine..................lb.	.80	.75	.85
m-Tolylenediamine........... lb	.82	.82	.88
Xylidine.....................lb.	.45	.45	.50



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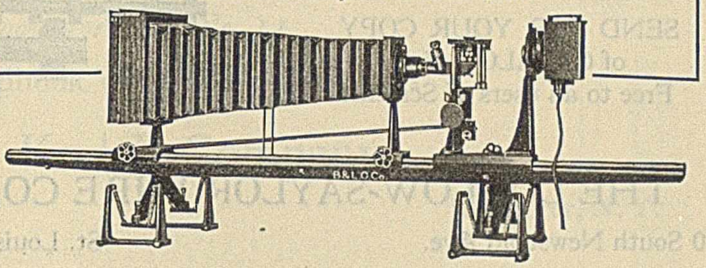

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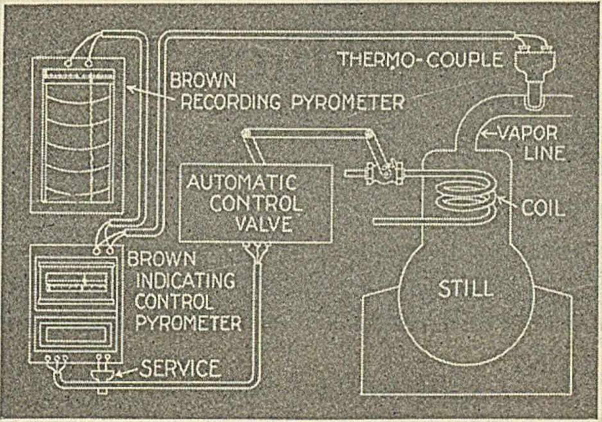

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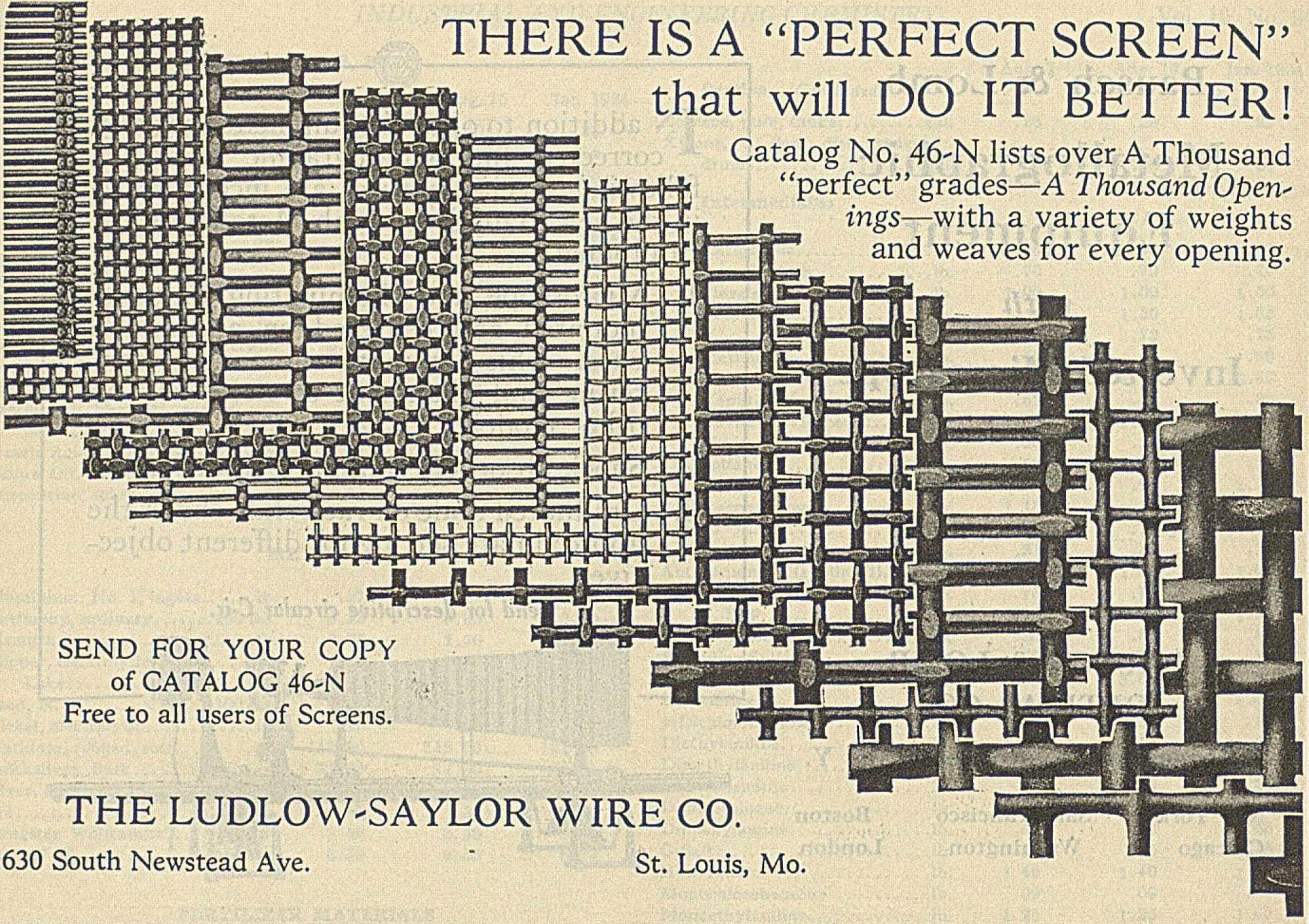

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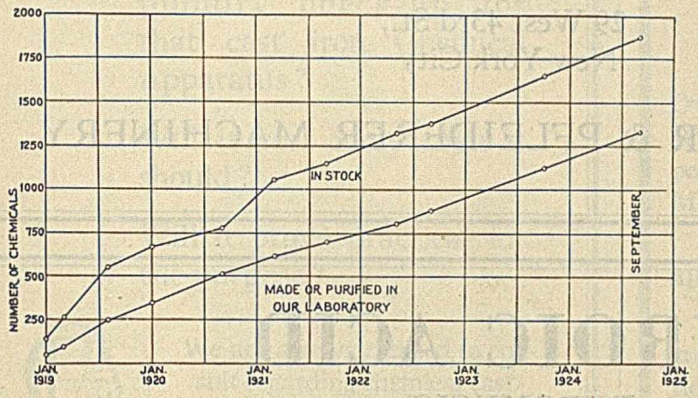

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America's Handbook of Organic Chemicals

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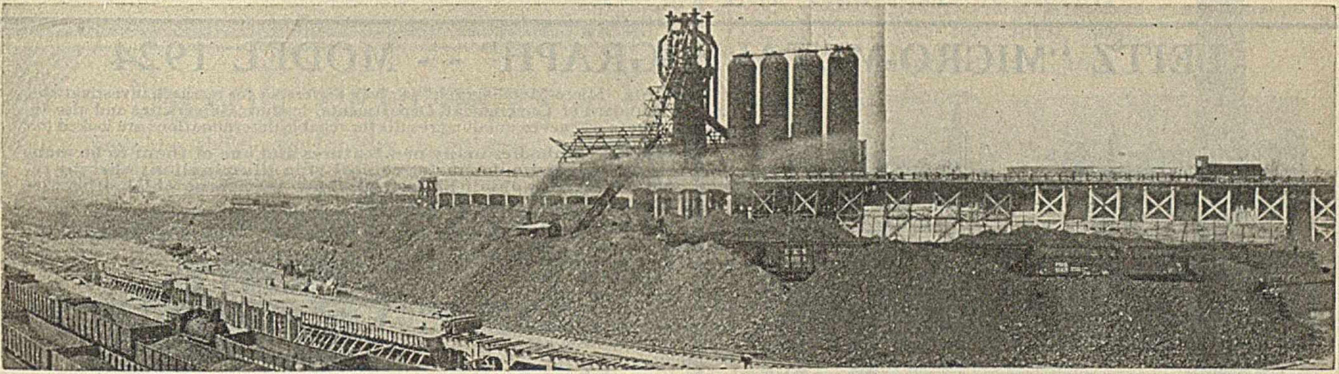

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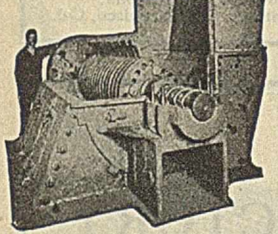

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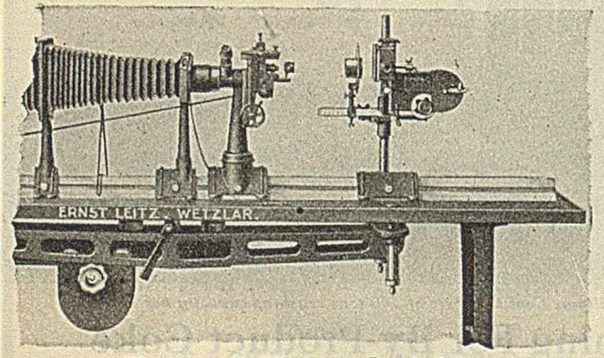

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have the ability and quality to withstand many heats as shown by the veteran below. They are uniform in construction and composition and embody knowledge gained only after nearly a century of experience.

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Built of PERFORATED RADIAL BRICK, manufactured expressly for the purpose.

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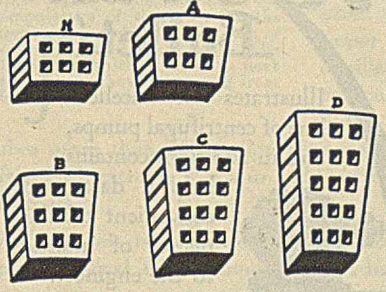

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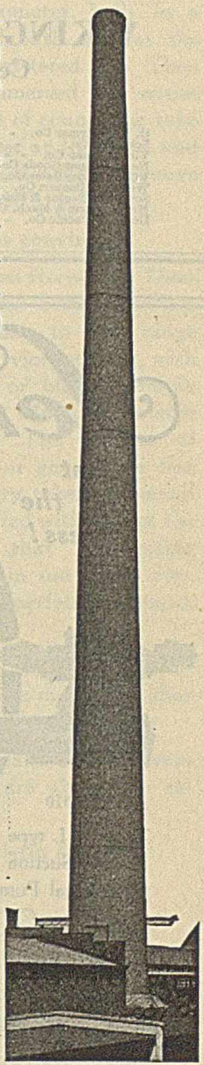
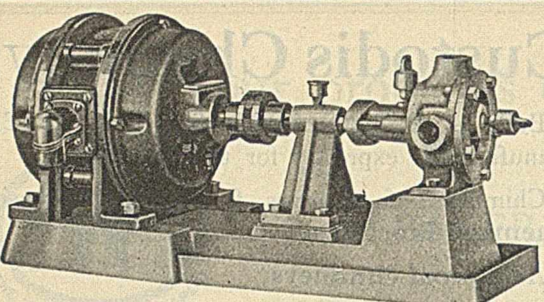


This chimney, 350 feet high, 8 feet inside at top, built by the Custodis Co. in 1904, has handled successfully acid gases for twenty years and is as good to-day as the day it was built.



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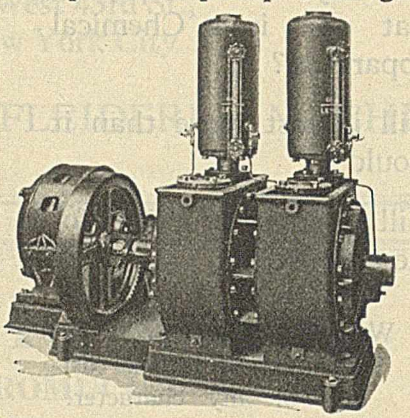

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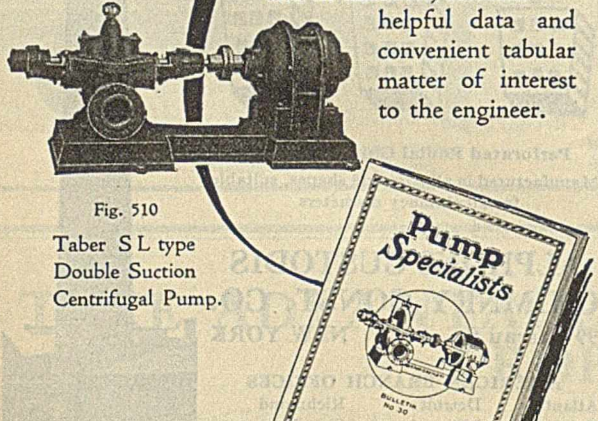

Fig. 510

Taber S L type
Double Suction
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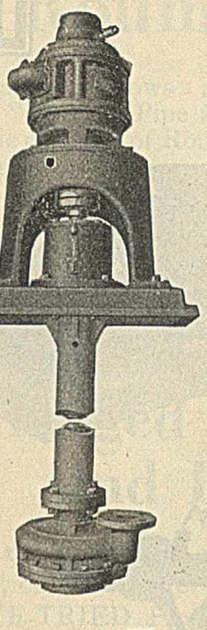

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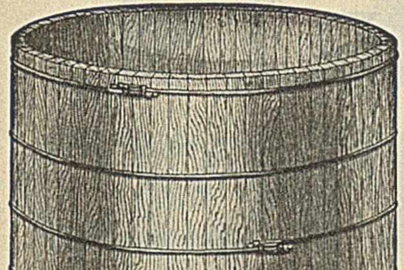

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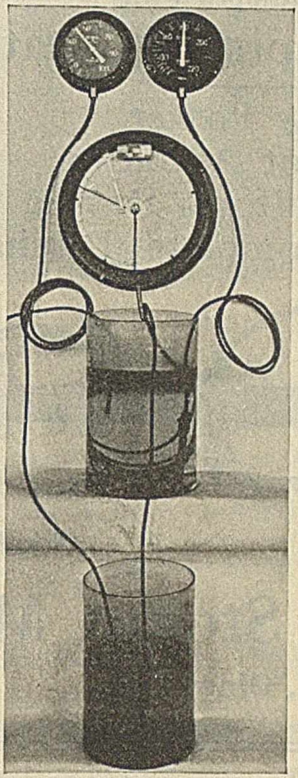

The indicating thermometer—upper left—reads 52° Fht., the temperature of the bath in the lower jar, in which the recording thermometer bulb is immersed.

The indicating thermometer—upper right—reads 180° Fht., the temperature of the water in the upper jar, in which the 20 feet of connecting tube is placed. The steam line which is used to heat the water is shown emerging from the left hand side of the jar.

"How can I expect accurate records from this Foxboro Recording Thermometer?" asked a customer. "There's 20 feet of connecting tube subjected to a high room temperature. You can't tell me that the record isn't affected by it."

This Test Showed Him He Was Wrong

We placed the recording thermometer bulb in a chilled bath so that the pen registered 52°. Then we immersed the entire 20 feet of connecting tube in water at 180° Fht. and the pen didn't move from 52°.

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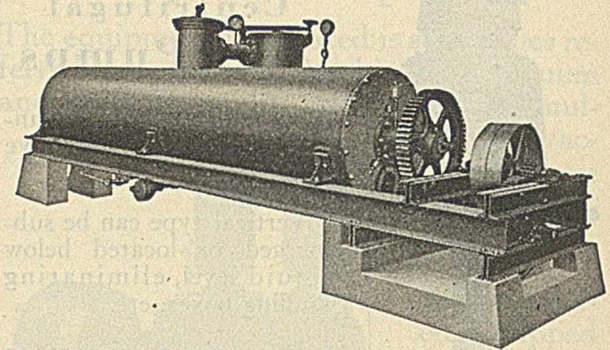

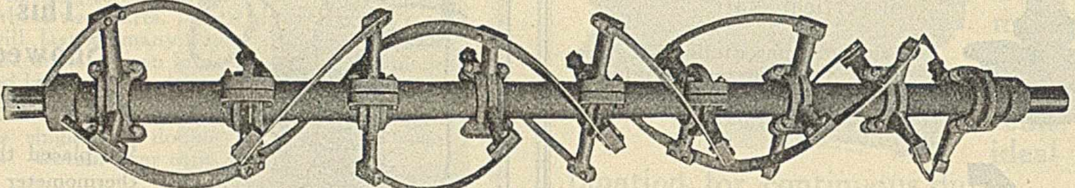

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Special sheet metal work.

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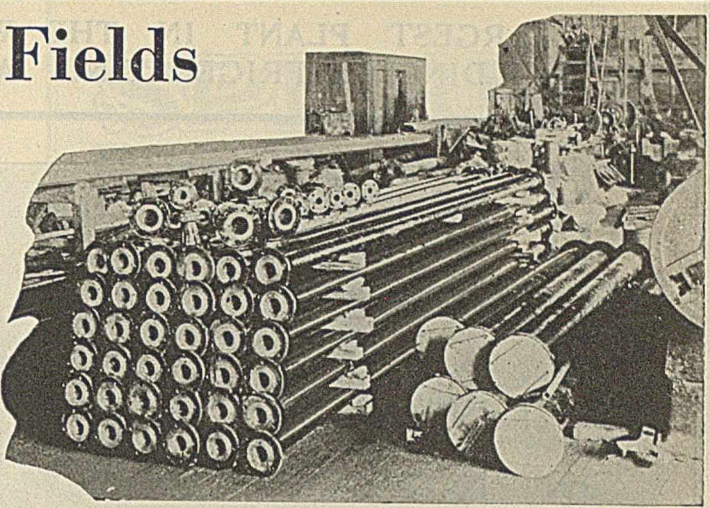
To Roumania's Oil Fields



The Illustration shows a small part of a large shipment of "United" Pipe and Fittings destined for use in the oil fields of Roumania. This material—consisting of

"United Tubond"
Lead-Lined
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—is for the handling of aluminum sulphate; and was specified, on the basis of the "United" reputation for SERVICE-TRIED Products.

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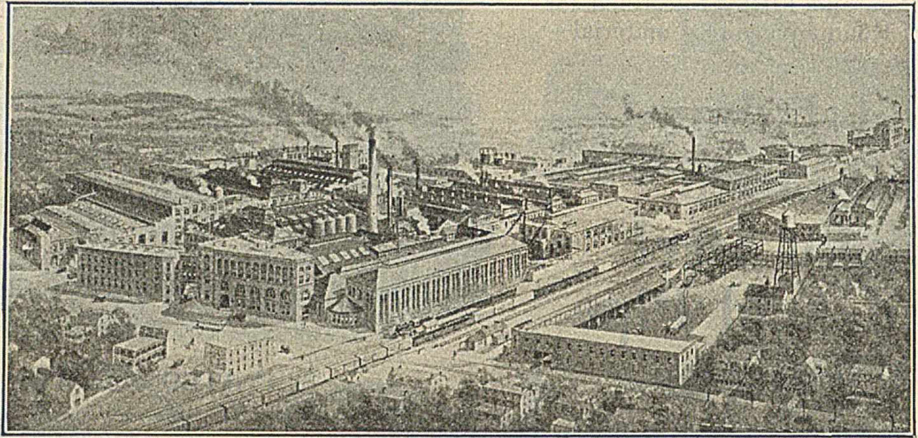

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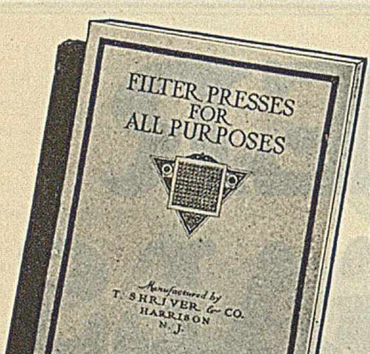

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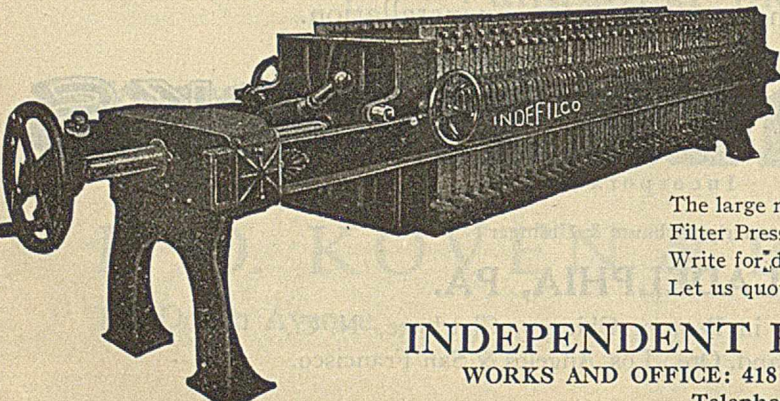

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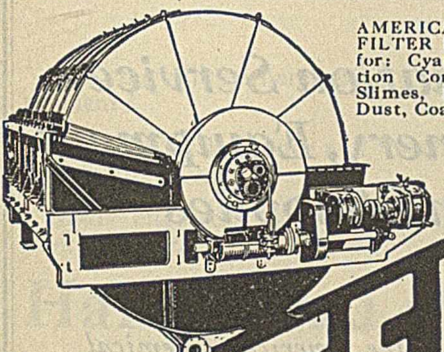

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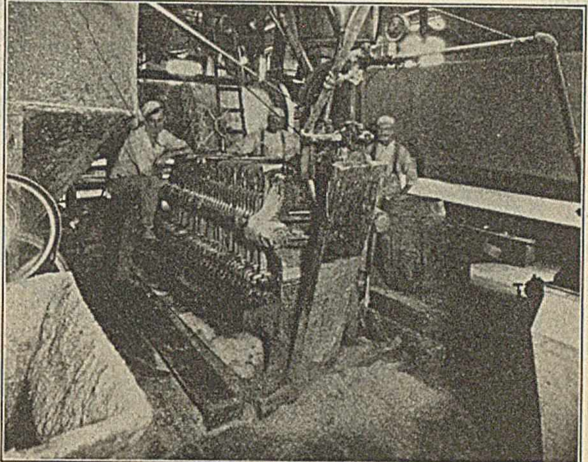

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It gave such complete satisfaction that they bought three others, making four in operation at their plant—filtering crude corn oil, refining corn oil and maltose syrup.

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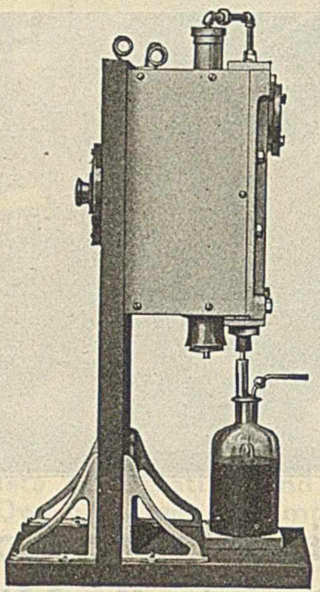

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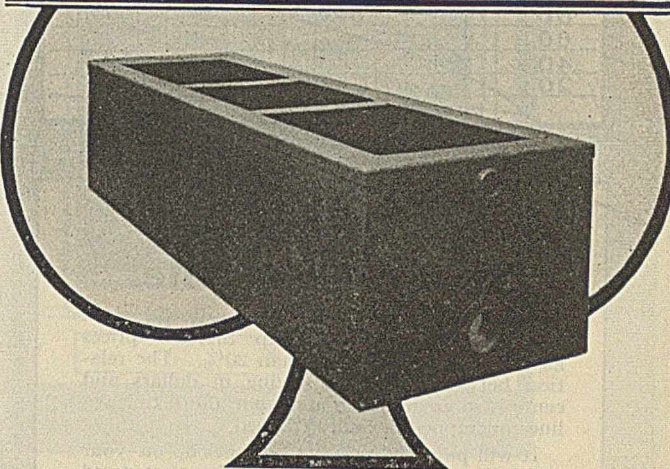

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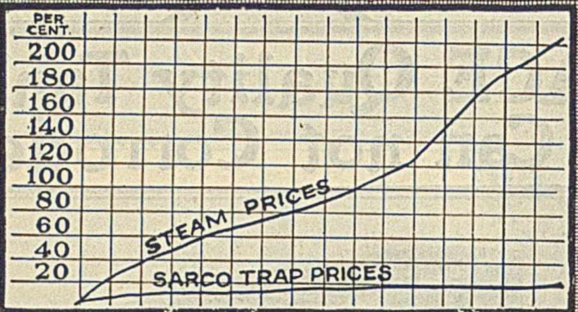

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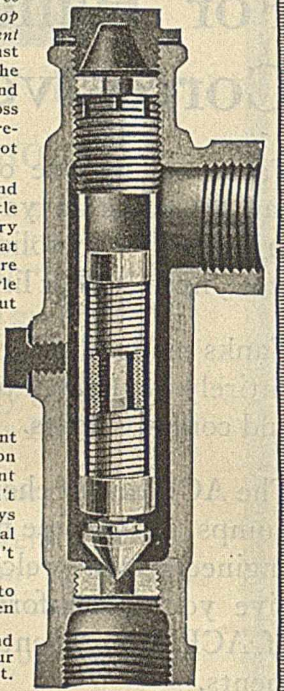

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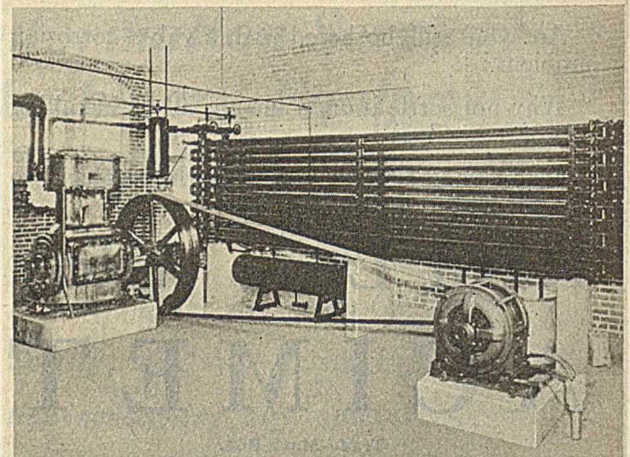

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