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EDITORIALS

Something for Nothing

IT REMAINED for our good friend, Arthur D. Little, to prove the incorrectness of the old adage that "you cannot make a silk purse from a sow's ear." It required a deal of patient research and persistent effort to accomplish the result. Our Government through the Civil Service Commission is now endeavoring to prove the incorrectness of another adage—namely, that "you cannot get something for nothing." But they propose to accomplish their result by the much simpler means of advertising and circularization by mail.

We refer to recent circulars announcing opportunities in government service involving some scientific training at salaries much lower than untrained men can command, and even less than unskilled labor is being paid in many parts of the country. It is proposed to offer \$540 per year for a junior aid in one of the government bureaus. To qualify for this desirable place the applicant must stand a satisfactory examination in physics and chemistry, mechanical drawing, algebra, and geometry. He must also be able to say that he has fourteen units of high school training toward entrance requirements to a university, or that he has completed a high school course.

Another position pays \$1000 per year. It is dignified by the title of Laboratory Assistant, and the applicant must stand examination in physics and chemistry, mathematics through trigonometry, and mechanical drawing, drawing to be made on the day of examination. Further, the applicant must show completion of sixty hours of college work with the grade obtained in each study pursued while in college.

These are typical requirements and salaries for a number of places for which applicants are desired. As the Commission points out, these are basic salaries, and if services prove satisfactory, a bonus of \$20 per month is granted in addition.

By inquiring in your own locality you will have no difficulty in finding many untrained people with very much less investment of time and money in preparation, earning far better wages than the Government is offering not only the grades given as examples above, but men in very much more responsible positions. In announcing the resignation of the Director of the Bureau of Standards, a man under whose administration the Bureau of Standards has been developed from a very modest beginning to the most important bureau of its kind in the world to-day, the Secretary of Commerce again called attention to the extreme difficulty of satisfactorily carrying on the nonpolitical work of the Government on the scales of salary now set by law.

It seems to us that if government bureaus are to render the greatest service, they should, in general, undertake fundamental research upon problems so broad that the greatest number of people are benefited. Organizations capable of doing this work must include many of our best trained and experienced investigators. There are many such men now in government service, who, day by day, make a real sacrifice in order to discharge their duties. The Government must provide adequate salaries for scientific men. This whole matter is involved in the reclassification program that has long been discussed, and it is a matter of importance which must be kept before us.

The Committee on Public Representation of the Chicago Section has taken up the present situation with the Civil Service Commission. Its example might profitably be followed by similar committees in other Sections.

Adaptability

STATISTICS indicate a slow but consistent improvement in business affecting the chemical industry, by the number of people employed in the industry month by month, and the volume of export trade. The very welcome information comes to us that the outlook for chemists, both young and old, is much improved. Men have been taken on at some of the plant laboratories, and the consulting chemists are finding an increased demand for their services. With this return of better times and increased demand for chemists, let us do whatever we can to prevent a repetition of the sad experiences of many chemists in the past. We refer to the great turnover in the men employed in chemical laboratories.

We have frequently discussed the question of maintaining research organizations in times of business depression, and we still believe that research on a sufficient number of well-chosen problems should be consistently and continually carried on under proper direction as the best insurance for the future of any manufacturing organization. There are, however, many variables which may not be considered by those who unfortunately find themselves required to seek employment in new fields.

In many research organizations which have been more or less disrupted lately, the men constituting them were secured in a somewhat hurried manner during the period of war-time stress. There was an urgent demand for every man, and applicants who could show a college diploma and a little laboratory experience were accepted pretty much at their own valuation. They were available; they said they were qualified; and they were put to work. Most of these men did the best that could be done under the circumstances, but when the rush was over and business took a somewhat different turn, employers began to evaluate their men and naturally found there were some square pegs in round holes. There are too few real research men. Some men, try as they may, never become fitted for research although they may be very useful in other lines of scientific endeavor. We believe that a careful investigation would show the large majority of men who have proved themselves to be qualified for research still busily engaged. Nevertheless, employers who deliberately curtail research solely in order to show quick profits or to temporarily curtail expenditures are not to be excused.

We have been much interested in such work as Prof. C. E. Seashore, of the University of Iowa, is conducting to develop ways for discovering and encouraging students with exceptional ability. Perhaps our teachers can emphasize more strongly in the future than in the past the fact that the single word "chemist" is a definition altogether too broad to be applied to all those who work in that field. There is a modifying adjective that will make it apply far better in each individual case. Any help that can be given a chemist in selecting that adjective which really describes his qualifications will save a great deal of unpleasantness and in the end benefit the whole profession.

Standardization

THIS is not a new word. There are some folks who fear standardization in the belief that it means the loss of cherished individuality. The majority know that through standardization wonders can be accomplished in convenience, economy, and real service. Germany looks upon standardization as a means by which a firm hold can be gained in the great importing countries and possibly the whole world, if she can only impress her industrial standards upon world trade. On one order placed in Germany for Russian locomotives, twenty firms coöperated to such an extent that every part in every one of the seven hundred locomotives was exchangeable with a corresponding part in all the others. Obviously, the next order for locomotives will specify that all parts must be readily interchangeable with those on hand.

From its inception in 1917, the American Engineering Standards Committee has made satisfactory headway. More than one hundred sixty bodies of national importance coöperate in its work, and over five hundred individuals serve on its several sectional committees. Its objects are:

1—To unify methods of arriving at engineering standards, and to secure coöperation between various interested organizations, in order to prevent duplication of work and promulgation of conflicting standards.

2—To receive or pass upon recommendations for standards but not to initiate or develop the details of any particular standard.

3—To act as an authoritative channel of coöperation in international engineering standardization.

4—To promote in foreign countries the knowledge of recognized American standards.

5—To collect and classify data on standards and standardization bodies in the United States and foreign countries, and to act as a bureau of information regarding standardization.

Of the one hundred six projects before the Committee, eleven are concerned directly with chemistry and principally with standard methods of analysis and specifications. The American Society for Testing Materials has been the principal sponsor.

What can be done through standardization in an industry closely related to chemistry is illustrated by the experience of the Glass Containers' Association. Two hundred ten styles and sizes of prescription bottles have been reduced to twenty, and similar simplification seems possible in the list of bottles and jars now comprising four thousand separate items, exclusive of special names and trade marks.

The Standards Committee maintains a regular interchange of information in the form of quarterly reports as to the status of work under way with the national standardizing bodies of Austria, Belgium, Canada, Czechoslovakia, France, Germany, Great Britain, Holland, Italy, Japan, Norway, Sweden, and Switzerland.

Industries are coöperating with the American Engineering Standards Committee, and the Government, through the Division of Simplified Practice of the Department of Commerce, is actively assisting in the work of eliminating excessive variety and achieving other simplifications which decrease cost of production and distribution. Chemists and chemical manufacturers have a direct interest in this work. Costs must be reduced wherever possible. Standardization will be an important step in this direction.

The Chemist and His Work

THE University of Pittsburgh has selected fifteen contemporary chemists of the United States as seminar topics during the first semester. The graduate student to whom the assignment is made is expected to present a biographical sketch of the chemist assigned to him and to discuss the work of that chemist as represented by his three most important published papers. At the conclusion of the semester an examination will be held and credit given for satisfactory standing.

We believe seminars of this character are well worth while and that such a course of study will do much to give the chemist pride in his profession as well as worthy traditions to uphold. Our science is a living human thing in which interest can no doubt be increased by better acquaintance with the men and women identified with its development. The facts and theories associated with people are those best remembered. Mention of any of our greatest dis-

coveries or inventions in any other field of endeavor immediately brings to the mind of the intelligent laity the name of the person credited with the work, and in nearly every other field manufacturers have not hesitated to advertise individuals until they are as well known as their creations. It should be so in chemistry, but chemists have not been so well advertised.

“Disarm or Perish”

LORD ROBERT CECIL sounded this warning in presenting the report of the Disarmament Committee to the Assembly of the League of Nations. In laying before the nations a choice between destruction and salvation, he stated that whatever agreements may be made—as at Washington—to limit the weapons of war, in a life and death struggle all weapons will be used.

In his discussion he mentioned the developments that have been continued as to size and effectiveness of aerial bombs, now said to be ten times as destructive as in the Great War, and laid stress upon the importance of poison gas and germs. It seems to be generally recognized, even by the League of Nations, that until the world really disarms those who would not be defenseless must give serious consideration to the purely scientific studies of poison gases and the methods of defense against them. In our country alone is the subject failing to receive that measure of support which means safety without aggression and without treaty violations. In the budget provided for another year, the item for our Chemical Warfare Service has been cut to the point where research is seriously threatened, if indeed is not made impossible. This is serious, not only from the standpoint of national defense, but because of the expert information which the Chemical Warfare Service is in position to supply on many questions of public welfare. We believe that the pendulum will eventually swing the other way, but it is very discouraging for those in that Service to endeavor to continue their work and maintain their trained organization under the present starvation policy.

November 9, 1922

DEAR MR. EDITOR:

In a few days my official connection with the Society will come to an end, and as I have been so happy in my relations with the entire membership, and so much genuine good and kindness have been showered upon me, I can't resist the impulse to send these lines of deep appreciation and gratitude with my

Goodbye!

EDGAR F. SMITH

Library Support

IT HAS been our experience that those in position to give financial support to scientific work are more easily interested in some investigation or research than in the publication of the results of such research. In many university departments one of the greatest difficulties is the maintenance of adequate library facilities, and doubtless much work is needlessly duplicated because records of the past are not accessible. Read again the letter on "Bibliography and Research," page 1085 of the November issue of THIS JOURNAL.

It is very encouraging to find that the Department of Chemistry of Ohio State University has just received a gift of \$17,000, the income of which is to be used in developing the library of the department. In addition, the department will continue to receive its share of the university library funds. This is a type of endowment which should be sought, and we hope that the example that has been set by Mr. C. C. Sharp, the donor, may be speedily followed in many other universities and colleges. The Ohio State University is to be congratulated upon its good fortune.

Technical Exhibits

NO EFFORT to acquaint the scientist and industrialist with comparative progress in a given field of applied science quite takes the place of a national or international exhibition. To realize the most from the opportunities presented by such an exhibition, manufacturers will always display their best wares, models, or animated illustrations of them, and put their exhibits under the auspices of their leading specialists. Under such circumstances the ultimate consumer may gain valuable information from the men he meets, receive answers to his verbal questions, and make comparisons on the ground. Chemists realize what an impetus has been given to their industry by the National Exposition of Chemical Industries.

Now comes the initial effort in the closely related specialty—power. Under the guidance of an advisory committee whose personnel guarantees success, the First National Exposition of Power and Mechanical Engineering opens at the Grand Central Palace on December 7, and will continue through the 13th. The moving machinery which will be exhibited is sure to attract the crowd, but the important thing is to give the public a better understanding of what power means and the need for the conservation of the resources upon which power development depends.

This is of direct interest to every chemist, and particularly the industrial chemist, for he plays a vital part in power production, transmission, and utilization. The chemist is the one who has contributed most on the evaluation of fuels and the development of methods to control their utilization and insure efficient use. He has coöperated in devising materials for constructing power plants and transmission lines. The insulating problem has been a field for his knowledge and research. Bearing metals are not successfully produced without the chemist. Lubrication, so vital in all machine operations, is peculiarly the chemist's field, and offers him one of the most important groups of research problems, especially in view of our diminishing petroleum resources. In many other ways he has been directly concerned with that control over the forces of nature which we call power.

The power show will bring together the latest devices, the foremost experts, and a mass of instructive data, all of which offer a splendid opportunity which the chemist should not overlook.

Science in Trade

OF THE several movements under way for spreading a better knowledge of the application of chemical science to everyday affairs, none is more important than that recently initiated to teach chemical salesmen the rudiments of the science underlying their work. Chemists and educators are often inclined to slight the profession of the salesman and to consider him as one who has no particular interest in the science. Frequently an intelligent salesman is embarrassed to find that his customer knows more about his product than he does, especially where ordinary articles are being offered under fanciful names. No doubt the salesman has looked upon the chemist as an unnecessary evil, since frequently it has been the chemist who has been able to tell the salesman just what it is he has to offer. There has been a lack of understanding, neither chemist nor salesman realizing how intimately the work of one is related to that of the other.

In this new course being offered by F. E. Breithut at the College of the City of New York under the auspices of the New York Chapter of the Salesmen's Association of the American Chemical Industry, we have an interesting experiment. The salesman as the representative of the manufacturer carries a responsibility which he cannot hope to discharge fully without familiarity with the scientific viewpoint. It is true he cannot be given a chemical education through the medium of ten lectures, but from the enthusiastic reception of the plan by the salesmen, there is reason to hope that their interest may carry them beyond the initial course. But if not, the discourses upon the various phases of chemistry included in the course will be certain to stimulate interest and to create a better sympathy for the science and to make the salesman a much better representative of the chemical industry.

Why not go a step further and plan a course in chemistry for purchasing agents? This should not be confined to the purchasing agents of chemical plants, for to-day if any purchasing agent or buyer is really to know materials, he must have something of a scientific background. New products constantly coming on the market are mostly created with the aid of science and present a new problem to the totally unscientific man. To be sure, the day has gone when a certain purchasing agent refused to buy B. t. u.'s because he wanted heat, but there are many new specifications and novel materials and in order to pass upon them intelligently at least a speaking acquaintance with chemistry is essential.

When all the salesmen and purchasing agents become appreciative of chemistry, we shall have gone a long way toward gaining that intelligent sympathy of the public which is essential to our profession.

Section Programs

IN OUR November issue we offered to assist Local Sections in the interchange of information relative to their scientific programs. The first program which reaches us is in the form of a pocket card issued by the Rochester Section. On one side it gives a list of the officials of the AMERICAN CHEMICAL SOCIETY and of the Section, a blank in which the name of the member may be written, and a second line for the signature of the Secretary-Treasurer to denote good standing and dues paid. The other side of the card gives details of the meetings from the 30th of September to the 21st of May, with the names of speakers and their connection. In addition, special announcement cards are sent out before each meeting. Interest and good attendance are the rewards of such enterprise. Who has a better plan?

Heat Transfer by Conduction and Convection^{1,2}

II—Liquids Flowing through Pipes

By W. H. McAdams³ and T. H. Frost⁴

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

In this article a review of the literature has been made, including Reynolds' analogy between heat transfer and friction.

A simplified form of the theoretical Boussinesq equation is proposed for the film coefficient of heat transfer, h , for liquid flowing inside pipes in turbulent motion. This equation is based on dimensional considerations, and shows the relation between the coefficient, h , and thermal conductivity, diameter, linear velocity, viscosity, and density. According to this equation, the coefficient varies directly as approximately the 0.8 power of the product of linear velocity and density divided by the viscosity of the film, directly as the first power of the thermal conductivity, and inversely as approximately the 0.2 power of the inside diameter of the pipe.

This equation has been tested, with experimental data for water from four sources, and with data for light oils from two sources by

plotting hD/k versus Du/ν . As shown by Fig. 3, a straight line may be drawn through the experimental points on logarithmic paper. The coefficient may be predicted by use of Fig. 3, or from the equation of the curve:

$$h = \frac{22.6k}{D} \left(\frac{Du\rho}{\nu} \right)^{0.796} = \frac{22.6k}{D^{0.204}} \left(\frac{u}{z} \right)^{0.796}$$

(For meaning of symbols, see Nomenclature Table.)

For water, since $k = 0.329$ and ρ is about 62, this equation becomes

$$h = \frac{199}{D^{0.204}} \left(\frac{u}{z} \right)^{0.796}$$

The fouling of pipes is discussed, and a factor of safety is suggested.

IN A PREVIOUS article^{1,*} on this subject the authors pointed out the advantages of studying heat transfer from the point of view of film coefficients rather than over-all coefficients; this discussion is on the same basis.

POSSIBILITY OF TWO TYPES OF FLUID MOTION

It is well established that a fluid flowing through a pipe may assume either of two types of motion—namely, straight line (viscous) motion or turbulent (eddy) motion. A full discussion of this matter is given in a recent paper,² and it is there shown that the "critical" velocity—i. e., the average velocity of flow at which straight line motion tends to break over into the more common turbulent motion—is figured by the following equation:

$$u_c = \frac{16\mu}{\rho d f_c} = \frac{942\mu}{\rho} \quad (1)$$

In this equation u_c is the critical velocity in ft. per sec.—namely, the cu. ft. per sec. flowing through the pipe divided by its cross sectional area in sq. ft.; μ represents the absolute viscosity of the fluid in lbs. per sec. per ft.; d represents the inside diameter of the pipe in feet, and ρ is the density of the liquid at its average temperature in lbs. per cu. ft. However, it was there shown that in some cases unstable viscous motion may develop, with the result that the break does not occur until the velocity becomes three times that calculated from the foregoing formula. In other words, the velocity at which one type of motion ceases and the other begins is rather uncertain. Nevertheless, calculations of critical velocity should be made in all cases, inasmuch as equations for the heat-transfer film coefficient for the common type of flow (turbulent motion) may not hold for viscous motion. This is because in turbulent motion the liquid at any cross section is continually being mixed by eddy currents, the main resistance being found in the relatively stationary film of liquid at the wall, whereas in viscous motion eddy currents are absent and the heat must flow between the pipe and the

main body of liquid solely by the process of conduction through a layer which is thicker than in the case of turbulent motion. Fig. 1 shows how the critical velocity varies with the "kinematic" viscosity (μ/ρ) for a pipe 0.625 in. in diameter.

(For other sizes multiply ordinates by $\frac{0.625}{\text{Act. D}}$)

SCOPE—The greater part of experimental data for the flow of liquids has been confined to the flow of water through pipes of various diameters. Fortunately, the velocities used in commercial practice are nearly always far above the critical velocity, and this paper will deal primarily with the flow of water under these conditions through tubes or pipes. The possibility of the two types of motion has been mentioned

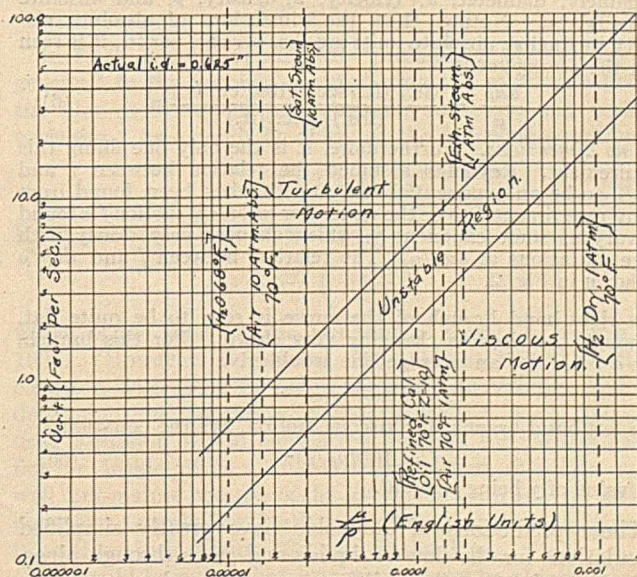


FIG. 1—CRITICAL VELOCITIES IN PIPES

at this point for two reasons: first, because occasionally the cooling pipes through which the water flows may be so small and the velocity so low that turbulent flow will not be found; and second, because the flow of liquids more viscous than water will be touched upon in this article.

¹ Received August 21, 1922.

² Published as Contribution No. 77 from the Department of Chemical Engineering, Massachusetts Institute of Technology.

³ Associate Professor of Chemical Engineering, Massachusetts Institute of Technology.

⁴ Instructor of Chemical Engineering, Massachusetts Institute of Technology.

* Numbers in the text refer to the Bibliography, p. 1104.

THEORETICAL DISCUSSION

REYNOLDS' DERIVATION: ANALOGY BETWEEN HEAT TRANSFER AND FRICTION—In 1874 Reynolds³ derived a *theoretical* equation for the coefficient of heat transfer for the case under discussion. This was based on the assumption of a certain relation between heat transfer and his law for the relation between the friction factor and a certain group of variables. The latter has been given a thorough test and found to be valid. His derivation is essentially as follows:

Consider a differential length, dx ft., of a pipe of inside radius r ft. through which water at the temperature t° F. is flowing at a rate of w lbs. per sec. and at an average velocity of u ft. per sec. The temperature of the inner wall of the pipe at this section is T° F., the specific heat of the water is C B. t. u. per lb. per $^\circ$ F., and the density is ρ lbs. per cu. ft.

1—By means of a heat balance, the rate of heat transfer per unit area of inner pipe wall ($Q/A\theta$), expressed as B. t. u. per hr. per sq. ft., may be equated to the heat picked up by the water.

$$\frac{Q}{A\theta} = \frac{3600 w C dt}{2 \pi r dx} \quad (2)$$

2—According to the familiar Fanning equation for friction, the loss of intensity of pressure is

$$dp = \frac{f dx \rho u^2}{gr} \quad (3)$$

where f is the experimentally determined friction factor and g equals the acceleration due to gravity, 32.2 ft. per sec. per sec.

3—Assume that the pressure lost due to friction ($\pi r^2 dp$) divided by the momentum of the water (wu/g) equals the heat transferred to the water divided by the heat which would have been transferred if the water had been warmed to the temperature of the wall.

$$\frac{\pi r^2 dp}{wu/g} = \frac{w C dt}{w C (T - t)} \quad (4)$$

By combining these equations one obtains

$$\frac{Q}{A\theta(T-t)} = h = 1800 C f \rho u \quad (5)$$

It should be noted that the last equation is Newton's law solved for the film coefficient of heat transfer, h , between the pipe wall and the water.

A careful inspection of Equation 3 shows that the friction factor has no dimensions. In 1883 Reynolds⁴ predicted that f should be some function of certain variables grouped so as to have no dimensions. It was known that four variables affected f —namely, diameter, d , velocity, u , density, ρ , and absolute viscosity, μ . Noting that the dimensions of absolute viscosity in English absolute units are lbs. per sec. per ft., it is seen that the arrangement

$$\frac{dup}{\mu} = \frac{(\text{ft.})(\text{ft./sec.})(\text{lbs./cu. ft.})}{(\text{lbs.})(\text{sec.})(\text{ft.})} \quad (6)$$

has no dimensions. Furthermore, it is the only one filling this requirement. Reynolds assumed the relation between f and dup/μ to be an exponential one, and this has been found from many experiments⁴ to be the case. For *turbulent* motion f is found to vary as some exponent y , which changes very slowly with large variations in dup/μ . The relation between f and dup/μ is shown in Fig. 2.

The right-hand branch of the curve is seen to be quite flat, although the slope is changing very slowly. For this branch, $f = a (dup/\mu)^y$, an average line would give

$$f = a (dup/\mu)^{-0.2} \quad (6a)$$

The left-hand branch, for viscous motion, has the equation

$$f = 16 (dup/\mu)^{-1} \quad (6b)$$

the value of y being constant.

These predictions of Reynolds have greatly simplified calculations for the flow of liquids and gases through pipes, as values of f for all conditions may be read as ordinates from a single plot (such as Fig. 2) with dup/μ as abscissae. Practical application of this relation has been made elsewhere, but it was introduced here for reasons which appear below.

Instead of using f in Equation 5 as a variable, Reynolds substituted its equivalent from Equation 6a, obtaining for *turbulent motion*:

$$h = \frac{1800 a C (\rho u)^{\mu^{1-n}}}{d^{1-n}} \quad (7)$$

where, for convenience, $1 + y$ has been replaced by n .

This equation states that the film coefficient of heat transfer should be a direct function of the linear velocity, density and viscosity, and an inverse function of diameter. For example, for turbulent motion where $n = 0.8$ (and $y = -0.2$), this becomes

$$h = \frac{1800 a C (\rho u)^{0.8} \mu^{0.2}}{d^{0.2}} \quad (7a)$$

In 1897 Stanton⁵ tested this relation with his data for water flowing through 18-in. lengths of several small sizes (0.29, 0.42, and 0.55 in.) of copper tubes. The value of n for Equation 7 was found to be about 0.83, and Reynolds' equation allowed satisfactorily for variations in h due to velocity and diameter, but did not allow for the actual effect of viscosity. Stanton found empirically that Equation 7a divided by the first power of the viscosity would fit his data—namely,

$$h = \frac{a_1 C (\rho u)^{0.83}}{d^{0.17} \mu^{0.83}} \quad (7b)$$

where a_1 is a new constant. However, Stanton abandoned Equation 7b, apparently because it was different from Reynolds' equation, and adopted the following *empirical* equation:

$$h = \frac{a_2 (C) (\rho u)^{0.83} \mu^{0.17} (1 + \alpha T)(1 + \beta t)}{d^{0.17}} \quad (8)$$

where a_2 , α , and β are new constants.

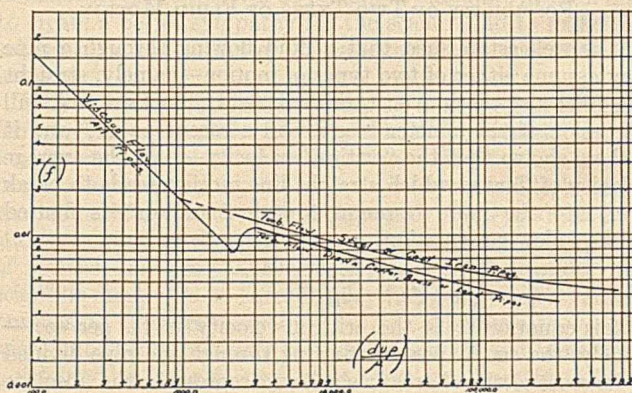


FIG. 2—VARIATION OF FRICTION FACTOR (f) IN EQUATION 3 WITH $\frac{dup}{\mu}$

DERIVATION OF RATIONAL FORMULAS—It seems strange that Reynolds did not apply the same process of "dimensional reasoning" to the heat transfer problem, which proved so valuable for the pressure drop relations. By definition, the film coefficient h equals the thermal conductivity k divided by the effective film thickness L —i. e., $h = K/L$. Values of k may be easily obtained from tables of physical constants,[†] so the only problem is the prediction of what variables determine L . L has linear dimensions. While both length and inside diameter fill this requirement, it does not seem reasonable that the length of the pipe has any effect on the coefficient. Since there are indications⁶ that the zone of *relatively* low velocity in a pipe—referred to as the film of effective thickness, L —is directly proportional to the diameter of the pipe, other things being equal, it will be assumed that L varies as d . The effective thickness of film is known to be a function of several variables, such as velocity and viscosity. Since the friction factor and the

[†] See also Reference 1 for means of predicting k by H. F. Weber's equation.

FILM COEFFICIENT FOR LIQUIDS (h_L) FLOWING THROUGH
PIPES IN TURBULENT MOTION

$$h_L = \frac{22.6 K}{D} \left(\frac{Du\rho}{z} \right)^{0.798}, \text{ where}$$

h_L = B. t. u. per hr. per sq. ft. of film area per ° F. drop,
pipe to liquid.

K = Thermal conductivity of stationary liquid, B. t. u.
per hr. per sq. ft. per ° F. per ft.

D = Actual i. d. of pipe in inches.

u = Av. velocity of liquid in ft. per sec.

ρ = Av. density of the liquid in lbs. per cu. ft.

z = Av. viscosity of liquid film relative to water at 68° F.

EXPLANATION OF POINTS

- Water
- O Clement and Garland (Univ. of Ill.) cold drawn 1 in. steel tubing. (Ref. 13)
 - X Wishnew (M. I. T.), std. 3/8-in. brass pipe. (Ref. 11)
 - ⊙ Trowbridge (M. I. T.), std. 3/8-in. copper pipe. (Ref. 12)
 - ⊖ Webster (Scotland), 1/2-in. copper pipe. (Ref. 13)
- Oil
- ⊙ Barton and Safford (M. I. T.), 1/2-in. std. steel pipe. (Ref. 14)
 - △ Voss (M. I. T.), 1 1/4-in. std. steel pipe. (Ref. 14)

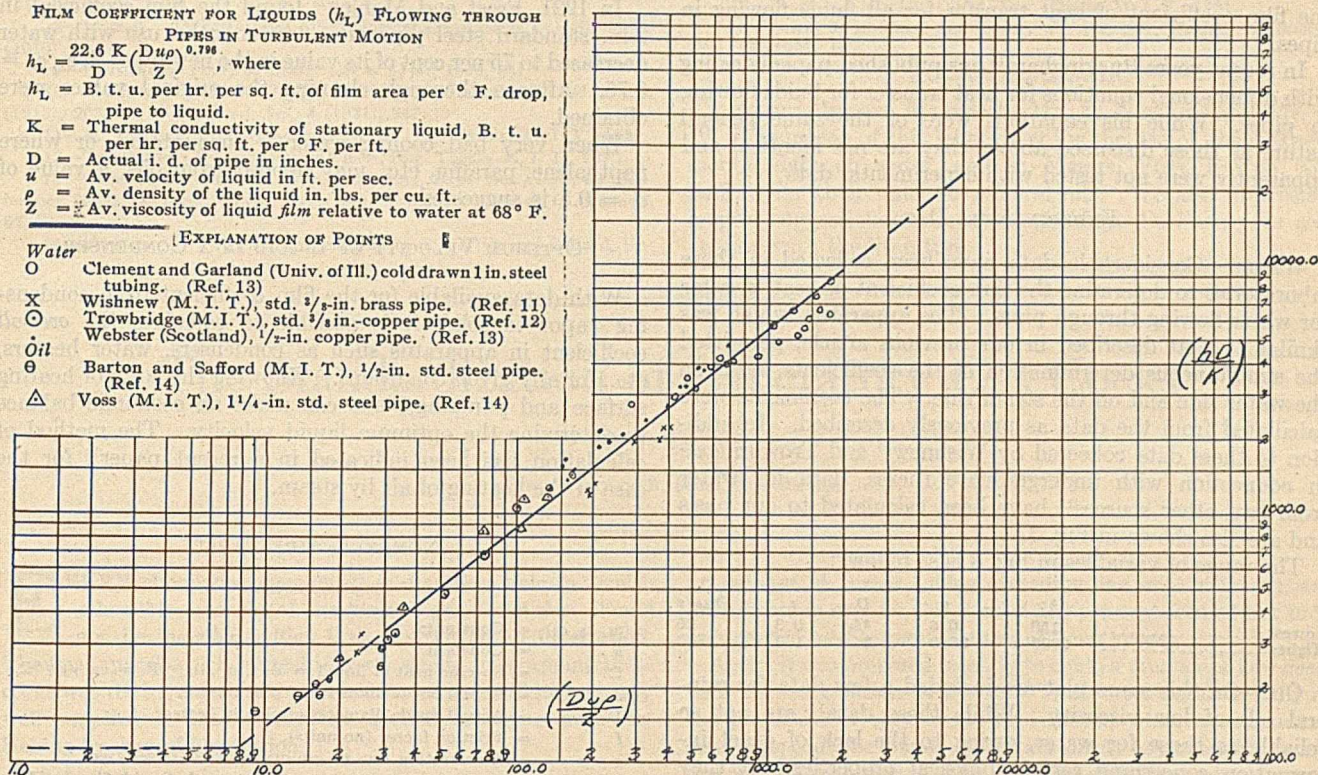


FIG. 3

film thickness are determined by the degree of turbulence (dup/μ), it seems reasonable to suppose that this same "dimensionless" ratio would determine the effective film thickness for heat transfer.

Hence, we assume

$$h = \frac{k}{L} = \frac{bk}{d} \left(\frac{dup}{\mu} \right)^n \quad (9)$$

where b and n are to be experimentally determined. It should be noted that this equation is a logical one, in that all dimensions cancel.

Rearranging,

$$h = \frac{bk (u\rho)^n}{d^{1-n} \mu^n} \quad (9a)$$

This checks with Stanton's experiments on viscosity. However, he apparently abandoned it and adopted Equation 8, which contains the two empirical correction factors for temperature. (In 1912, Stanton⁷ derived Equation 9a for gases from Equation 7a by assuming that $C = a_3 \gamma k / \mu$, neglecting variations in γ , the ratio of specific heat at constant pressure to that at constant volume, and assuming a_3 to be substantially constant.)

Equation 9a indicates that the film coefficient h for a given sized pipe and fluid varies directly as the product of the linear velocity and the density to the power n , and inversely as the viscosity to the same power. Furthermore, the slope of the curve or value of the exponent n theoretically may be predicted from the friction factor plot, since $1 + y = n$. Equation 9 indicates the general relation between the film coefficient h and linear velocity, density, viscosity, diameter, and thermal conductivity. It is obvious that the logical method of testing this theoretical relation is to plot hd/k versus dup/μ on logarithmic paper. If the theory is correct, the slope will be practically constant over a considerable range of dup/μ , and b may be determined from the ordinate where dup/μ equals unity.

As a matter of convenience, diameter in feet, d , has been replaced by diameter in inches, D , and absolute viscosity

in lbs./sec./ft., μ , has been replaced by relative viscosity in centipoises, z . Since water at 68° F. (20° C.) has a viscosity of 1.00 centipoise, the viscosity in centipoises is numerically the same as viscosity relative to water at 68° F., a concept which may be readily visualized. (It should be noted that z is the reciprocal of the relative fluidity f used in our preceding article.) Hence, we shall plot hD/k versus $Du\rho/z$ to determine the value of b and n in the expression

$$h = \frac{bk}{D} \left(\frac{Du\rho}{z} \right)^n \quad (9b)$$

In 1909, Nusselt⁸ applied the "principle of physical homogeneity" to the problem of predicting the relation between the film coefficient of heat transfer for gases and certain variables. As a result he obtained the following equation:

$$h = \frac{a_4 k}{d} \left(\frac{dup}{\mu} \right)^n \left(\frac{C\mu}{k} \right)^m \quad (10)$$

He then assumed $n = m$, giving

$$h = \frac{a_4 k}{d} \left(\frac{dupC}{k} \right)^n \quad (10a)$$

which is the same as the Boussinesq⁹ equation derived in 1905. (However, Boussinesq did not test this theoretical equation with data in order to prove its validity and to determine the constants necessary for its use.) Nusselt used Equation 10a in correlating his data for various gases flowing inside pipes. This equation fitted the data very well, but mainly because of the use of the term $(u\rho)^n$. Other equations, employing $(u\rho)^n$, but containing terms different from those in Equation 10a, also fit the data.

It should be noted that Equation 9 may be obtained from the Boussinesq equation by placing $m = 0$. Instead of m being equal to n , or m being equal to zero, it may be that both m and n are finite, which would require a three-coordinate or "space" diagram instead of the one employed in Fig. 3. If this is true, the coordinates would be (hd/k) , (dup/μ) , and $(C\mu/k)$. It is possible that the Boussinesq equation may prove to be the ultimate general equation for

the film coefficient of heat transfer for all fluids flowing in pipes.

In recent years Buckingham¹⁰ has published papers dealing with dimensional equations for heat transfer for fluids flowing in pipes. While his equations were of the same general nature as those discussed above, they are not identical and apparently were not tested with experimental data.

EXPERIMENTAL DATA

WATER—Considerable data have been collected in these laboratories to determine the film coefficient of heat transfer for water flowing through pipes. The apparatus, which was similar to that described in our previous article, permitted the simultaneous determination of the coefficients, both on the water side and on the steam side. The coefficients were calculated from the data as previously described. In addition to these data collected by Wishnew¹¹ and Trowbridge¹² in connection with undergraduate theses, data for water from two other sources¹³ have been calculated to our basis and are also shown in Fig. 3.

The range of variables in Fig. 3 is as follows:

	h	u	D	z	Dup/z
Lowest.....	150	0.6	$\frac{3}{8}$	0.3	25
Highest.....	2700	20.0	2	1.0	1800

OIL—On this same plot are included a few data for mineral oils of low viscosity. While these data¹⁴ are not so reliable as those for water, owing to the lack of exact information concerning certain physical properties, yet they are compatible with them. Hence, in the lack of additional data for oil, the use of Fig. 3 is recommended for purposes of estimation.

Below the critical velocity $y = -1$, and since $y + 1 = n$, n should be equal to zero for viscous motion. Under these conditions Equation 9b reduces to

$$h = \frac{bk}{D} \quad (9c)$$

No data are at present available to determine whether Equation 9c will hold under these conditions. Hence, the use of the plot below the critical velocity is not recommended. As shown by Equation 1, $dup/\mu = 16/f_c = 942$, at the theoretical critical velocity, which is equivalent to an abscissa in Fig. 3 of Dup/z of about 7.6.† If unstable viscous motion develops, Dup/z might be as high as 23. However, the probability of unstable viscous motion where heat is being transferred is remote. Hence, the curve in Fig. 3 should not be used below an abscissa of 8.

FOULING OF PIPES—It has long been known that in heat-transfer apparatus the inner surfaces of the pipes carrying certain liquids become covered with a deposit of solid matter. For example, where the cooling water contains dissolved bicarbonates such as calcium, these decompose under the action of heat and a scale of carbonate is formed. Further, a slime is often deposited, due to dirt in the cooling water. In the case of oils, deposits containing naphthalene, paraffin, and other materials may form. The scale or deposit in any case adds another resistance to heat transfer, which varies directly with the thickness and nature of the deposit. Allowance made for this should be by adding another resistance term to the denominator of Equation 1 of our previous article. Instead, it is customary to multiply the liquid film coefficient by a cleanliness factor, c_1 , which never exceeds unity. The use of such a cleanliness factor is not theoretically sound, as in a given pipe containing a definite scale, the value of c_1 might be 0.4 with a very high liquid film coefficient and 0.8 with a very low coefficient.

† For smooth pipes f_c is about 88.3 per cent that in rough pipes, hence these values would be increased about 13 per cent.

In 1921, Frost and Manley¹⁵ found the film coefficient in 2-in. standard steel pipe after two months' use with water decreased to 75 per cent of its value in the new pipe—i. e., $c_1 = 0.75$. After a thorough cleaning the original values were obtained.

When very bad cooling water is encountered, or where naphthalene, paraffin, etc., may deposit from oils, a value of $c_1 = 0.5$ is suggested.

OPTIMUM VELOCITY OF LIQUID IN A CONDENSER

With data available for the film coefficient from condensing vapor to solid, it is possible to calculate the *over-all* coefficient in apparatus such as condensers, water heaters, etc., for any given conditions. Knowing the costs of heating surface and pumping,§ one can make an economic balance to determine the optimum liquid velocity. The method of calculation has been indicated in a recent paper¹⁶ for the case of the heating of air by steam.

NOMENCLATURE TABLE

English Symbols

a (a_1, a_2, a_3)	= Constants.
b	= Constant.
C	= Specific heat of liquid = B. t. u. /lb. ° F. = cal./g. ° C.
d	= Actual inside diameter of pipe in feet.
D	= Actual inside diameter of pipe in inches.
f	= Friction factor (no units).
g	= Acceleration due to gravity = 32.2 ft./sec./sec.
q	= Coefficient of heat transfer through liquid film inside of pipe = B. t. u./hr./sq. ft. of inner wall of pipe per ° F. difference in temperature between inner wall of pipe and liquid at the center line of pipe.
$k(K)$	= Thermal conductivity of stationary liquid = B. t. u./hr./sq. ft./° F. per foot of thickness.
L	= Effective thickness of film, in feet.
m	= Exponent.
n	= Exponent = $1 + y$.
p	= Intensity of absolute pressure, lbs./sq. ft. of cross section.
Q	= Quantity of heat transferred at right angles to heat transfer surface, B. t. u.
r	= Inside radius of pipe in ft. = $d/2$.
T	= Temperature of inner wall of pipe, ° F.
t	= Temperature of water at center line of pipe, ° F.
u	= Average water velocity, ft./sec.
w	= Average rate of flow of water, lbs./sec.
x	= Length of pipe in ft.
y	= Exponent at average film temperature.
z	= Viscosity of liquid at average film temperature relative to water at 68° F. (20° C.) as unity = centipoises.

Greek Symbols

α	= Constant.
β	= Constant.
γ	= Ratio of specific heat of gas at constant pressure to that at constant volume.
π	= 3.14.
ρ	= Density of liquid at center line temperature, lbs./cu. ft.
μ	= Absolute viscosity of liquid. lbs./sec./ft., = 0.0672 poises = 0.000672 centipoises.

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ACKNOWLEDGMENTS

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The Standardization of Laboratory Gas Cocks¹

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EVERY chemistry department is doubtless able to furnish a horrible example of the kind of gas cocks that should not be installed. Fig. 1 may serve as an illustration. The final appeal which seemed to carry weight in scrapping these cocks was the argument of a serious fire risk in a building already well supplied in that particular. Actual examples were not lacking by way of illustration.

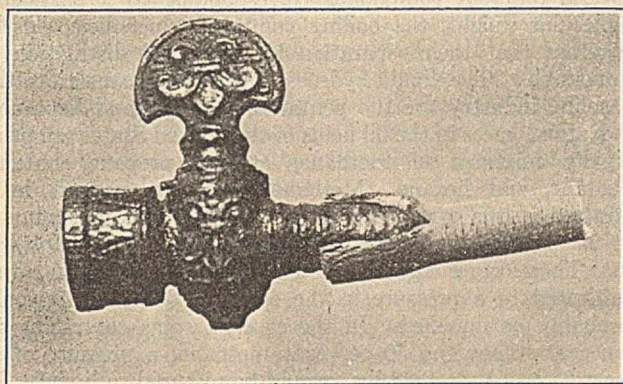


FIG. 1

The replacement of these old cocks by new ones of acceptable pattern, however, was found to be not a simple matter. One of the largest firms specializing in this sort of equipment recently filled an order in this laboratory for several hundred, of which Fig. 2 is an illustration. These were rejected as unsatisfactory, the reason being that rubber tubing, after serving for a time on cocks of the Fig. 1 pattern, or on burners of equally unfortunate dimensions as to hose connections, would form no attachment

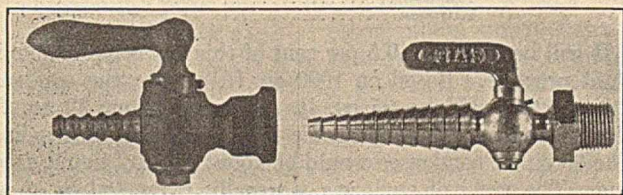


FIG. 2

FIG. 3

whatever for gas cocks like those of Fig. 2, and the fire risk would be again evident. The manufacturers argued that better tubing should be used; but the annual order in this laboratory is for

an amount of burner tubing exceeding one mile in length, and an increase in cost for this item of 200 per cent seemed not to be appreciated by the manufacturer of brass goods.

Again, it was proposed recently to equip a number of new desks with the cock shown in Fig. 3. These were admitted only on the promise that they would be removed when a satisfactory substitute could be found. They are chiefly objectionable for the reason that a laboratory fully equipped with these cocks, including gas, air, and vacuum, is suggestive of the fretful porcupine. If the extravagant and useless waste of metal in the hose extension were put into an enlargement of the key and barrel, it would be an improvement. Fig. 4 presents a working sketch of a cock which one of the large factories has agreed to adopt to meet our own needs at least. With an order for approximately 500 cocks, it should be possible to obtain the exact pattern desired. The sketch is self-explanatory. The diameter of the smallest and largest corrugation in an extension length of 1 1/4 in.

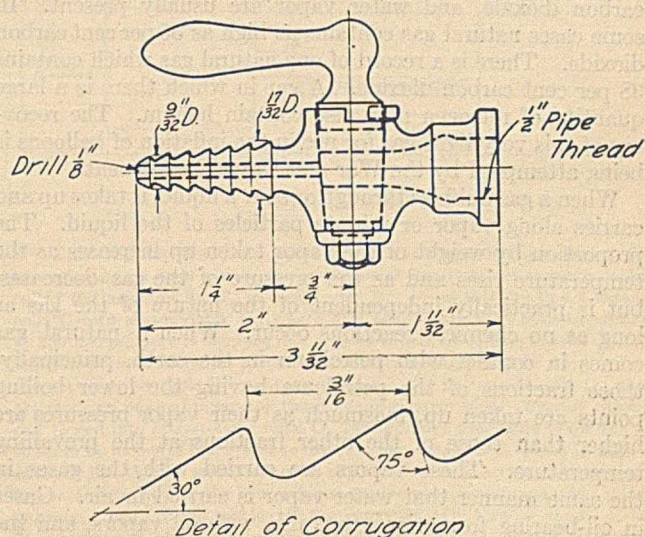


FIG. 4

affords ample range for all reasonable variations of condition and size of rubber tubing. Attention may also be called to the fact that the outer edge of each corrugation has a slight angle and not a rounded surface. This operates with a sort of barb-like effect which permits of easy slipping on of the tubing and positive resistance to its removal. At the same time these angles are not so sharp as to produce cutting of the tubing.

¹ Received September 20, 1922.

Some Recent Developments in the Manufacture of Natural Gas Gasoline¹

By F. E. Hosmer and F. M. Seibert

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THAT gasoline can be extracted from natural gas and casinghead gas has long been known, but its production has only within the past few years become of commercial importance, owing to the increase in the number of internal combustion engines.

In 1904 there were only two small plants producing casinghead gasoline. Both of these plants were somewhat crude, and their production for the year was only 400 barrels. At that time there was very little demand for gasoline, the products mostly desired being kerosene, lubricants, and fuel oil. In 1911 there were 176 plants in operation, and the production was 7,425,000 gal. In 1920 there were 650 plants, with a production of 483,000,000 gal. These figures portray the rapid growth of the industry.

CHEMISTRY OF NATURAL GAS

In the gasoline industry, natural gas is popularly classified in two great divisions—wet gas and dry gas. The gas coming from gas wells is generally classified as dry gas, and that coming from oil wells, if carrying any gasoline vapors, is considered as wet gas.

Natural gas is a mixture in which the hydrocarbons of the paraffin series predominate. Small proportions of nitrogen, carbon dioxide, and water vapor are usually present. In some cases natural gas contains as high as 35 per cent carbon dioxide. There is a record of one natural gas which contains 98 per cent carbon dioxide. A gas in which there is a large quantity of nitrogen may also contain helium. The recovery of this very light gas for use in the inflation of balloons is being attempted by the War and Navy Departments.

When a gas bubbles through or over a liquid, it takes up and carries along vapor or minute particles of the liquid. The proportion by weight of the vapor taken up increases as the temperature rises and as the pressure of the gas decreases, but is practically independent of the nature of the gas as long as no chemical reactions occur. When a natural gas comes in contact with petroleum in the earth, principally, those fractions of the petroleum having the lower boiling points are taken up, inasmuch as their vapor pressures are higher than those of the other fractions at the prevailing temperature. These vapors are carried with the gases in the same manner that water vapor is carried in air. Gases in oil-bearing formations thus mix with oil vapors, and the content of vapor in the gas in these formations is dependent upon the pressure and temperature, as well as upon the intimacy of contact between gas and oil. The effect of pressure is largely exerted through its influence upon the rate of diffusion of the vapor.

Obviously, gas from an oil well yielding a crude that

From the following discussion it is evident that wide choice of methods for recovering gasoline from casinghead gas is available. Most of the developments in recent years have been along the line of absorption. A comparison of the costs of installation and operation of the various methods, and a consideration of the yields of marketable product, indicate clearly (in the opinion of the writers) that absorption methods are the most practical. For those companies which have sufficient oil production and which run the oil to their own refineries, the best method to use is that of crude oil absorption. The plant construction is very simple and the shipping losses are considerably reduced, particularly so in case the oil is transported in pipe lines to the refiner.

contains no gasoline will not pick up any vapors. This condition exists in wells in the Gulf Coast District.

Other factors controlling the amount of vapor picked up by gas are as follows: the porosity of the oil-bearing strata, the depth of the well, and the rapid expansion of the gas which causes variations in temperature.

Inasmuch as the yield of gasoline from natural gas is largely dependent upon the proportion of the vapor of the liquid paraffins in the gas mixture, the character of the oil in a sand is of considerable importance. Crude oil is a mixture of several series of closely related complex hydrocarbons and of various other organic substances. There are often present several different compounds corresponding to a particular molecular weight, the boiling points of which lie so closely together that their separation by fractional distillation is impossible. The liquid hydrocarbons of chief concern to the gasoline industry are the pentanes, hexanes, and heptanes.

Natural gases in the oil fields of the United States are principally mixtures of methane, ethane, propane, butane, pentane, and hexane. Methane is always present in a stratum in the gaseous condition. Ethane becomes a liquid at 95° F. if the pressure reaches the value of 664 lbs./sq. in. Therefore, if a gas consisted of ethane alone and was subjected to a pressure in the earth of 664 lbs., it would probably be liquefied. In the case of a gas containing 50 per cent ethane and 50 per cent methane, a pressure of at least 2 × 664, or 1328 lbs., would be required to liquefy the ethane at 95° F. This fact is explained by discussion of the effect of partial pressures.

FRACTIONATION OF A TYPICAL WET GAS

	Per cent
Methane.....	36.8
Ethane.....	32.6
Propane.....	21.1
Butane-pentane.....	5.8
Hexane.....	3.7
	9.5

FRACTIONATION OF A TYPICAL DRY GAS

	Per cent
Methane.....	87.1
Ethane.....	5.0
Propane.....	6.5
Nitrogen.....	1.4

It will be seen that 9.5 per cent of this gas is liquefiable in plant practice. Based on 1000 cu. ft. of gas, the condensable portion will be 95 cu. ft. It takes about 32 cu. ft. of pure vapor of this character to make 1 gal. of gasoline. The 95 cu. ft. condensed would be about 3 gal. of liquid gasoline. The yield of such gas is usually expressed as about 3 gal. per 1000 cu. ft.

DESCRIPTION OF METHODS

The two most important methods of producing gasoline in the natural gasoline industry are the compression and the absorption processes. When using compression at pressures

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less than 100 lbs. the discharge from the compressors is passed through water-cooled coils into an accumulating tank where the condensate collects. The gas then passes out into the fuel lines, and gasoline is trapped off into stock tanks. Where high pressures are used, two-stage compressors are employed. Low-pressure cylinders compress the gas to about 50 lbs./sq. in., pass it through water-cooled coils and then through an accumulator where a portion of the vapor is condensed and trapped off to stock tanks. The gas passes out from the top of this accumulator and into the suction line of the high-pressure cylinders. It is then discharged through high-pressure water-cooled coils where additional condensate is obtained. In most cases the gas is next discharged into the fuel system. Compressing the gas to 250 lbs. pressure and cooling with water-cooled coils does not entirely strip it of its gasoline; therefore, further means of extraction are employed. One of them is to refrigerate the gas by means of an ammonia plant. Another way is to cool the gas by means of expansion in the following manner:

The gas, after leaving the water-cooled coils and accumulating tanks, passes through the inner pipe of a set of double pipe coils and into an accumulator. This takes place at 250 lbs. pressure. The gas then is used to drive an expander, which, in effect, amounts to using gas at 250 lbs. pressure to drive a prime mover, and this in turn compresses the exhaust gas from the power cylinders of the expander after it has been used as a cooling medium to compress the gas for distribution through the residue fuel system. By using high-pressure gas in this manner, heat is extracted from it in proportion to the work done, and the exhaust gas is consequently brought to a temperature in the neighborhood of -75° F. This exhaust gas, or expanded gas passing through the outer pipe of the double pipe coils, refrigerates the gas passing through the inner pipe. This causes it to drop out additional gasoline as it passes through the accumulator tank on its way to be used to drive the expander.

The temperature of the gas to be cooled may be lowered by this means to the neighborhood of 0° F.

Instead of using an expander, some plants use an absorber on the gas leaving the plant, in order to strip the remaining gasoline from the residue gas. The medium used as an absorbent is put through either steam or fire stills after it has scrubbed the gas, and the gasoline is driven off through condenser coils and blended with the regular plant product.

In order to understand changes that take place in a mixture of gases as it passes through the compressor, knowledge of the principles governing the pressures exerted by gas mixtures is essential, and it is necessary to become familiar with the general thermal relationships encountered.

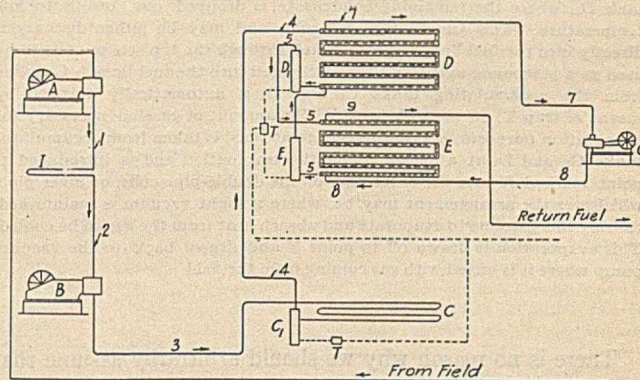
One physical law must be explained—namely, that of partial pressures. We say that at sea level atmospheric pressure is about 15 lbs./sq. in. Three pounds of this pressure are due to oxygen in the air and 12 lbs. to nitrogen. When a vapor is mixed with other gases or other vapors and pressure applied, only a part of the total pressure is exerted on the first-named vapor, or, more correctly, is exerted by the first-named vapor. In case this vapor constitutes 10 per cent by volume of the mixture measured at total pressure, then the pressure on this vapor alone, or exerted by this vapor, is 10 per cent of the total pressure. A total pressure of 150 lbs. is required in order that a pressure of 15 lbs. be exerted on the first-named vapor and that condensation be made possible at the temperature of its boiling point. If we take noncondensable gas and add gasoline vapor to it to the extent that the mixture includes 10 per cent vapor and 90 per cent other gas, then, in order to place 15 lbs. pressure on this vapor, it would be necessary to place 150 lbs. pressure on the entire mixture; or,

if the percentage were increased so that of the total mixture 20 per cent of this was condensable vapor, it would be necessary to apply only 75 lbs. pressure to obtain 15 lbs. pressure on the vapor. It must be understood that it is assumed that these vapors in question will be the first to condense, and that, of course, under these conditions condensation merely begins.

A LOW-PRESSURE METHOD

Under suitable conditions, gasoline vapor is condensed by removing its latent heat of condensation. In turn, gasoline will be evaporated by supplying the latent heat of evaporation. If by any means, therefore, we cause the evaporation of a given amount of gasoline, it must absorb heat from some source, and if we cause the evaporation of the gasoline to occur in heat-extracting relationship to a gasoline vapor (radiation losses being disregarded), the latent heat of condensation of the gasoline would be absorbed by that gasoline being evaporated. Approximately equal weights of gasoline and gasoline vapor must change state, the two processes occurring simultaneously.

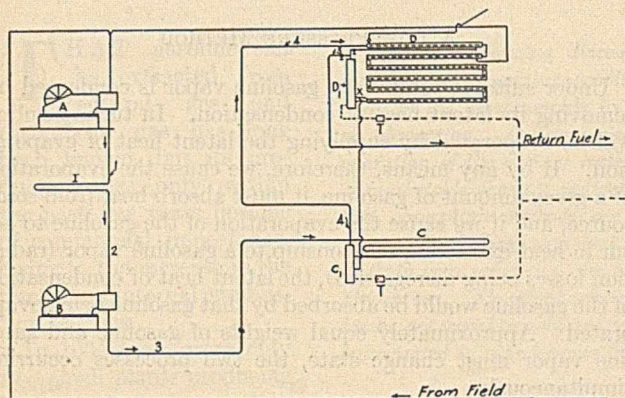
It has been shown that an increase of partial pressure will decrease the total pressure required to produce liquefaction at a given temperature. By evaporating gasoline for its cooling effect and by returning this gasoline vapor through vacuum pumps and compressor, it becomes intimately mixed with the gases entering from the field, thereby increasing the gasoline content of the gas to be handled by the plant. Such



EXPANDER SYSTEM

This diagram shows the operation of the expander system. A is a gathering pump from which gas, by means of line 1, passes through cooling coils I by means of line 2, to compressor B. From this, by line 3 through coils C into accumulator C₁, where any condensate that may be realized at 250 lbs. pressure is dropped out. Coils C will, of course, consist of high- and low-pressure coils, as at this pressure two stages will be used. From the accumulator tank C by means of line 4 the gas enters coils D, which are made up of smaller pipe on the inside of a larger pipe. Passing through coil D and into accumulator tank D₁, the ordinary procedure is for the gas to leave by means of line 5 and go direct to the expander G, which is nothing more or less than a means of using gas at 250 lbs. pressure as a means of power and to obtain the low exhaust temperatures accompanying its expansion. The exhaust gas leaves the expander cylinders by means of line 7, entering the other pipe of the double-pipe coils D, and after passing through this coil is allowed to escape into the fuel system, or, if the pressure makes it necessary, it goes into the compressor cylinders, driven by expander G, which are directly connected to the expander. Sometimes the gas, after passing through the double-pipe coils D, and out of the accumulator tank 5, will be very cold and used as a cooling medium before entering the expander. This means that its temperature will be higher when entering the expander and will be probably somewhat higher upon leaving the expander than it is in the case of the first-named arrangement. By this arrangement the gas, after leaving accumulator tank D₁ by means of line 5, enters the double pipe coils E, going into accumulator tank E₁, then through coils D, and by means of line 7 is led to the expander to be used as power, and the exhaust gas, by means of line 8, is used to cool gas going through coils E.

an increase in gasoline content provides that a greater percentage of the total pressure exerted on the gas is applied to the condensable part. It is then necessary that we extract from the gasoline vapors present in casinghead gas, only enough heat to reduce the kinetic energy to a value corresponding to that of the liquid state.



LOW-PRESSURE EVAPORATION

This diagram shows the arrangement used when the low-pressure evaporation system described in this paper is used. A represents a vacuum pump which gathers gas in the field. B is a single stage compressor. Gas passes from A through inner-cooled coils by means of line 1 and by means of line 2 enters compressor B, being discharged through line 3, is passed through coil C, into accumulator C₁, where any gasoline that may be condensed at this pressure and temperature is collected. By means of line 4 the gas enters double-pipe coil D, passing downward through this into accumulator tank D₁, where the remaining condensate is dropped out, owing to low temperature. This gas is dry and cold, and may be either discharged directly into the fuel lines or passed back through the top sets of coils to be used as a precooling agent and then delivered into the fuel lines. Gasoline from the accumulating tanks C₁ and D₁ is automatically trapped by means of trap T, off to stock tank. The amount of gasoline necessary for evaporation purposes, in order to refrigerate gas, is taken from accumulator tanks C₁ and D₁ at a point above the trap outlet, and is introduced at point marked X into the outer pipe of the double-pipe coils, or inner pipe, whichever the arrangement may be, where a slight vacuum is maintained, causing this gasoline to evaporate and absorb heat from the gas to be cooled. This evaporation is drawn off to point Y and drawn back to the vacuum pump where it is mixed with gas coming from the field.

There is no reason why we should arbitrarily assume that any particular pressure is necessary to condense gasoline from gas. We may take, for example, pentane, a constituent of casinghead gasoline. As a pure vapor, it would be necessary only to hold pressure on it which would equal its vapor tension at any given temperature. For instance, pentane has the following vapor pressures: 11.8 lbs./sq. in. at 86° F.; 8.1 lbs./sq. in. at 68° F.; 5.4 lbs./sq. in. at 50° F.; and 3.5 lbs./sq. in. at 32° F. Any one of these pressures suffices at the corresponding temperature.

The above-mentioned principles have been applied in several commercial plants, one of the writers having installed five of them.

It has been found in some instances that the boiling point of the liquid evaporated is as low as -60° F. The loss due to radiation through insulating material is overcome to a certain extent by precooling with cold dry gas expanded to field pressure, and it is assumed that the cooling realized by this cold dry gas is sufficient to offset the loss due to radiation in the evaporation coils proper. The amount of gasoline which it is necessary to evaporate is calculated, therefore, from the amount of gasoline recovered in the double-pipe coils. If a million cubic feet of gas which carries one-half gallon to the thousand are to be handled, and no water-cooled coils are used, it is then necessary to evaporate only slightly more

than 500 gal. (0.5 of a gal. for each thousand cubic feet) of gasoline. The evaporation of the excess over 500 gal. provides for cooling the gas. This amount is very small, however, owing to the low specific heat of the gas.

The benefit of the principle of partial pressures and the advantages to be derived from increasing the partial pressure on the condensable part of the gas, are realized by the intimate mixture of the vaporized gasoline drawn from the evaporation coils with the gas coming from the field. This has the effect of increasing the amount of gasoline produced by the low-pressure coils, makes less work for the high-pressure cylinder of the compressor, at the same time effecting a greater amount of condensation even in the high-pressure coils. Results so far obtained indicate that the greater part of the gasoline evaporation in the double-pipe coils is recovered in the water-cooled coils, together with that part which would be recovered in the water-cooled coils if the evaporation coils were not in operation. If this were not the case the process would not be practical, since the gasoline recovered in the evaporation coils is due to evaporation of other gasoline, and this evaporated gasoline, if not recondensed before it reaches the evaporation coils, would make it necessary to evaporate twice as much, since there would be twice as much gasoline to recover. This gasoline would continually accumulate and in a very short time the apparatus would become inoperative. By increasing the percentage of condensable vapor in the gas, a greater percentage of the total pressure is exerted on the condensable part and, as explained before, because of this pressure more gasoline is condensed. The possibility of low temperature causing freezing of these coils was at first considered serious, but all inconvenience due to this source has been eliminated. One hundred and twenty-five pounds is the maximum pressure required under any circumstances in plant operation. In some instances, 70 lbs. has been found sufficient.

The question may be raised as to the horse power required to handle the additional amount of gas due to the evaporation of gasoline in the evaporation coils. As stated before, about 1 gal. of gasoline is evaporated in these coils for every gallon condensed, and in the case of a gas carrying 1 gal. per 1000 cu. ft. for a million feet there would be approximately 1000 gal. evaporated. This would amount to only 32,000 cu. ft. of gas for the entire million feet handled.

As to the actual horse-power requirements (based on the pressure of 125 lbs. which is used as a maximum), the following figures are presented in order to show the least possible difference we could expect to realize between the power necessary to operate this process compared with that necessary to operate under the high-pressure method.

Fifty horse power are required to compress 375,000 cu. ft. of gas per day of 24 hrs. from atmospheric pressure to 125 lbs./sq. in. 210,000 cu. ft. may be compressed to 250 lbs. pressure with the same amount of horse power. This figure is based on the practice of installing a 165-h. p. engine to drive a 660,000-cu. ft. compressor. However, we are giving this installation the benefit of an extra 40,000, assuming that it might handle 700,000 cu. ft. with this same 165-h. p. unit.

During a recent test at one plant, a meter-proving apparatus was installed which could be used at any time to serve the same purpose as a meter, and at different times the amount of gasoline being evaporated was checked. Since a gallon of gasoline will yield 32 cu. ft. of vapor, it was found that when the plant was handling 250,000 cu. ft. of gas per day, 22,000 cu. ft. of gas was the excess handled. These results would indicate that we could handle with 50 h. p., 345,000 cu. ft. of gas per day from the field. This test was made under average conditions—a temperature of 80° F. cooling in the water-cooled coils, and a very rich gas. The data show

that 110,000 cu. ft. more gas can be handled per day than with a 50-h.p. unit at 250 lbs. pressure.

On the basis of one million cu. ft. for a vacuum station and gasoline plant under the same roof, the capacity would be as follows, the gas carrying $2\frac{3}{4}$ gal. per cu. ft. (vacuum taken at 18 in., which is the pressure generally used in designing a vacuum plant):

LOW-PRESSURE METHOD	
1,000,000 cu. ft. from 18-in. vacuum to atmospheric pressure.....	77 h. p.
88,000 cu. ft. from 18-in. vacuum to atmospheric which would be the excess due to evaporation	6.8 h. p.
	83.8 h. p.
1,000,000 cu. ft. from atmospheric to 125 lbs.....	127.4 h. p.
88,000 cu. ft. from atmospheric to 125 lbs.....	15.4 h. p.
Total required to handle from 18-in. vacuum to 125 lbs. pressure and extract the gasoline.....	142.8 h. p.
	226.6 h. p.
HIGH-PRESSURE METHOD	
1,000,000 cu. ft. from 18 in. to atmospheric.....	77 h. p.
1,000,000 cu. ft. from atmosphere to 250 lbs. pressure.....	239 h. p.
Total required from 18 in. to 250 lbs. pressure and extract the gasoline.....	316 h. p.

In addition, an expander would be required to secure maximum extraction with high-pressure method.

The amount of excess gas necessary to be handled is determined by the amount of gasoline left in the gas upon entering the evaporation coils, and no consideration is given here to the advantage derived from the removal of additional gasoline in the low-pressure side of a compressor, thereby causing the high-pressure side to do less work. It is quite probable that the greater part of the excess vapor is condensed in the low-pressure coils.

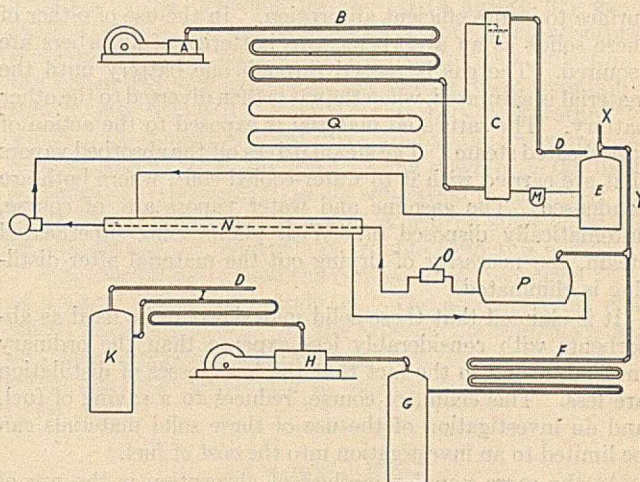
It was found at one of the gasoline plants, that when operating at 125 lbs. without the evaporation coils, 80° Bé. gasoline was made in the water-cooled coils. In a few minutes after placing the evaporation coils in operation, the gravity of the gasoline made in the water-cooled coils was 90° Bé., indicating that considerably more gasoline is recovered in both the low- and high-pressure cylinders at 125 lbs. pressure in the water-cooled coils with evaporation coils in operation, than is recovered without them. This is due to the increased partial pressure of gasoline vapor corresponding to the increased content of gasoline, which makes possible the recovery of the additional gasoline.

It must be understood that the evaporation coils can be installed in connection with high-pressure as well as with low-pressure installations, and constitute a less expensive installation than an additional expander, besides having a greater heat-extracting capacity than the expander.

The advantages derived from the process herein described are: The installation cost is reduced in proportion to the horse-power requirements; with 125 lbs. maximum pressure the horse-power requirements indicate that a 40 per cent saving is to be realized in the initial expense, and a proportional saving in operating expense. In some instances where a lower pressure than 125 lbs. is adequate, there will, of course, be savings running up to as high as 60 per cent. The necessity of using an expander is eliminated, high pressure fittings and tanks are unnecessary, and an opportunity is offered to make installations of this process where the uncertainty as to the supply of gas would preclude the adoption of the high-pressure process. In most cases a plant of this type is assured of profits in a comparatively short time. on account of the relatively low cost of installation.

ABSORPTION METHOD

This method consists in bringing the gas in contact with an absorbing medium in such a manner as to enable the absorbent to pick up the gasoline vapors. Plants of the usual type use an absorbing tower partially filled with absorbing



ABSORPTION SYSTEM

This sketch shows diagrammatically the principles employed in absorption system. Gas is compressed by means of compressor A, passed through a set of water-cooled coils to the bottom of absorber C, out of the top of this absorber by means of line D, to be disposed of as dry gas. The absorbent oil is pumped by means of pump O, through a set of water-cooled coils, Q, into the top of the absorber, and is sprayed downward to point L. The oil leaves the bottom of the absorber, being trapped off automatically by M, into weathering tank E. From this weathering tank E the oil is passed through a heat exchanger where it comes in heat extraction relationship to oil leaving the stills. From this heat exchanger it goes direct to a still, P, where gasoline vapors are driven off through a set of water-cooled coils condensing these vapors and accumulating them in tank G. The oil leaves the still, passing through N on its way to pump O, and has been cooled somewhat by the oil leaving the weathering tank E on its way to the still. The oil, before going into the absorber, is further cooled by means of water-cooled coils Q. Vapors driven off in still P may not all condense in coils F; therefore, if this is of a sufficient amount, a compressor is installed which takes the vapors from accumulator tank G, which fail to condense in coils and discharge them through another set of water-cooled coils, I, where they are condensed and accumulated in tank K. If there happens to be any noncondensable vapors, these escape from the tank K into the air or fuel system by means of line D. Weathering tank E may be connected so that any vapors allowed to escape go into the atmosphere by means of line X or Y, being passed through water-cooled coils F, and in turn pass through condensing unit consisting of H, I, and K.

medium, the gas being passed in at the bottom and out the top, while the absorbing medium passes in at the top and out the bottom. In addition, the absorbers are sometimes equipped with baffle plates, which assist in the further distribution of the gas and effect intimacy of contact between the absorbing medium and the gas.

Absorption processes may be divided into two classes—those using solid absorbing materials that present large surfaces for contact, and those employing liquid absorbents. Activated charcoal and silica gel have been used in processes usually designated as absorbents of the first type. Crude oil, mineral seal oil, naphtha or low-grade gasoline may be used in processes of the second class. Everyone is familiar, of course, with the general character of these liquid absorbents.

The solid absorbents, however, need further discussion. During the war, chemists and physicists were called upon to develop an efficient gas mask. In their investigations charcoals were prepared which were found to be capable of

absorbing condensable gases, because of the extensive surfaces within the body of the charcoal.

Investigations along these same lines have been carried out with silica gel. This gel is made by the coagulation of sodium silicate with an acid. The gel is washed and dried and is then ready for use. Certain very important precautions must be taken to prepare this material so that it will have sufficient surface to insure efficient absorption. In the use of either of these solids as an absorbent, two batteries of absorbers are required. The gas is passed through one battery until the material is saturated, when the gas is then diverted to the other battery. The saturated material is exposed to the action of superheated steam. The steam drives off the absorbed vapors that are carried with it to water-cooled coils, where both are condensed. The gasoline and water vapors are, of course, automatically disposed of. With plants using superheated steam, the necessity of drying out the material after distilling is eliminated.

It is claimed that these solid materials can be used as absorbents with considerably less expense than the ordinary method, owing to the fact that the heat losses of distillation are less. This claim, of course, reduces to a saving of fuel, and an investigation of the use of these solid materials can be limited to an investigation into the cost of fuel.

As the more popular method of absorption is the use of liquid absorbents, more detailed information is available than on the use of solids. The system is similar to that used for extracting benzene, toluene, and other vapors from gas made by destructive distillation. The gas under high or low pressures enters the absorbing towers placed in either vertical or horizontal positions and passes out the top. The oil used as an absorbent enters at the top, is sprayed downward, and leaves the absorbers at a point close to the bottom.

The absorbers usually consist of steel shells varying in diameter from 12 in. to 4 ft., although in some cases still larger diameters are used. The height varies from 15 to 45 ft. It is generally advisable to fill these absorbers partially with baffling material of some kind. In some cases there may be 6 ft. of baffling material and in others there may be 20 or 25 ft. Although the general plan has been to allow sufficient open space at the top of the absorbers for the separation of the oil and gas, one of the writers has recently installed absorbers 30 in. in diameter and 35 ft. high, filled to within 6 ft. of the top. A small separator for the outgoing gas, which removes any oil which may have been carried over, is superimposed. The baffling material varies—broken bottles, mineral-wool, broken stone, and bricks, etc., have been used. In some cases the baffling is made of wooden slats, and in still others flat revolving disks with small holes have been used successfully.

In the writers' opinion, the best baffles are steel plates. These may be about $\frac{1}{32}$ in. thick and from 6 in. to 12 in. high, and, of course, will be of varying lengths. The plates are bolted together with about $\frac{1}{2}$ -in. space between. The lengths can be made to conform to the inner circumference of the shell. If sets of these baffles are placed one on the other, each set is at right angles to the one adjacent to it, or they may be placed so as to create a whirling motion, although such a motion does not present any advantage. The object of the baffling is to present a large surface for the oil to trickle over, thereby accomplishing intimate mingling of the gas and absorbent.

By using this steel baffling, arranged as described above, the area of the cross section of the absorbers is reduced by only approximately 3 per cent, thereby insuring a low velocity of the gas passed through the absorbers, without sacrificing contact surface.

The gas passing out of the top of the absorbers goes into the

fuel system or into the air, depending upon the requirements. The oil after leaving the absorbers goes to stills, passing through heat exchangers in such a manner that it will be heated by hot oil leaving the stills, which in turn is cooled somewhat. The oil leaving the stills is then passed through water-cooled coils before being pumped into the absorbers.

The apparatus for separating gasoline from the absorbent has been frequently described and will not be considered here.

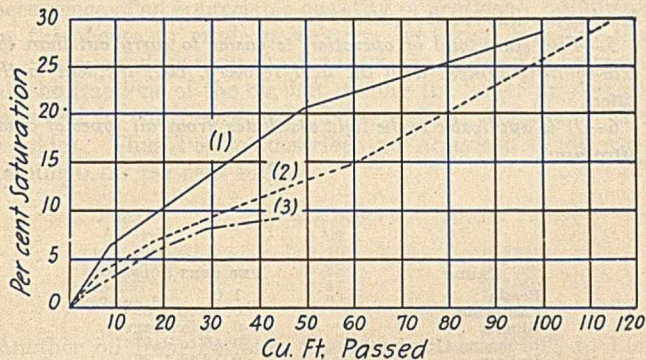
The most important part of the absorption process is the action of the absorbers themselves. The amount of liquid absorbent necessary to be circulated depends upon the efficiency of the absorbers; this, in turn, depends upon the temperatures, pressures, and lengths of time of contact between oil and gas.

Henry's law states that the amount of vapor that will be absorbed by a liquid is proportional to the partial pressure of the vapor. This relationship is true, but the length of time of contact is of considerable importance in practice. For instance, the writers have noted in a plant operated at a certain pressure, and with gas of constant gasoline content, and using any given absorbent, etc., that if the length of time of contact alone was increased, the absorbent would dissolve increased quantities of vapor. This further absorption must be understood as not being of the same efficiency from the standpoint of stripping the gas of its content of vapor, as will be realized if low saturation percentages are maintained. We may assume, for example, that in an absorber in which the gas and oil are in contact for 15 sec. all the gas passing through will be entirely stripped of its gasoline. If this same oil is recirculated in the absorbers, however, and a further amount of gas brought into contact with it for an additional 15 sec., the oil will still absorb but the saturation percentage will not be doubled. By using the oil the second time, the saturation percentage will be approximately 80 per cent of that realized during the first period of absorption. If the operation is repeated, using this saturated oil and new gas, the oil will be further saturated, but will be increased only by about 50 per cent of that realized during the first period of contact. This latter ratio will prevail approximately, decreasing slightly until about 30 per cent total saturation is reached.

It has been customary in absorption plants to use saturation percentages varying from less than 1 per cent to about 6 per cent, depending upon pressures and temperatures. There is no reason, however, why this percentage could not be higher in practice. This would be accomplished primarily by increasing the length of time of contact, either by increasing the height of baffling or by operating absorbers in series. In doing this, the counterflow principle should be used. The rich oil leaving the absorbers meets rich gas entering and the lean gas leaving comes in contact with the lean oil entering. The effect of using this high saturation percentage would be to cut down the still capacity required, since there would be considerably less oil to be heated and the quantity of heat necessary to furnish the latent heat of evaporation would be the same. For example, if a plant with a capacity of 1,000,000 cu. ft. per day with a total gasoline content of 1000 gal. were running at a saturation of 4 per cent, 25,000 gal. of oil per day would have to be circulated through the absorbers, and the stills would have to supply sufficient heat to raise the 25,000 gal. of oil to the required temperature—in addition to latent heat of evaporation to be supplied for the 1000 gal. of gasoline. Now, if the saturation percentage were maintained at 20 per cent, it would be necessary to circulate only 7000 gal. of oil and to supply heat sufficient to raise the temperature of approximately 5000 gal. of absorbent to the temperature necessary to drive off the gasoline vapor, plus the latent heat of evaporation of 1000 gal. of gasoline. This would reduce the still capacity required, as well as that of the

circulating pumps, by approximately 75 per cent. The same reduction would apply to the fuel requirements for the stills.

The writers have built commercial plants that employ these high baffles and absorbers in series, obtaining the high saturation percentages previously described. In actual plant practice, when handling in the neighborhood of 2,000,000 cu. ft. of gas per day at pressures between 20 and 30 lbs./sq. in. and saturation percentages up to 25 per cent, these baffles and absorbers have been found to be entirely satisfactory. It is noticeable that the increase in gravity is approximately one degree for each 5 per cent additional saturation. This applies also to crude oil when used as an absorbent. We have found in one particular case, with crude oil of 38° Bé.



COMPARISON OF MINERAL SEAL, CRUDE OIL, AND DRIP GASOLINE AS ABSORBENTS

ABSORBENTS	Temperature—° F.		Gravity—° Bé. at 60° F.	
	Start	Finish	Start	Finish
(1) Mineral Seal	60	70	37.5	46.1
(2) Crude Oil	52	62	41.7	48.8
(3) Drip Gasoline	68	72	64.8	67.9

gravity and an initial boiling point of 118° F., that the crude oil, after being used as an absorbent, had a gravity of 43° Bé., and an initial boiling point of 80° F. This change in gravity represents an increase of approximately 25 per cent in volume, which was indeed the actual increase of volume observed. The temperature of the oil entering the absorbers was slightly less than 80° F., so that under this condition the temperature of the oil was about equal to the initial boiling point of the rich liquid, and the temperature of the oil leaving the absorbers was about 110° F. Since the oil leaving the absorbers was set at a temperature exceeding the boiling point of the absorbent at that place—i. e., original absorbent plus absorbed gasoline—its ability to dissolve further vapors was reduced. This effect was offset to some extent by increased pressures. The boiling points referred to above were determined at atmospheric pressure, and naturally, if the pressure were held at 20 or 30 lbs./sq. in., the initial boiling points would be somewhat higher. An absorbent will absorb vapor until the partial pressures of the dissolved gasoline constituents equal those of the same constituents in the wet natural gas at the common temperature.

CRUDE OIL ABSORPTION

A means of reducing expense incident to recovering gasoline is the use of crude oil as an absorbent and pumping the rich liquid through pipe lines to a refinery. Some companies are at present blending the natural gasoline product with their crude oil runs.

Crude oil absorption is the same in principle, of course, as that obtained by the use of any other medium, the stripping stills in this case being eliminated, or rather replaced, by the regular crude stills of the refinery. It is necessary, in order that maximum efficiency be realized with a small amount

of oil, to cool the oil after it leaves the absorbers. This requirement is due to the great amount of heat generated by the process of absorption. If the oil from the absorbers were put into tanks at these high temperatures, a considerable amount of the absorbed vapors would be driven off when the pressure is relieved.

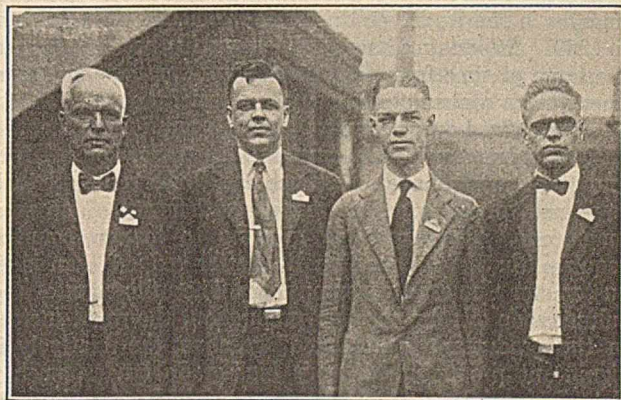
An interesting feature in connection with crude oil absorption is the tendency for the oil to absorb dry gas in small amounts. However small in amount, such absorption is undesirable. A method for overcoming this objection is the use of the heat generated by absorption to maintain in the oil just before it leaves the absorbers temperature that will be high enough to offset this action at the pressures used. The oil coming in at the top trickling down over the baffles increases in temperature as its saturation is increased, and by the time it reaches the outlet it will be sufficiently high in temperature to prevent any trouble from this source.

It is interesting to note the comparative absorption values of mineral seal oil and crude oil. The accompanying chart shows this comparison. All the experiments were made with the same apparatus, using the gas from the same source, and under the same condition as to weather, etc.

A Chemical Family

Nine universities have contributed to the education of the chemical family of Swan, which sent a 100 per cent delegation—a father and three sons—to the Pittsburgh meeting of the AMERICAN CHEMICAL SOCIETY. These nine universities have already conferred upon this family ten degrees, including three Ph.D.'s, and the youngest son, Thomas, expects soon to qualify for his doctor's degree at Ohio State University.

The father, John N. Swan, is now head of the Department of Chemistry at the University of Mississippi. He has held professorships at three colleges, and has built a new laboratory at each.



Stewart D. Swan is connected with the Dentists' Supply Company of New York City, and William O. Swan is at present Acting Assistant Professor of Analytical Chemistry at the University of Virginia.

We wonder if this is not a record contribution to chemistry?

One of the important recent developments in the feldspar industry has been the rapid rise of New Hampshire as a feldspar-producing state. The unusual size and purity of the deposit now being worked near Keene, and the improved methods of mining and milling used have been responsible for this situation. The ore body stands nearly vertical between walls of mica schist. Between the feldspar body and the schist walls on each side occurs the mica for which the deposit was opened. The width of the pegmatite dike varies from 40 to about 200 ft. The total depth has not been proved, but mica workings to a depth of more than 200 ft. showed no apparent change in the nature of the deposit. Mica workings have also been extended over a length of 750 to 1000 ft. along the vein, with no change in the deposit indicated.

Refining of Gasoline and Kerosene by Hypochlorites¹

By A. E. Dunstan and B. T. Brooks

THE ANGLO-PERSIAN OIL CO., LONDON, ENGLAND, AND THE MATHIESON ALKALI WORKS, INC., NEW YORK, N. Y.

Sulfur, though often present in relatively very small proportions, is the most objectionable impurity in motor fuel, and it is with the removal of sulfur that the present paper deals, although it should be pointed out that the refining method here described does a great deal more than merely remove sulfur. This method is not an academic process, but has been in successful large-scale operation a little over one year and is now in operation in several refineries.

The advantages of the hypochlorite process for the refining of gasoline and kerosene, which are pointed out in this discussion, may be summarized as follows:

1—Lower refining cost.

2—Less loss on refining, adding materially to the total money saved.

3—No acid sludge is formed and no acid to be recovered.

4—The operation can be carried out in ordinary steel apparatus; one year's experience has shown that the corrosion of apparatus, piping, etc., is much less than when acid is employed. Lead-lined apparatus is not required.

5—The sum total of operation is easier to carry out than the acid-refining process with the acid recovery, etc., incident to the latter.

6—It is applicable to the light distillates from all types of crude petroleum.

IT WAS inevitable that with the tremendous growth of the petroleum industry and particularly the production of gasoline for motor cars, considerable attention would be given to better methods of refining. Considerable impetus has been given to this general problem by the automobile industry and, during the war, by the necessity of finding superior motor fuels and lubricants for aeroplanes. Petroleum refiners, or at least their sales departments, have also come to realize that superior goods are appreciated by the consumer.

The question of good motor fuel is certainly one of universal interest. This country, owning 85 per cent of all the automobiles in the world, produced 5,145,000,000 gal. of gasoline in 1920. At certain seasons the demand has been so great and the lapse of time from the production of gasoline at the refinery to its consumption has been so brief that refiners have often sacrificed everything to "through put." Shipments of gasoline from America to England, Australia, South Africa, and other points, have sometimes had to be returned to be re-refined, or have led to money settlements of no small magnitude. The export of gasoline to foreign countries requires that such gasoline be better refined than is the custom for domestic consumption. The utilization of high sulfur crude oils for gasoline production, the rapid increase in the production of "cracked" gasoline, the relatively insignificant production of very high-grade crudes, such as light Pennsylvania oil, the known merit of benzene in motor gasoline, and the very large losses resulting in the refining of crude benzene, have also been factors in the search for better refining methods.

Although the proper refining of gasoline involves more than the removal of sulfur compounds, the removal of such compounds can, nevertheless, be taken as a fair index of the degree of refining. The nature of the sulfur compounds present in a crude petroleum, or its distillates, makes a great deal of difference, for example, with respect to odor (mercaptans) and corrosive properties, but comparatively little is known as to their exact nature. Figures for the percentage of sulfur in unrefined gasoline distillates are not generally available, but average about one-tenth of the amount present in the original crude petroleum. The percentage of sulfur in a number of crude oils is given in the following table:

CRUDE	PER CENT SULFUR
Persia	1.0
California	0.55 to 3.55
Illinois	0.40 (average)
Louisiana (Jennings)	0.40 to 0.57
Indiana	0.72 to 1.26
Ohio (Lima)	0.65
Texas, Beaumont	0.94 to 2.40
Texas, San Antonio	1.52 to 2.02
Texas, Reeves County	1.00
Texas, Medina County	2.09
Texas, Travis County	1.26
Mexico	1.9 to 4.8

Engler and Höfer give the following sulfur contents of crude petroleum:

CRUDE	SULFUR PER CENT	CRUDE	SULFUR PER CENT
Tegernsee	0.044	Pechelbroun	0.650
Olheim	0.580	Wietze	0.58
Galicia	0.21	Roumania	0.170
Montechine	0.045	Bi-bilibat	0.220
Balachany	0.147	Palembang	0.212
Java	0.473	Sumatra	0.066
Roem Koot	1.166	Pennsylvania	0.049
Burmah	0.121		

Persian crude oil contains about 1.02 per cent and Burmah (Yenan Yung and Singu) about 0.1 per cent sulfur.

Free hydrogen sulfide has been identified in the crude petroleum from Canada, Ohio, Texas, Galicia, and Persia.² The natural gas accompanying sulfurous crudes sometimes contains upwards of 10 per cent of hydrogen sulfide. The hydrogen sulfide which frequently appears during distillation is probably partly expelled from solution and partly results from the decomposition of sulfur compounds in the oil.

Free Sulfur—Elemental sulfur has been recognized by Richardson and Wallace³ in Texas petroleum, which, after being freed (at ordinary temperatures) from hydrogen sulfide and filtered through kaolin, deposited crystals of this element.

The natural gas accompanying petroleum rich in sulfur is usually rich in hydrogen sulfide, and the slow evolution of dissolved hydrogen sulfide from certain crudes has apparently been the cause of no small number of fatalities. Kraemer and Spilker⁴ state that the presence of sulfur in petroleum is due to activity of certain bacteria, contemporaneous with the algae which these authors regard as the source of petroleum. It is well known that sulfur reacts readily with

² Mabery, *Proc. Am. Acad. Arts Sci.*, **31** (1894), 1743; Thiele, *Chem.-Ztg.*, **25** (1901), 433.

³ *J. Soc. Chem. Ind.*, **27** (1902), 316.

⁴ *Ber.*, **35** (1902), 1212.

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

hydrocarbons to give hydrogen sulfide, and Friedmann⁵ has shown that thiophenes are also formed. It is not difficult to conceive that such reactions have occurred in nature and would afford an explanation of the presence of sulfur derivatives in petroleum. However, a strong explanation against this explanation is the fact that thiophenes are rarely found in petroleum and then only in traces. Free sulfur is frequently observed in the neighborhood of petroleum wells, and it is not unlikely that this occurrence is due to reduction of sulfur compounds—e. g., mineral sulfates—by the oil or its antecedents. The observations of Steinkopf⁶ that acetylene when passed over heated pyrites yields thiophene and that butadiene in a similar way generates methyl thiophene are of interest, though there is no satisfactory evidence of the occurrence of an appreciable quantity of acetylene, butadiene or thiophenes in crude petroleum. Speaking broadly, the thio compounds present in petroleum are distributed between all the fractions of the oil, but usually the larger proportion is found in the heavier distillates and particularly in the residues. Thus Perkin⁷ describes an American crude containing 0.727 per cent sulfur:

Fraction	Per cent Sulfur	Specific Gravity
to 90° C.	0.02	
110–150° C.	0.10	0.7282
152–220° C.	0.38	0.7669
220–257° C.	0.41	0.7940
257–300° C.	0.37	0.8138

Another oil from Petrolea, Canada, containing 0.98 to 1.06 per cent sulfur gave the following results:

Fraction	Per cent Sulfur	Fraction	Per cent Sulfur
115–150° C.	0.28	250–300° C.	0.51
150–200° C.	0.42	300–350° C.	0.86
200–250° C.	0.50	Residue	0.70

ELIMINATION OF SULFUR FROM PETROLEUM DISTILLATES

It has long been established that sulfur compounds occurring in petroleum products are objectionable, and are largely responsible for the properties which refining seeks to remove. While this statement applies to nearly all⁸ petroleum products, it is particularly true of gasoline and kerosene. The offensive odors possessed by most unrefined gasolines are due chiefly to very small proportions of mercaptans, and perhaps to a lesser extent to nitrogen bases and simple naphthenic acids. Unrefined gasolines are also usually corrosive to metal, copper being usually employed for the test, and this also is attributed to sulfur derivatives or perhaps to dissolved elementary sulfur. Gasolines and kerosene of offensive odor also usually show a positive "Doctor" test (with alkaline litharge solution). In addition to the effects of sulfur just mentioned, the use of high sulfur gasolines, particularly benzene blends which are apt to have a high percentage of sulfur, results in the formation of acids on combustion in a motor, and this causes serious corrosion. The discoloration and development of acidity in gasoline that is stored for some time is also frequently attributed to sulfur compounds, although these effects are certainly more pronounced in the case of cracked oils which have been refined by sulfuric acid, as pointed out below. Sulfur is probably not such a serious impurity in kerosene as in gasoline, although it is known to cause filming of lamp chimneys and charring and uneven burning of the wick. It is also probably responsible for discoloration during storage.

The best known and one of the most successful processes for desulfurizing oils is the Frasch process, developed to sweeten the so-called "skunk" oils of northern Ohio, Indiana, and

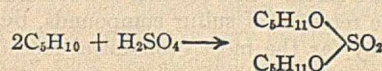
Ontario. The production of this crude has now sunk to very insignificant proportions, and other oils which are now of the greatest industrial importance—for example, the high sulfur Mexican oils—cannot be successfully desulfurized by the Frasch method. Frasch also took out a patent⁹ for *dechlorinating* oil which had been treated with bleaching powder. The Frasch method of dechlorinating consisted in heating the oil with alkaline litharge or Doctor solution, but so far as the authors are informed this process was never operated on an extensive scale. Colin and Amend¹⁰ patented a method of refining petroleum distillates which consisted in treating the oil with hypochlorites in the presence of catalytic agents, such as manganese, nickel, or cobalt salts, which evolve oxygen from the hypochlorite. However, the only desulfurizing process other than that of Frasch which has been employed on a large scale is the alkaline litharge method; but, like the Frasch method, this process eliminates only certain classes of sulfur derivatives and is of little or no value on distillates from certain crudes. It is frequently noted that gasolines may be negative to the alkaline litharge test and yet show very marked corrosion of copper and rapid discoloration on standing.

The method of refining by dilute hypochloric solutions described below seems to be universally applicable to desulfurizing all the gasoline and kerosene distillates from all types of crudes. For example, it can be successfully applied to the desulfurizing and refining of naphtha from Mexican crudes, which are not amenable at all to the Frasch method. It should be pointed out also that under the conditions as defined below no chlorine is introduced into the oil. Refining by hypochlorite can be carried out according to either of two principles: (1) complete desulfurization, or (2) refining so as to pass the usual tests and be satisfactory as regards odor, color, and keeping qualities. The latter method requires the employment of much less reagent and is accordingly cheaper. Although the copper corrosion and Doctor tests may be negative and the oil may be quite satisfactory in other respects, not all the sulfur present is actually removed; the corrosive and offensive sulfur compounds present are converted to very stable compounds which are odorless and noncorrosive. The amount of hypochlorite required to refine the gasoline distillate from the average American crude petroleum is remarkably small.

The savings effected by the hypochlorite method vary widely with different oils and according to the degree to which the refining is carried out. Thus, a good quality of crude gasoline distillate may be refined to pass the corrosion and Doctor tests with only 2 or 3 lbs. of chlorine in the form of hypochlorite per 1000 gal., but complete desulfurization of a gasoline, such as that from Persian crude, requires about 1 lb. of chlorine per 50 gal.

REFINING OF CRACKED DISTILLATES

It is probable that labil sulfur compounds in oils that have been treated by sulfuric acid are responsible for discoloration when such oils are permitted to stand; this is particularly true of gasoline which has been made by thermal cracking methods and which has been refined by sulfuric acid. When small proportions of sulfuric acid are employed for treating such cracked gasoline, it is possible to bring about a substantial increase in the sulfur content, the sulfur thus introduced being in the form of alkyl esters of sulfuric acid, formed according to the equation—using amylene as an example—



⁹ U. S. Patent 525,811 (1894).

¹⁰ U. S. Patent 723,368 (1903).

⁵ Ber., 49 (1916), 1344, 1551.

⁶ Ann., 403 (1914), 11.

⁷ J. Inst. Petroleum Tech., 3 (1917), 229.

⁸ The presence of sulfur appears to be an advantage in the case of residuum, which is to be blown by air for conversion to asphalt; sulfur accelerates the process, producing a harder product in a given time.

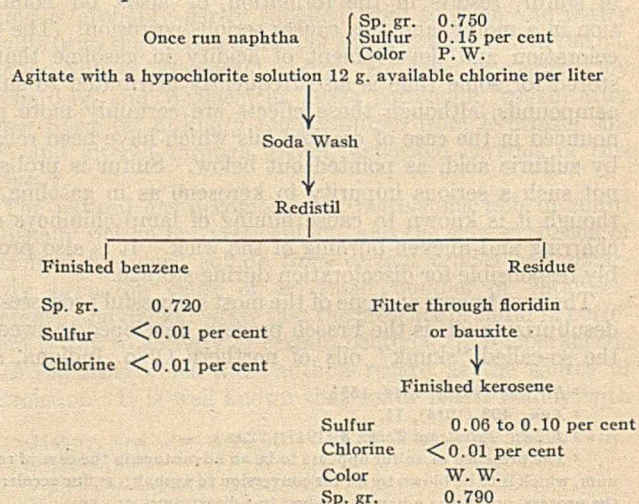
Such esters are not readily removed from the oil by washing with alkali; and it is common experience that such oils, treated in this way, yield free sulfur dioxide when redistilled, even when the alkali wash has been as effective as possible.¹¹ On the other hand, if large proportions of sulfuric acid are employed for treating, large losses result, varying from about 3 per cent up to 20 per cent, the latter figure being about the average loss on treating Scotch shale oil distillates with sulfuric acid. Very large losses are also experienced in refining crude benzene losses by solution and polymerization frequently amounting to 20 per cent. However, it is now very generally recognized that simple olefins are not objectionable as constituents of motor fuel. It has accordingly become the almost universal practice to refine such cracked naphthas with a small proportion of acid and then redistil to free the gasoline of the sulfuric esters and polymers formed by the acid.

The total loss on refining cracked gasoline, however, is always greater than the observed loss of volume, since a large proportion of the unsaturated hydrocarbons are polymerized to higher boiling hydrocarbons. (When such cracked distillates are not redistilled they quickly become discolored on standing, even for a comparatively short time, and frequently develop a brown sediment and a strongly acid reaction.) This procedure obscures the actual total loss of gasoline. Since polymerization is the principal result with unsaturated hydrocarbons above hexylene in the olefin series,¹² the polymerization loss on treating cracked gasoline is always greater than the observed solution loss. Thus, a cracked gasoline giving a solution loss of 3 per cent will have a polymerization loss of *at least* an equal amount, or a total gasoline loss of at least 6 per cent. This point is worth emphasizing, because it is by no means universally recognized to be a fact. A number of cracked gasolines made by distilling Oklahoma fuel oil under 100 to 150 lbs. pressure showed polymerization losses of 15 to 30 per cent and the dry point was not reached at 260° C. (500° F.). Although these particular gasolines contained a higher percentage of unsaturated hydrocarbons than commercial cracked distillates made to-day, and were treated with more acid, they do demonstrate that such losses are very real and may be comparatively large. This is still further demonstrated by the action of ordinary concentrated sulfuric acid, 66° Bé., on a mixture of amylenes and hexylenes at -5° C., in which case the loss by solution in the acid was only 11 per cent, but 75 per cent of the mixture was converted into high boiling polymers. Small proportions of acid may bring about a very extensive polymerization. Thus, a pure olefin, C₁₂H₂₄, of known purity, showed a loss to 85 per cent sulfuric acid of only 4.4 per cent and was almost entirely polymerized; ordinary 96 per cent acid gave a loss of about 10 per cent, and the remainder was *completely* polymerized. The highest solution losses occur in the lighter fractions containing amylenes and hexylenes. In view of the facts just mentioned, it is certain that a careful investigation of the polymerization losses in the present American practice, of refining cracked gasoline by sulfuric acid and redistilling, are very real and probably amount to 3 to 6 per cent of the gasoline treated. The refining of such cracked gasolines by filtering through fuller's earth or similar material also is known to effect some polymerization, and therefore loss, but treatment in this manner has not been very successful or widely adopted. The only published data bearing on this are those of Gurwitsch¹² who noted that amylene was rapidly polymerized by fuller's earth. The refining of such cracked gasoline, including the removal of sulfur compounds, by hypochlorite solutions is by far the most economical method of refining such products.

That the hypochlorite method of refining petroleum distillates had not been worked out many years ago is probably due to the fact that the first attempts resulted in introducing chlorine into the oil. The natural conservatism surrounding a long-established process (sulfuric acid and soda refining), together with the fact that only in recent years has liquid chlorine become a really cheap, bulk staple of the chemical industries, have also been factors in retarding the development and adoption of the new method. Special methods for the cheap and safe transportation of liquid chlorine have also been developed—i. e., specially designed tank cars—and consequently liquid chlorine has rapidly been replacing bleaching powder among consumers of large quantities of bleach.

The active agent in the new process is probably hypochlorous acid. As originally carried out, the hypochlorite solution was generated by the partial electrolysis of salt in specially designed hypochlorite cells. This is unsatisfactory on account of the low utilization of salt, cost of current, rapid deterioration of the cells, and other difficulties which have been the common experience with such cell installations, and the hypochlorite solution is better made up from liquid chlorine, which greatly simplifies the operation and necessary supervision.

The sulfur derivatives in petroleum distillates are rapidly oxidized by dilute hypochlorite solutions, 2 hrs. being the time allowed in the case of the Persian distillates. A concentration of 12 to 15 g. of available chlorine per liter is employed and agitation is accomplished by circulating the aqueous solution through centrifugal pumps discharging below the surface of the oil. The agitators are iron and are not lead lined, experience having shown that corrosion of the iron agitators does not proceed beyond a slight filming of the metal. Part of the sulfur is removed in the form of oxidation products soluble in water. The best procedure, when it is desired to eliminate the sulfur, is to refine the crude naphtha distillate containing both the gasoline and kerosene, then steam-distil the gasoline and pass the kerosene residue through a filter containing dehydrated bauxite or similar adsorbing material to remove the slight color. The oxidized sulfur compounds are much more readily removed by the bauxite than in their original condition. The combined losses amount to about 0.5 per cent in the case of Persian oil, and the refining losses on the same oils as formerly treated by sulfuric acid were 3 per cent. The spent hypochlorite solution is practically a 1 per cent solution of calcium or sodium chloride, and can be disposed of without causing stream pollution or other nuisance. This procedure thus avoids the recovery of acid, burning the acid tars, or other troublesome methods of caring for the acid wastes involved in the old sulfuric acid process.



¹¹ Brooks and Humphrey, *J. Am. Chem. Soc.* 40 (1918), 822.

¹² *J. Chem. Soc. (London)*, 1915, 933.

When gasoline only is to be treated, the filtering operation may, of course, be dispensed with. The foregoing is an outline of the process as carried out on the distillate from Persian oil. The purification is so effective that with gasoline from Persian oil, containing originally the percentage of sulfur indicated above, the regular commercial output passed the following tests:

1—100 cc. gasoline + 1 cc. KMnO_4 (0.1 *N* soln.) + 2 cc. 10 per cent sulfuric acid, and vigorously shaken retains the permanganate color for 10 min., usually much longer.

2—When a sample of the gasoline is treated with sodium and alcohol and, after the reaction is over, slightly acidified and tested with lead acetate, no film of lead sulfide can be detected.

3—The copper dish test is entirely negative.

4—The Doctor test is negative.

The Composition of Erythrosin¹

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ALTHOUGH tetraiodofluorescein was discovered in 1875, the commercial purification of its sodium salt was not well understood even in 1909, as is evidenced by the statement of E. G. Kohnstamm² before the Seventh International Congress of Applied Chemistry in that year: "Of twelve samples of erythrosin examined, ten were not erythrosin at all, and of the other two, one was low in iodine, and one contained arsenic." To-day, with the dyestuff standing as one of the seven permitted food colors and receiving important consideration as a sensitizer of photographic plates, the subject of its preparation has attained considerable importance. When intended for use as a food color, it is obviously necessary to place the requirements in regard to purity as near the theoretical as technical practice will allow. The failure, however, of carefully made and apparently pure technical erythrosin to conform to the standards set by the United States Bureau of Chemistry³ has made it seem doubtful if the formula $\text{C}_{20}\text{H}_6\text{O}_5\text{I}_4\text{Na}_2$, as given in Schultz's *Farbstofftabeln* for 1914, page 200, and as adopted by the Bureau of Chemistry, is correct.

In this communication are submitted the results of a study concerning: (a) the preparation and purification of tetraiodofluorescein, (b) the conversion of this into the sodium salt—i. e., erythrosin, (c) the composition of pure erythrosin, and (d) the composition of the technical product.

PREPARATION OF TETRAIODOFLOURESCIN

Fluorescein was prepared in the usual manner from phthalic anhydride, resorcinol, and zinc chloride, and was carefully purified. Its purity was further confirmed by converting a portion into the diacetate, and this was found to melt at 199° to 200° C.⁴

Three methods are described in the literature for the preparation of tetraiodofluorescein: (1) the electrolysis of an alkaline solution of fluorescein containing a little excess of iodine,⁵ (2) the treatment of a comparatively cool alkaline solution of fluorescein and sodium iodide with ammonium or potassium persulfate,⁶ and (3) direct halogenation in hot dilute acetic acid with an excess of iodine.⁷ For laboratory preparation this last method seemed to offer the best possibilities.

Twenty-four grams of fluorescein were dissolved in a hot mixture of 24 cc. of 30 per cent sodium hydroxide and 240 cc. water. One hundred grams of iodine and 240 cc. of water were treated with just sufficient 30 per cent sodium hydroxide solution (105 cc.) to cause decolorization, and the two solutions were mixed and heated nearly to boiling. One hundred grams of glacial acetic acid were allowed to flow in drop by drop, with good stirring, the temperature being maintained at nearly the boiling point. The liquid was then partially neutralized with 55 cc. of the sodium hydroxide solution, and, after short standing, made strongly acid with 200 cc. of 1:1 hydrochloric acid. After boiling for a minute, the mixture was diluted with hot water to 3 liters, and the whole allowed to stand for several hours. The yield of crude, amorphous product was 95 per cent.

It was found that the method of Mühlhauser—namely, repeated digestion with dilute hydrochloric acid—did not remove all the adhering iodine. Treatment of an alkaline solution of the dye with sodium sulfite apparently removed some of the halogen even from the molecule itself. Repeated digestion with sodium iodide gave a product very light in color, but which still retained some iodine, as could be demonstrated by heating the acid at 135° C., whereupon vapors of iodine were given off. Treatment with 5 per cent sodium thiosulfate solution was not efficient, and there always resulted a slight precipitate of sulfur. The following procedure was finally adopted for securing a product which, while amorphous, was free from occluded and adsorbed iodine: four washings of the crude substance with water containing a little sulfuric acid in order to repress the solubility of the iodo compound, two extractions with warm alcohol, then solution in dilute sodium hydroxide (50 g. dye in 3 l. of water), and precipitation, hot, with dilute sulfuric acid; then again washing with water, and finally with alcohol. The final product was very light in color and did not give off iodine vapors when heated for one hour at 150° C.

The product thus purified, while entirely free from occluded iodine, contained about 6 per cent of diiodofluorescein, as was evidenced by its iodine content—59.74 instead of 60.75 per cent. It is almost impossible to separate completely the tetraiodo from the diiodo compound by recrystallization of the mixture of the acids, because the two are nearly alike in respect to solubility, or rather insolubility, in the usual solvents. Nor can one depend upon the melting point as a criterion of purity, for this is very indefinite. In order to obtain perfectly pure tetraiodofluorescein, we have therefore converted our product into the diacetate, purified the latter by recrystallization until the melting point was constant and iodine analysis indicated a compound of unques-

¹ Received May 8, 1922.

² *Proc. 7th Internat. Cong. Appl. Chem.*, 1909, Sec. 4b, p. 122.

³ "Coal-Tar Colors Used in Food Products," *U. S. Dept. Agr., Bull.* 147, 206.

⁴ *Baeyer, Ann.*, 183 (1876), 2, 13.

⁵ *Chem. Zentr.*, 1900, II, 1176. Société chimique des Usines du Rhone, Anct. Gilliard, P. Monnet, et Cartier, D. R. P. 108,838.

⁶ Winther, "Patente der Organischen Chemie," 2 (1877-1905), 169.

⁷ Mühlhauser, *Dinglers polytech. J.*, 263 (1886), 99; 283 (1892), 258.

tioned purity. This diacetate upon saponification gave us the pure tetraiodofluorescein.

TETRAIODOFUORESCEIN DIACETATE—25 g. of tetraiodofluorescein, 100 cc. of acetic anhydride, and 5 g. of fused sodium acetate were heated in an oil bath under a reflux condenser for 2 hrs. at 150° C., and the solution was then poured while still hot into ice water. The solidified mass, washed with water and dilute sodium hydroxide, and dried, was recrystallized from boiling bromobenzene. It then became soluble in cold acetone, from which, however, it almost immediately reprecipitated as a beautifully crystalline white powder, nearly insoluble in all solvents of low boiling point. By three crystallizations from bromobenzene, alternated with the above-mentioned solution and precipitation from acetone, a pure white product was obtained which melted at 293° to 294° C. Yield, 14 g.

Calculated for diacetate $C_{24}H_{12}O_7I_4$: I, 55.20 per cent.

Found: I, 55.27; 55.46; 55.08; 54.90. Av. 55.18 per cent.

SAPONIFICATION OF THE DIACETATE—Of several methods tried, the following was found most suitable: 10 g. of erythrosin diacetate were suspended in a mixture of 600 cc. of acetone, 45 cc. of water, and 90 cc. of ammonium hydroxide solution at room temperature for 8 to 10 hrs., complete solution having been effected in about one-third of this time. The filtered solution was diluted with one-fourth its volume of water and, after partial neutralization with dilute acid, heated to 40° to 50° C. Upon complete acidification, pure acid precipitated crystalline. In this condition the air-dried material retains only 0.5 per cent of solvent. Yield, 95 per cent. The acid purified through the diacetate could readily be obtained in crystalline form even from its warm aqueous ammoniacal solution by dilute acetic acid, complete separation being insured by finally adding a little sulfuric acid. The same material precipitated in the cold was amorphous, but when sufficiently washed was equally pure.

		Per cent			
Calculated for $C_{24}H_{12}O_7I_4$:	I,	60.75			
Found: Lot 1	I,	60.44	60.51	60.67	Av. 60.54
Lot 2	I,		60.62		
Lot 3 Hot pptn.	I,	60.43	60.27	60.73	Av. 60.54
Cold pptn.	I,	60.65	60.56	60.65	60.81 Av. 60.67

Tetraiodofluorescein thus prepared is insoluble in all the usual solvents which boil below 100° C., with the exception of alcohol and moist acetone, and only slightly soluble in these. Ethylene chlorobromide and dibromide dissolve a little on heating, as does bromobenzene, but the precipitates obtained on cooling are not fully crystalline. The solubility in ethyl salicylate is low. Nitrobenzene dissolves 1 g. per 15 cc. at 160° C., but at best only half of this is precipitated on long standing, and the product is somewhat low in iodine content. *m*-Cresol proved an unusually good solvent at its boiling point, but here again the yields were never better than 50 per cent and the product analyzed only 59.37 per cent iodine.

METHOD OF IODINE ANALYSIS—For the determination of the percentage of iodine, the Pringsheim method, fusion with sodium peroxide, proved entirely unsuitable. The chromic acid oxidation according to Baubigny and Chavaunne⁸ was applicable and has been used to some extent, but the results were inferior in constancy to those obtained by the method of Seeker and Mathewson,⁹ as is shown on the same sample in both cases, in the following table:

		Per cent Iodine			
Baubigny and Chavaunne		50.09; 47.89.	48.29;	48.99	
Seeker and Mathewson		48.90;	48.99;	48.94	

Some slight modification of the second method, however, was found advisable, especially in the case of acid dried

for a long time. 0.2 to 0.3 g. of tetraiodofluorescein was dissolved in 20 cc. of water and 10 cc. of 10 per cent sodium hydroxide by heating gently for a few minutes. (With the sodium salt, only 2 cc. of sodium hydroxide are necessary.) While still hot, 40 to 60 cc. of a saturated solution of halogen-free potassium permanganate were added, followed by 12 to 15 cc. of concentrated nitric acid. The subsequent treatment was identical with that given by Seeker and Mathewson. It was found that this method of halogen estimation could be applied to the diacetate also, if the sample were dissolved in 30 cc. of 70 per cent alcohol and 15 cc. of 10 per cent hydroxide, and heated on the water bath until all alcohol was removed and saponification was complete before the addition of permanganate and nitric acid.

PREPARATION OF ERYTHROSIN

For the preparation of the disodium salt of tetraiodofluorescein, a suspension of the acid in water could be exactly neutralized by the addition of the requisite amount of standard 0.02 *N* alkali and the solution evaporated to dryness. It was found, however, that products obtained in this manner were difficult to get dry and were invariably low in iodine. Sodium carbonate gave us better results, and accordingly the following method was adopted: 3 g. of tetraiodofluorescein and an equal weight of dry sodium carbonate were suspended in 150 cc. of absolute alcohol and, after standing some hours, the whole heated to boiling for a few minutes. The undissolved carbonate was filtered off and the liquid concentrated under reduced pressure until the separation of the salt commenced. The small amount of precipitate was removed by filtration and the evaporation of the solution continued further. When the volume had reached approximately 30 cc., an equal amount of absolute ether was slowly added and crystallization allowed to proceed overnight. The red crystals were separated rapidly by filtration, washed with alcohol and ether, and dried in a vacuum desiccator over fresh sulfuric acid. Erythrosin prepared as described contains solvent of crystallization which, however, is not all alcohol, but in part water. The water has partially resulted from the neutralization of the erythrosin acid by the sodium carbonate, and in spite of the fact that the amount of water is exceedingly small as compared with the large amount of alcohol, nevertheless erythrosin takes up that water, so great is the avidity of the sodium salt to form a hydrate. Completely hydrated erythrosin is obtained when the pure sodium salt, freed from alcohol by drying at 130° C., is dissolved in water, the solution evaporated to dryness under reduced pressure, and the dry residue further dried in a vacuum desiccator.

PURE ERYTHROSIN

In the following table are given the results of analyses of several samples. The relative proportions of alcohol and water in erythrosin were obtained as follows: A weighed sample of the salt (3 to 4 g.) was put in a large boat, placed in a glass tube and heated at the desired temperature, a stream of air carrying the vapors into a combustion tube. From the quantities of carbon dioxide and water produced, the relative amounts of the two solvents in the sample of erythrosin can be calculated. All samples, whether from alcohol or from water, were dried, prior to analysis, over sulfuric acid in a vacuum desiccator for 2½ to 3 hrs., which period should be amply sufficient to free crystalline material from any adhering volatile solvent.

These results indicate clearly that erythrosin combines with both alcohol and water. The actual number of mols of each of the two solvents per mol of dye could only be determined approximately, since in the initial stages of dry-

⁸ *Chem. Zentr.*, 1903, II, 69; 1904, I, 609; 1908, I, 2111.

⁹ *Chem. News*, 103 (1911), 161.

No.	SOLVENT	PRELIMINARY DRYING IN VACUUM DESICCATOR AT ROOM TEMP.	HEATED Temp. °C.	Hrs.	Loss, PER CENT		
					Alcohol	Water	Per cent
1	Alcohol	10 hrs.	Room	10	..	1.10	..
			120-130	1	..	7.01	..
			130	4	..	0.09	8.20
2	Alcohol	4 days	125	9	2.50	..	1.02
			170	4	0.14	..	0.39
			170	4	2.85	..	1.67
3	Alcohol	4 days	170	4	1.67
			170	4	4.52
4	Water	2 1/2 hrs.	Room	9	1.02
			130	1	5.23
			130	3	0.48
			160	16	0.32

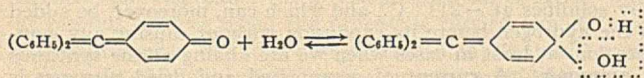
ing in the desiccator, some of the solvent is undoubtedly lost. Approximately, from water the salt contains: 1 mol erythrosin + 4 mols H₂O; from alcohol, 1 mol erythrosin + 2 mols C₂H₅O; from alcohol containing but a very little water, some of each solvent is taken up. But whatever the composition of the hydrated salt, it is obvious that in drying the last portion of the water is retained with extreme tenacity. The question arises—what assurance does one have, outside of the analysis of the dried salt, that all the water has been driven out even when the salt is heated for hours at 160° to 170° C.? May not a state of equilibrium be established at that temperature, wherein liberation of water from the salt proceeds at a very slow rate? Much higher temperatures for drying are inadvisable, for decomposition of erythrosin is likely to set in, evolution of iodine becoming quite noticeable at 200° C. We have analyzed Sample 3 after it had received the treatment described—namely, 4 hrs. at 170°, and Sample 4, which had been dried 5 hrs. at 130° C. and 16 hrs. at 160° C. The results in per cent iodine are:

Sample 3	57.10	56.84	57.01	Av. 56.98
Sample 4	57.20	56.80		Av. 57.00

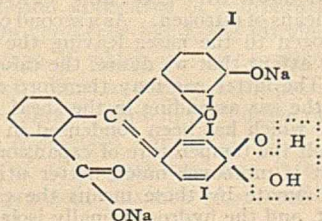
Calculated for C₂₀H₂₄I₂O₅Na₂: 57.70; C₂₀H₂₄I₂O₅Na₂ + H₂O: 56.55

That the long heating in the process of drying the two samples at the temperature recorded did not induce decomposition of erythrosin with possible loss of iodine, is evident from the fact that the acid regenerated from the salt was found to contain the right amount of iodine—viz., 60.51 against 60.75 per cent calculated. The conclusion, therefore, seems to be that the low iodine content—approximately 57.00 instead of 57.70 per cent—of our erythrosin, which had been prepared from very pure acid and had been thoroughly dried, must be due to the retention of water by the salt to the extent of about 1.2 per cent (calculated for 1 mol H₂O, 2.00 per cent).

With regard to the manner in which the water is held, little may be said with certainty. In a series of papers from this laboratory, it has been shown that diphenyl fuchsones and many analogous compounds possess the tendency to combine with water and give rise to quinonoid tautomers of the carbinols of varying degrees of stability.



Erythrosin, on the basis of its constitution and in analogy with the other and simpler fuchsones, may act in a similar manner. The constitution of the salt, then, is as follows:



TECHNICAL ERYTHROSIN

A sample of commercial erythrosin acid of reliable manufacture was subjected to the same analysis as our sample which had been completely purified through the diacetate. The acid, upon digestion with alcohol, was found to be practically free from adsorbed iodine. Dried in a vacuum desiccator and for a few minutes at 130° C., it contained 60.61 per cent of iodine against the theoretical 60.75. The acid was converted into erythrosin, in absolute alcohol with sodium carbonate, just as described for our own sample, and the resulting salt was dried in a vacuum over sulfuric acid at room temperature.

(1) One portion of this erythrosin, which had been dried at room temperature for 12 hrs., was heated at 120° to 130° C., and it lost in alcohol and water, during the first hour and a half, 6.27 per cent, and during the next 4 hrs., 0.3 per cent.

(2) A second portion was recrystallized from water, and the sample, after 13 hrs. in a vacuum desiccator, lost at 130° C., during the first hour, 5.65 per cent, and in the next 3 hrs., 0.36 per cent; after that in 16 hrs. at 160° C., 0.09 per cent.

(3) A third portion, from alcohol, lost in 11 hrs. at 135° C., 7.36 per cent as alcohol and 1.36 per cent as water.

(4) A fourth portion, also from alcohol, lost in 4 hrs. at 170° C., 7.57 per cent as alcohol and 1.2 per cent as water. Now, just as in the case of our own erythrosin, this technical product, in spite of the drastic treatment, did not apparently lose all its water. Here again the salt contained less iodine than it should if it were completely dehydrated. Sample 4 gave 57.27, 57.14, 56.92 per cent; average, 57.09 per cent iodine.

CONCLUSION

The conclusion seems justified that the true composition of erythrosin is C₂₀H₂₄I₂O₅Na₂ + H₂O, and that it is almost impossible to dehydrate it completely without risk of decomposition of the salt. In view of this, we suggest that the specifications of purity be based upon the following principles: (1) Erythrosin should be dried to approximately constant weight at 120° to 125° C., weighings being made at the end of the second hour and every hour thereafter; it should, then, on solution in very dilute ammonia and careful precipitation, hot, with acetic acid followed by a little sulfuric acid, give 93.5 ± 0.5 per cent of its weight of dry erythrosin acid, after adding a correction of 0.4 per cent for each 100 cc. of water used with a 1-g. sample. This solubility correction was found necessary in experiments upon pure erythrosin acid. (2) The precipitated erythrosin acid should give up no iodine to alcohol, and should, when dry, contain about 60.75 per cent of iodine.

Fire Hazards in Oil Refineries

Fires in oil refineries may be caused by lightning or other mishap, or by carelessness in allowing the oil or vapors to become ignited, states the Bureau of Mines in Serial 2400 just issued. Probably the most frequent cause, however, is the failure of refining equipment. Stills are designed to be safe, and usually are safe. Nevertheless, defects sometimes occur, as in all metal structures, and unless promptly discovered and remedied may result in serious fires and explosions. The dangers of refining crude oil are well recognized, and all modern refineries have developed highly efficient systems of inspection and fire prevention.

Further tests have been conducted at Pittsburgh, Pa., by the Bureau of Mines to obtain data as to the comparative sensitiveness of gasoline vapors and methane with respect to their ignition from electric flashes. This work has a bearing on the degree of protection that will be necessary for electric motors used in and around buildings where gasoline vapor may be present.

The Manufacture of Hydrogen by the Partial Liquefaction of Water Gas and Coke-Oven Gas^{1,2}

By Georges Claude

SOCIÉTÉ DE GRANDE, PAROISSE, NEAR MONTREAU, FRANCE

FOR A NUMBER of years already I have been engaged in the manufacture of hydrogen by the partial and direct liquefaction of water gas and its analogues. For this purpose water gas, compressed to a suitable degree, is in the first instance deprived of its carbon dioxide and is dried. The gas is then sent into a heat exchanger, E (Fig. 1), in which it is cooled by circulating in the opposite direction to the hydrogen and carbon monoxide which have already been separated. The gas then enters, by the collector C, the bottom of a sheaf of vertical tubes, F, the lower portion of which plunges into a bath of carbon monoxide boiling under atmospheric pressure. By the combined influences of the pressure and of the temperature of the liquid bath, a large portion of the carbon monoxide of the ascending gases is liquefied; it flows back into the collector C. Owing to the pressure this liquid is forced out through the tube T and the cock R, into the vaporizer V, where it replaces the liquid which is being evaporated. The remaining gas, containing hydrogen and a little of the residual CO, continues to rise in the sheaf of tubes F. There the gases encounter a temperature which is more and more being lowered, by means which I shall presently explain. Under that influence the rest of the carbon monoxide is liquefied. *Theoretically*, therefore, it is a sensibly pure hydrogen which escapes from the top of the tubes, and it is this cold and compressed hydrogen which is expanded in the nozzle D, and further cooled by this expansion to be sent back around the sheaf F, in order there to produce the very low temperatures of which I have just spoken.

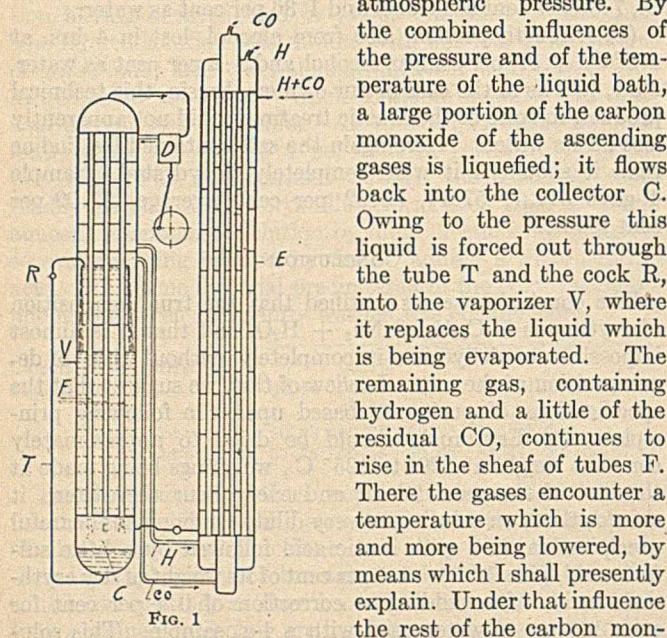


FIG. 1

oxide is liquefied. *Theoretically*, therefore, it is a sensibly pure hydrogen which escapes from the top of the tubes, and it is this cold and compressed hydrogen which is expanded in the nozzle D, and further cooled by this expansion to be sent back around the sheaf F, in order there to produce the very low temperatures of which I have just spoken.

In working this process two sources of inconvenience were experienced which I have only recently been able to overcome. In the first instance, when the hydrogen is arriving at extremely low temperature in the nozzle, as indicated, the frigorific efficiency of the expansion will be very low. There is in that case a "loss" of liquid, unless we go up to pressures regrettably high from the point of view of energy expenditure and this all the more so because none of the customary lubricants can be employed at these temperatures. Hence there is abnormal friction in the nozzle which will again lower the frigorific efficiency. In the second instance, the calorific mass of the gases leaving the tubes, and afterwards

the nozzle D, and circulating about the rising gases, will be smaller than that of the latter by the whole mass of the carbon monoxide which had been liquefied by their action. As a consequence the ascending gas cannot, even assuming a perfect heat exchange to take place, leave the sheaf of tubes at the temperature at which the expanded gases entered the tubes. The final temperature of the expansion of hydrogen will, therefore, not be very low, and in addition this temperature will be badly utilized for the purification of the ascending gases.

These various troubles have been overcome in the following manner:

1—Part of the compressed gas which is entering the system is withdrawn from the heat exchanger E, at a point, M (Fig. 2), before it arrives in the cold portion; it is thus relatively little cooled. It is sent through the tube *t* into an auxiliary system of tubes, G, around which the hydrogen, leaving the bundle and passing on to the nozzle, is being circulated by means of the pipes L and K. This relatively warm gas will then reheat the hydrogen before its expansion and will hence increase the efficiency of the expansion process.

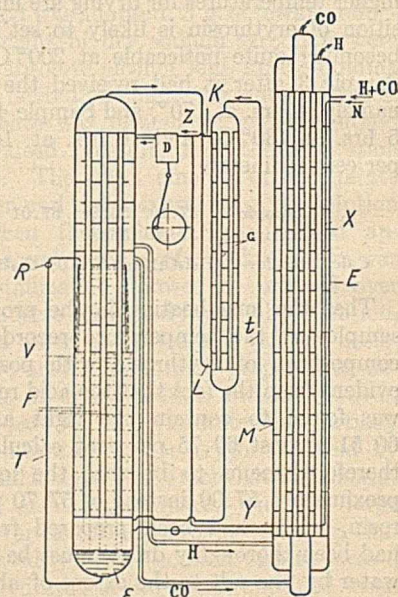


FIG. 2

2—If we relied exclusively upon this means, the final temperature of the expansion would remain bad owing to the want of lubrication and to the eventual freezing out of the residual CO (-206°C). We must manage to lubricate the machinery by a substance which will remain liquid when the temperature sinks below -206°C . That body cannot be petrol ether, or some similar substance, since they would all be solidified at this temperature. I have, therefore, made use of nitrogen which only solidifies at -211°C , and which can, moreover, be added to the hydrogen before its expansion without causing any complication, at least in cases when we are aiming at the synthesis of ammonia. A current of compressed and dried nitrogen is cooled down to about its condensation point in the heat exchanger E by means of the tube system XY; it is then added to the hydrogen at Z, before the hydrogen enters into the nozzle. In this way then we secure acceptable conditions for the lubrication. As a first consequence, the temperature of the escaping gas is easily lowered down to -208° and -210°C , as soon as we lubricate by means of nitrogen. As a second consequence, this addition of nitrogen to the gases leaving the tubular system increases, to any extent that we desire, the calorific mass of the expanded gas. The latter gas may therefore equal or surpass in mass that of the gas ascending in the sheaf F, including the carbon monoxide which has been condensed in this part of the tubes. As a result the temperature of expansion is considerably improved, and it is moreover much better utilized. We can, indeed, easily eliminate by these means the carbon monoxide within 1 per cent, and the hydrogen finally isolated can without

¹ A contribution to a general discussion on "The Generation and Utilization of Cold," held by the Faraday Society and the British Cold Storage and Ice Association, October 16, 1922. Reprinted by permission of Faraday Society.

² Translated by H. Borns.

any difficulty be used in my *hypercompression* process for the synthesis of ammonia.

This process has been developed and put into practice in the works of the Grande Paroisse, near Montereau, where an apparatus for the production of 500 cu. m. of hydrogen per hour is in operation, feeding a unit for 5 tons of ammonia per day. The carbon monoxide containing all the nitrogen of the water gas, it should be noted, is discharged at a percentage which may easily be raised to 85. The hydrogen efficiency is therefore excellent. The carbon monoxide may be utilized either for the manufacture of various chemical products or for driving the internal combustion motors of the installation.

The process which I have outlined requires the compression of the gases to degrees varying with the size of the apparatus from 15 to 30 atmospheres. The first figure applies to apparatus of a capacity of 2000 cu. m. of hydrogen per hour. This process necessitates the command of a relatively high motive power, and one might draw attention to the advantages offered by processes based upon the catalysis of CO into CO₂, such as are, for instance, employed in the Haber process. I have, therefore, studied and tried this process only with a view of its ulterior application to a particularly interesting case—that of the *coke-oven furnaces*, in which the presence of a considerable portion of methane renders catalytic processes inoperative. The complexity of the gas mixtures we have to deal with in this case and the diversity of the freezing points of the constituents might make us fear that we should have to meet serious difficulties in the working of this process. As a matter of fact, however, an apparatus has already been constructed for this purpose and has, after very short trials, been put successfully to service in the Béthune mines. The essential cause of the success is the very high reciprocal solubility of the diverse condensable constituents. This first apparatus has a productive capacity of 350 cu. m. of hydrogen per hour, and it is operating with a compression of about 25 atmospheres. An installation for the utilization of the hydrogen produced by means of this apparatus in the manufacture of ammonia by the application of hyper-compression has already been erected and is actually being put in working order. I hope that this installation will be the point of departure for a much more important installation in which I intend to make use of apparatus for the production of 2000 cu. m. of hydrogen per hour.

One of the essential reasons that make me count upon a development of this process in the coke-oven industry lies in the multiple indirect advantages which the process promises.

On the one hand, since the gases to be treated must already be compressed for the extraction of the hydrogen, we are naturally led to effect the stripping of the gas of its benzene likewise *under compression*. All the benzene, which at present escapes when the process is carried out at atmospheric pressures, will then easily be retained; that will constitute a gain which in certain cases may come up to 1 kilogram of benzene per ton of coke. This improved recovery will, moreover, be attained by means of an infinitely reduced amount of solvent and of heat energy, and at much diminished losses of solvent. The recovery will be effected in absorption and distillation apparatus of comparatively very small dimensions. On the other hand, the ethylene, this precious gas the percentage of which in furnace gases is too low for its successful extraction at atmospheric pressure, may easily be collected to a large extent in the course of the operations. For it will be condensed almost alone in the preliminary cold-exchanger of the apparatus, and it can be extracted as a 40 or 50 per cent mixture which will very readily be

utilizable, either for the manufacture of alcohol or for use in autogenous welding or similar apparatus. To give an idea of the possible importance of this by-product, I may state that, supposing the furnace gas is treated to contain 1.5 per cent of ethylene and that it can all be extracted—that would correspond to our obtaining 200 liters of alcohol per ton of ammonia in addition to other products.

Finally, I should remark that, from the calorific standpoint, hydrogen must be regarded as the very worst of all combustible gases. One cubic meter of hydrogen represents only about 2600 calories (lower calorific power) against the 3000 calories of carbon monoxide and the 10,000 of methane. When we, therefore, extract the hydrogen from coke-oven gases, we, in fact, enrich the gases in a true sense, and it is a considerable enrichment which they undergo, since they become fit for uses for which they would otherwise be unsuitable. When the gas is to be distributed, it will be free of every trace of the condensable impurities that cause so much mischief in our actual gas distribution systems; when it is to be utilized as industrial gas, it will enable us to obtain extremely high temperatures and to combine, under specially interesting conditions, the production of nitric oxide by the Häusser process with the synthesis of ammonia.

These are the principal advantages of the process which I have the honor to describe before you. I should like to emphasize that one of the characteristic essential features of the process is the extreme smallness of the necessary apparatus. An apparatus for 1000 cu. m. of hydrogen per hour requires a sheaf of liquefaction tubes 40 cm. in diameter and 3 m. in height.

Lectures at Naval Academy

The lectures by members of the AMERICAN CHEMICAL SOCIETY before the Naval Academy at Annapolis, Md., have again been arranged for 1922-1923. The officers of the Navy have expressed most cordial appreciation of the efforts which the AMERICAN CHEMICAL SOCIETY has been making to see that they are supplied annually with instructive chemical information from some of its prominent members. The lectures given for the present year are as follows:

- OCTOBER 21 AT 11 A.M.—“The Role Played by Cellulose in the Late War,” by Prof. Harold Hibbert, Yale University, New Haven, Conn.
- NOVEMBER 18 AT 11 A.M.—“The Economic Independence of the United States,” by Dr. Edwin E. Slosson, Head of Science Service, 1115 Connecticut Ave., Washington, D. C.
- DECEMBER 9 AT 11 A.M.—“Nitrogen Fixation and Its Relation to the Production of Food and Explosives,” by Prof. A. H. White, University of Michigan, Ann Arbor, Mich.
- JANUARY 13 AT 11 A.M.—“Chemistry as a Key to International Relations,” by Mr. H. E. Howe, Editor of *The Journal of Industrial and Engineering Chemistry*, 810 Eighteenth St., Washington, D. C.
- JANUARY 27 AT 11 A.M.—“Use of Chemical Agents in Warfare,” by Major E. J. Atkisson, Edgewood Arsenal, Edgewood, Md.
- FEBRUARY 17 AT 11 A.M.—“Helium, Its History, Properties, and Use in Aeronautics,” by Dr. R. B. Moore, Chief Chemist, Bureau of Mines, Washington, D. C.
- MARCH 17 AT 10.30 A.M.—“The Chemical Control of Gaseous Detonation with Particular Reference to the Internal Combustion Engine,” by Mr. Thomas Midgley, Jr., General Motors Research Corporation, Dayton, Ohio.

Platinum Theft

During the past summer platinum thieves twice visited the State University of Iowa. On the first occasion two platinum crucibles with their covers were stolen from the physical laboratory, and on the second a desk in the analytical laboratory was broken open and several crucibles and their covers taken. A further unsuccessful attempt was made between November 4 and 6, 1922, when a desk was forced open and an effort made to open the safe in the storeroom. The university has not yet succeeded in tracking down the thieves.

The Measurement of the Plasticity of Clay Slips^{1,2}

By Robert E. Wilson and F. P. Hall

RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

The paper emphasizes the great need of a quantitative measure of the physical properties commonly included in the term "plasticity" of clays and clay slips. Various indirect methods previously suggested are likely to lead to erroneous conclusions, while measurement of the flow or apparent viscosity of clay slips made up with a constant amount of water is shown to give misleading results.

The work described in this paper is preliminary in nature, and has been confined to a study of the properties of clay-water mixtures in the casting rather than in the molding range. In the light of these results, it is recommended that, instead of the vague term "plasticity," the properties of a given clay, at least for casting purposes, be expressed in terms of (a) the water content required to give proper working consistency, and (b) the resistance of the resulting slip to small deforming forces—such as gravity. Specifically, use is made of a modified Bingham plastometer, and the figures reported are: (a) the amount of water required to give a slip of a specified mobility, and (b) the yield value of the slip thus obtained.

The method is shown to be capable of giving quantitative figures

for the yield values at constant mobility which correspond well with the customary qualitative ideas as to the plasticity of clays. The amount of water required to give constant mobility varies to a surprising extent, and does not seem to bear any definite relationship to the usual classifications of more and less plastic clays. It probably does parallel fairly well the shrinkage or drying.

Small amounts of acid or alkali are shown to have a negligible effect on the mobility of a clay slip but a very large effect on the yield value, the variations being greater than the difference between a nonplastic kaolin and a highly plastic ball clay. This brings out the necessity, and indeed the potential value, of carefully controlling the hydrogen-ion content of the water used in making the slips.

Some preliminary data are given on the effect of additions of flint and similar nonplastic materials to clay slips.

It is recommended that an attempt be made to agree upon standard dimensions for the capillary and the desirable mobility for various purposes, and that the plastometer then be used as a standard method of test in the ceramic industry.

FROM a practical standpoint, "plasticity" is one of the most important properties, or rather combination of properties, possessed by any clay. Different clays are known to vary greatly in plasticity. Furthermore, in practical clay working substances are frequently added for the express purpose of increasing or decreasing the plasticity of the final mix.

In spite of these facts, however, no unit of plasticity has ever been defined, and there is no generally accepted method of measuring or comparing the plasticity of different clays. To be sure, many indirect methods have been suggested for its quantitative measurement—for example, the amount of adsorption of malachite green, the adsorption of alkali from various salt solutions, the strength of clay bodies after drying, the amount of water required to bring the clay to proper consistency, etc., etc. These factors are undoubtedly in some way related to plasticity, being common results of similar causes, the main factors probably being the fineness of subdivision of the ultimate particles and their affinity for water. It is nevertheless true that in many cases clays—e. g., fuller's earth—possess high adsorptive power for dyes, etc., and yet low plasticity. Such indirect methods of measuring plasticity have therefore not met with any general acceptance, and experienced clay workers still place ultimate reliance on empirical tests, although even such individuals do not consistently agree with one another.³

It is obvious that the ultimate solution of the problem must involve a measurement of the physical properties of a clay slip with a water content approximately correct for practical use. Some efforts have been made in this direction by determining the flow of a clay slip through an orifice or by the use of paddle wheel viscometers, but these have not

given satisfaction, partly because of the difficulty in determining just how much water should be added before making the test, and partly because it is not possible to measure the true viscosity of clay slips, as is evidenced by the subsequent discussion.

The most promising possibility for making the desired measurement is the use of a device such as the plastometer, recently developed by Prof. E. C. Bingham, and well described in *Scientific Paper 278* of the Bureau of Standards. Professor Bingham has shown that when a plastic substance flows through a capillary of constant dimensions, the amount of flow is not directly proportional to the pressure used, as in the case of viscous liquids, but departs therefrom by giving abnormally low rates of flow for low pressures and then increasing more rapidly at higher pressures. The two different types of flow curve are illustrated very clearly in Fig. 1, which presents results for a very viscous oil and for a clay slip, in the capillary used in the work described in this paper.

It is Professor Bingham's belief that the rounding off in the curve in the lower portion may be due to slippage or seepage, and that the laws of plastic flow may for all practical purposes be represented by a straight line intersecting the abscissa axis at some point to the right of the origin. The

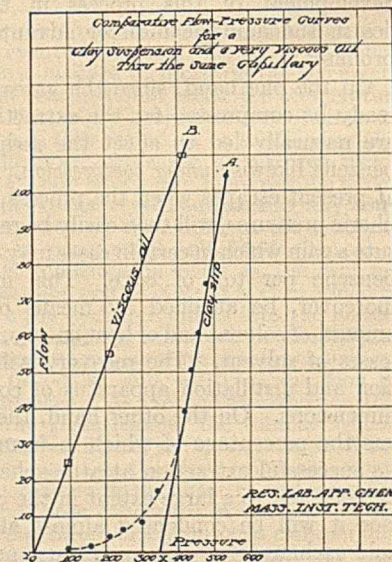


FIG. 1

¹ Received October 5, 1922. Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, September 6 to 10, 1921.

² Published as Contribution No. 63 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

³ This has been strikingly confirmed by a paper by Bole which appeared after this paper had been written—see *J. Am. Cer. Soc.*, 5 (1922), 469.

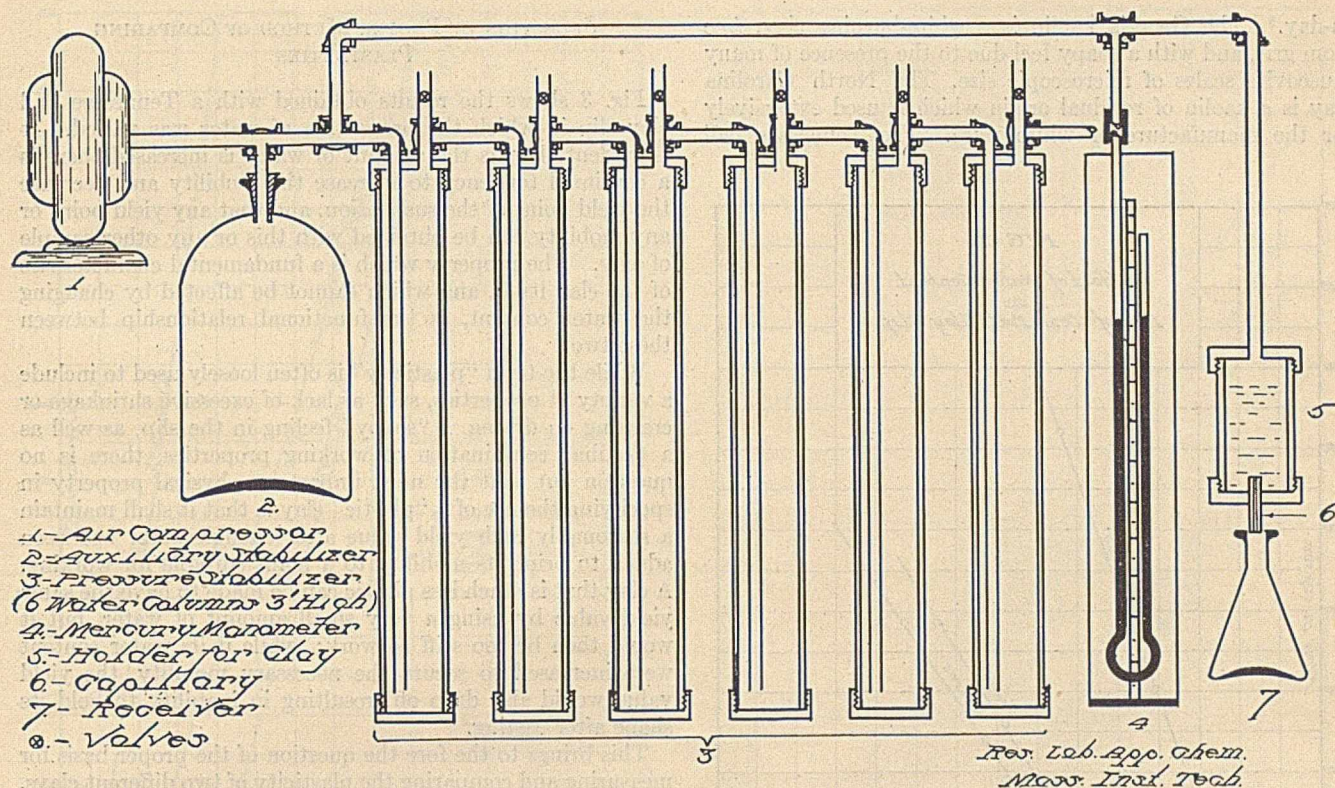


FIG. 2—MODIFIED BINGHAM PLASTOMETER

distance to the point of intersection, in proper units, is defined as the yield value, and the slope of the line is a measure of the mobility of the suspension. It is not the purpose of this paper to discuss the rather involved points with regard to the cause and equation for the lower curved portion of this line, or the questions that have arisen as to the degree of dependence of the results on the size of the capillary used. Both these factors, while of considerable theoretical interest, may for practical purposes be eliminated by agreement upon a standard capillary and by working with proper pressures, just as has been done in practical viscometry by using the Saybolt instrument.

Thus, the reason for the difficulties and apparent contradictions encountered in measuring the "viscosity" of clay slips becomes apparent. The calculation of viscosity from a single flow-pressure observation tacitly assumes that flow is directly proportional to pressure. For example, in the two curves in Fig. 1 a measurement at very high pressure would indicate that the clay slip had a lower viscosity than the oil, while measurements at pressures of 100 or 200 g./sq. cm. would indicate that the clay was more than ten times as viscous as the oil. By determining the complete curves and separating the apparent viscosity into its two components, mobility and yield value, the whole matter becomes clear. An attempt along somewhat similar lines was made by Bleininger and Ross,⁴ who measured the flow through an orifice of various clay mixes under variable pressure, but they drew no conclusions as to the significance of the results, or possible ways of measuring or expressing the two separate factors involved.

APPARATUS AND MANIPULATION

The apparatus used was a modified Bingham plastometer, shown diagrammatically in Fig. 2. It consists chiefly of a

pressure stabilizer for maintaining constant pressure of several different magnitudes, a container for holding the material to be tested, into the lower end of which is fastened a capillary, and a manometer for measuring the pressure. A general description of the apparatus is given by Bingham in *Proceedings of the American Society for Testing Materials*, 19 (1919), Part II. The flowmeter as described by Bingham and Green was not used in these measurements, but the weight of the discharge and the density of the clay slip were used to determine the volume. The instrument is limited to materials having a very slow "settling time." Furthermore, for very stiff pastes the pressure range must be great enough to permit the linear portion of the curve to be determined.

A number of preliminary trials were made to determine what size of capillary seemed most suitable for use on slips in the casting range. The smaller capillaries, such as used by Professor Bingham, were not found satisfactory in working with clay slips, especially when coarser particles were admixed. When the most suitable capillary was finally selected, its dimensions were carefully determined—the diameter by filling it level with mercury and weighing. It was found to have the following dimensions: length, 5.020 cm.; diameter, 1.3624 mm.

The capillary was later measured at the Bureau of Standards with a high-power micrometer microscope, which gave a figure of 5.021 cm. for the length and 1.3636 mm. for the average diameter.⁵ This capillary was used in all the tests discussed in this paper except where otherwise noted.

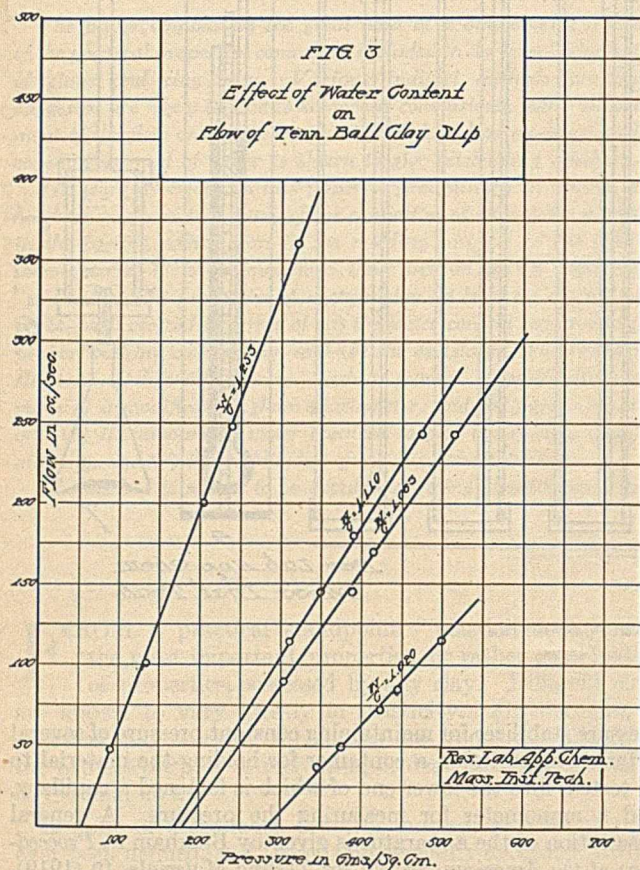
SOURCE AND TREATMENT OF CLAY SAMPLES

The clays used in these experiments were selected as representative of the clays used in the ceramic industry

⁵ Calculated from major and minor axes of tube, cf. *Z. physik. Chem.*, 80 (1912), 683.

⁴ *Trans. Am. Cer. Soc.*, 16 (1914), 392.

to-day.⁶ The Georgia kaolin is a white-burning clay, free from grit, and with a soapy feel due to the presence of many muscovite scales of microscopic size. The North Carolina clay is a kaolin of residual origin which is used extensively for the manufacture of white ware. The Tennessee ball



clay is a very plastic clay of sedimentary character and possesses very good bonding-power. The English ball clay is similar to the Tennessee ball clay. The English china clay is a very lean, white-burning kaolin. Several fire clays were tested, but their history was not known. All except the ball clays were subjected to a washing process before they were used. This is the same treatment that they receive before being put on the market.

The clays were prepared for use by grinding until the entire mass passed the 65-mesh sieve. No attempt was made to separate the clay into different fractions. It is known that very fine grinding affects the plasticity, so it was thought best to use a large capillary in the plastometer and avoid grinding the clay so fine that its character would be changed.

All the slips were made by adding weighed amounts of distilled water to a sample of the ground clay as received, but the ratio of water to clay was calculated to a bone-dry basis by making determinations of total water content up to 900° C. on separate small samples of each clay. The losses on ignition thus determined were as follows:

CLAY	Loss on Ignition Per cent
English china.....	14.20
Georgia kaolin.....	11.80
Tennessee ball.....	10.25
English ball.....	13.00
North Carolina.....	12.00

⁶ They were obtained from B. F. Drakenfeld Co. of New York City as representative samples of commercial clays.

SELECTION OF PROPER METHOD OF COMPARING PLASTICITIES

Fig. 3 shows the results obtained with a Tennessee ball clay slip in which the proportion of water was varied. It is evident that as the amount of water is increased there is a continual tendency to increase the mobility and decrease the yield point of the suspension, and that any yield point or any mobility can be obtained with this or any other sample of clay. The property which is a fundamental characteristic of the clay itself, and which cannot be affected by changing the water content, is the functional relationship between these two.

While the term "plasticity" is often loosely used to include a variety of properties, such as lack of excessive shrinkage or cracking on drying, a "soapy" feeling in the slip, as well as a peculiar combination of working properties, there is no question but that the most important physical property in specifying the use of a "plastic" clay is that it shall maintain a reasonably high yield value after enough water has been added to bring its mobility to a point suitable for working. A clay that is much less plastic can be made to have the same yield value by using a very small amount of water, but it would then be too stiff to work; while if its water content were increased to secure the necessary mobility, the yield value would also drop off, resulting in inability to hold its shape after casting.

This brings to the fore the question of the proper basis for measuring and comparing the plasticity of two different clays. One suggestion is the addition of a definite amount of water to the clay, followed by a determination of the flow curve. Fig. 4 shows the results obtained on three different clays with a constant ratio of water to clay of 1.253.⁷ It is impossible, however, from an inspection of such results, to decide which is the most plastic clay, because the question immediately arises—if less water had been added to the Tennessee ball clay, thus moving the line to the right, how would its slope compare with that of the other two?

It is therefore apparent that constant water content tests, though quite frequently employed in comparing clays, do not afford a suitable basis for comparison. Instead, the amount⁸ of water required to give suitable working properties to the clay is in itself an important property of the clay, which should certainly be determined, but which is distinct

⁷ All the figures in this paper are plotted in terms of the actual flow (cc./sec.) and pressure (g./sq. cm.) used with the specified capillary. It would be desirable to express these in terms independent of the particular capillary employed, but in view of the previously mentioned uncertainty as to the precise validity of Bingham's simple equations, this has not been done. However, for purposes of comparing results between capillaries that do not vary widely in dimensions, use can well be made of the formula: (see Bingham, "Fluidity and Plasticity," McGraw-Hill, 1922, p. 233.)

$$\mu = \frac{1.273 \nu}{R^2(F-f)}$$

where μ = mobility

f = friction or yield value

ν = volume of flow in cc./sec.

F = shearing force applied at the wall of the capillary in dynes/sq. cm.

$$= \frac{980.6 RP}{2L}, \text{ where}$$

R = radius of the capillary in cm.

P = applied pressure in g./sq. cm.

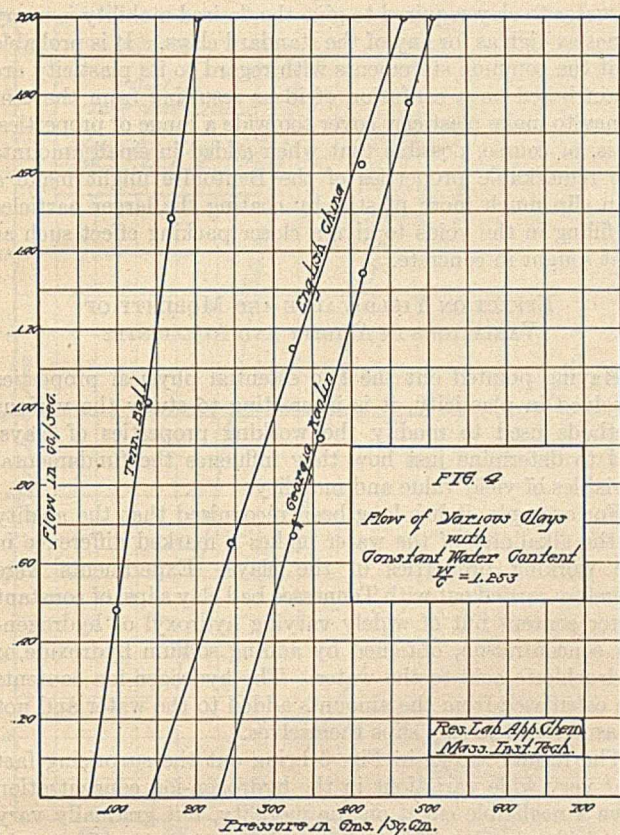
L = length of the capillary in cm.

The calculated yield values for the capillary used in the foregoing work in terms of shearing force in dryness per sq. cm. may therefore be obtained by multiplying the graphically determined yield values given in this paper by

$$\frac{980.6 \times 0.06815}{2 \times 5.021} = 6.65$$

and the mobilities by substituting in the above equation.

⁸ In the molding range this quantity is sometimes designated by the ceramists as the "water of plasticity."



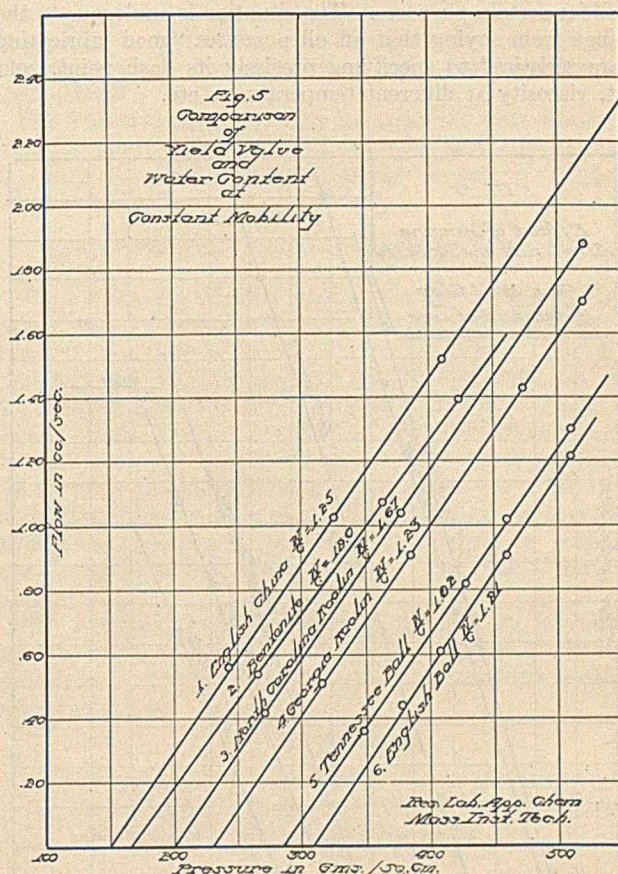
from plasticity. It is probably related to the amount of shrinkage on drying.

The question next arises as to how to determine when enough water has been added to give the resulting slip-working properties suitable for a given purpose. Several clays of quite different plasticities were made up to possess as nearly as possible similar working properties, and from this test—which should be further confirmed by investigators more closely familiar with ceramic practice—it appears that clays of *constant mobility* possess substantially identical working properties. The correct mobility value naturally varies with the purpose for which the clay slip is used, that selected for these tests being considered approximately correct for casting purposes before “freeing out” with alkali.

Clays should therefore be compared on the basis of (a) the amount of water required to give a specified mobility, and (b) the magnitude of the yield value when this amount of water has been added, this value presumably being higher the more “plastic” the clay. The testing of clays by this method unfortunately necessitates working by trial and error, and determining two points on the flow curve for each change in the amount of water added, but once the worker is fairly familiar with it he can approximate the proper mobility quite closely by estimation.

It is, of course, conceivable that by studying a large number of clays to which different amounts of water had been added, a definite functional relationship between mobility and yield value would be found to hold for a given type of clay, regardless of the water content, in which case only one measurement would have to be made. For example, it has been found as a rough approximation that for two samples of clay over a twofold range of mobilities the yield value \times mobility^{1.7} = a constant, but tests on a third kind of clay did not bear this out.

While the foregoing method of defining and measuring the more important physical properties included under the vague



term “plasticity” has thus far been applied only to the casting range, there seems to be no fundamental reason why it should not be extended to the molding range, although the high pressures required and the maintenance of steady flow may present rather serious experimental difficulties.

It should be noted that this method of analyzing “plasticity” into its more important components crystallizes the whole problem and avoids such inconsistencies as the statement of some ceramists that clay passes through a narrow region of “maximum plasticity” in the molding range as the water content is increased. It is certainly highly improbable that any physical property really passes through a maximum with increasing water content, and the popular conception is again believed to be due to the attempt to include too many properties in a single term. In other words, the region of “maximum plasticity” is in reality simply the region of the most desirable working properties (for molding) between the point where the clay is too stiff on account of insufficient water and too sticky or fluid from too much water.⁹

On account of the loose use of the term “plasticity,” which can probably never be eradicated, the writers are inclined to recommend that, instead of considering the yield value at constant mobility as a direct measure of “plasticity,” the term be dropped entirely when referring to the physical properties of the slips. If water content and yield value at constant mobility should not be found to comprise all the important properties now included under “plasticity,” an additional quantitative measurement and term could be added, but the separate properties of the clay should be accurately measured and uniquely defined rather than using a vague general term which means essentially “good working proper-

⁹ A very recent paper on “The Plasticity of Clays,” by J. W. Mellor (Communication from the Clay and Pottery Laboratory, Stoke-on-Trent, No. 53), has thrown interesting light on this question from a somewhat different point of view.

ties" for certain purposes. The situation is analogous to the change from saying that an oil possesses "good lubricating characteristics" to specifying precisely its flash point, cold test, viscosity at different temperatures, etc.

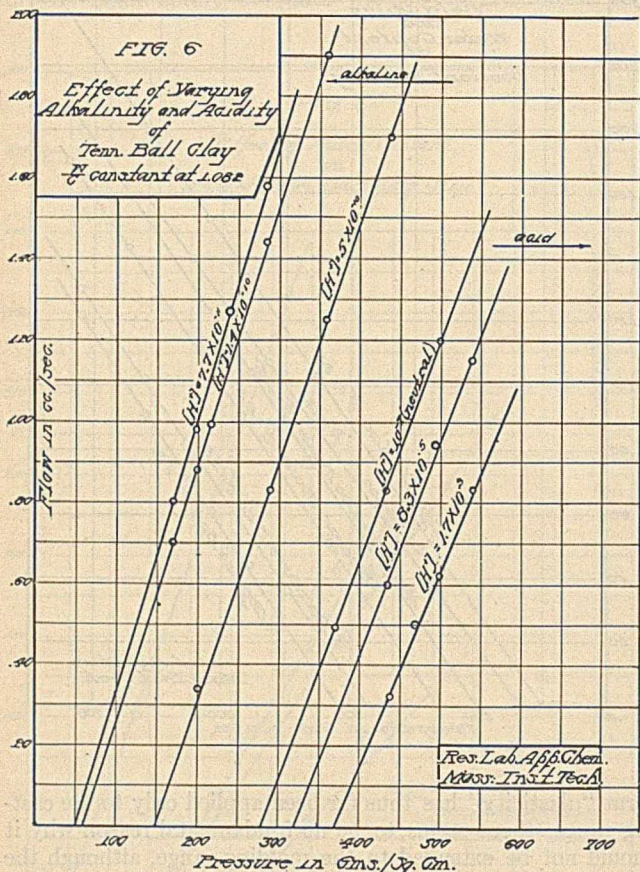
of water to clay required to give the desired mobility is many times as high as for any of the standard clays. It is probable that the common statements with regard to its plasticity are again based on a confusion of ideas resulting from the tendency to make plasticity cover too wide a range of properties. It is, of course, possible that when added in small amounts the remarkable properties of the Bentonite might make a lean slip much more plastic, by coating the larger particles or filling in the voids to give a closer packing effect such as that sought in concrete.

EFFECT ON YIELD VALUE AND MOBILITY OF VARIATIONS IN ACIDITY AND ALKALINITY

Having pointed out the two essential physical properties involved in plasticity, it is interesting to study the various methods used to modify the working properties of clays, and to determine just how they influence the fundamental variables of yield value and mobility.

For example, it has long been recognized that the acidity or the alkalinity of the water makes a marked difference in the working properties of the clays. Experiments were therefore carried out with Tennessee ball clay slips, of constant water content but of widely varying hydroxyl or hydrogen-ion concentration, obtained by adding sodium hydroxide or hydrochloric acid to the water. The hydrogen-ion contents are calculated from the amounts added to the water and not measured in the clay slips themselves.

The results shown in Fig. 6 bring out the surprising fact that very wide variations in the hydrogen-ion concentration have a negligible effect on the mobility, but gradually vary the yield value from 50 in alkaline solutions up to 370 in acid solutions. The function of alkalis in "freeing out" the clay, and of acids in "setting up" the clay, thus becomes quite apparent. It is also worthy of note that the yield value of at least this sample of clay can be varied by moderate additions of acids or alkali to cover a wider range than the whole



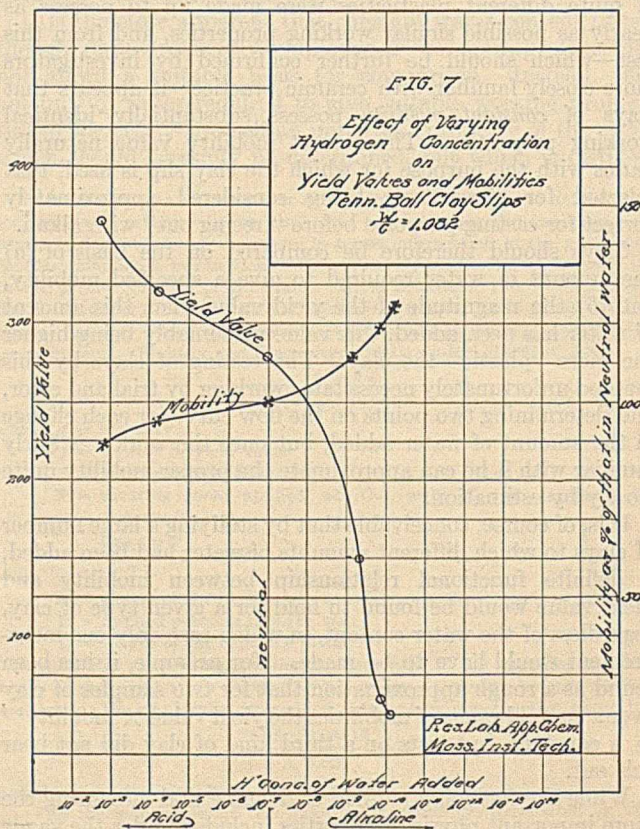
COMPARISON OF YIELD VALUES AND WATER CONTENTS AT CONSTANT MOBILITY

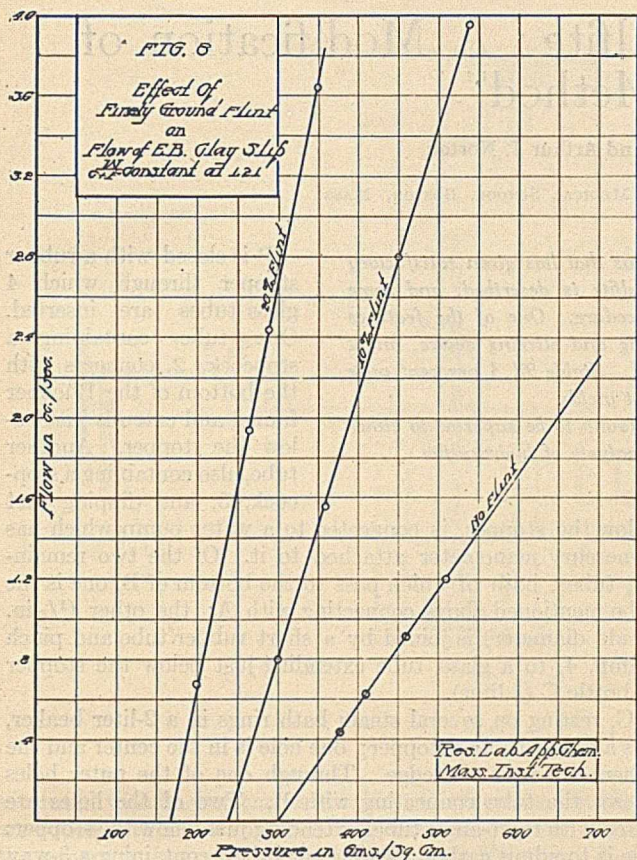
For the reasons previously discussed, the water content of six samples of clay was adjusted to give a constant mobility suitable for casting, and the yield points and water contents at these mobilities were compared. The results are shown graphically in Fig. 5.

Neglecting for the moment the sample of Bentonite, it will be noted that the order in which the clays arrange themselves with increasing yield value is as follows: English china clay, North Carolina kaolin, Georgia kaolin, Tennessee ball clay, and English ball clay. This corresponds very well with the customary belief as to the relative plasticity of these clays, and thereby confirms the essential validity of the test. It will be noted that the ratio of water to clay required to give these mobilities is quite variable, being as low as 1.02 for the Tennessee ball clay and as high as 1.67 for the North Carolina kaolin. Of the samples tested, the kaolins on the average required more water than the ball clays. The futility of comparing different clays at constant water content is obvious.

One very interesting sample is the Bentonite, a peculiar soapy clay of which there are large deposits in Wyoming.¹⁰ Although the Bentonite is customarily spoken of as being extremely plastic, it will be noted that on the selected basis of comparison its yield point is rather low, but that the ratio

¹⁰ The tests on the Bentonite were made later by Mr. C. E. Ronneberg of this laboratory with a capillary differing slightly in dimensions, but the results were corrected to make them comparable.





series of commercial clays when mixed with distilled water. The necessity, and indeed the potential value, of controlling the hydrogen-ion concentration of clay slips therefore becomes obvious.

Fig. 7 shows graphically how the observed yield value and mobility vary with the H-ion concentration—the sharpest change in the yield value is obviously between a calculated pH of 8 and 10.

EFFECTS OF ADDITIONS OF NONPLASTIC MATERIALS

Fig. 8 shows the effect of adding varying amounts of finely ground sand (Potters flint) to the clay slip, keeping constant, however, the ratio of water to total dry solids. The flint obviously does not hold nearly as much water as the clay, and the effect of replacing clay with flint is therefore similar to that of adding water to the slip, increasing the mobility and decreasing the yield values. It seems, however, in comparing the results with the addition of water alone, that the effect of the flint on yield value is less than that on the mobility. Additional tests should be made on mixtures of constant mobility and constant ratio of water to clay, but of variable amount of flint.

The foregoing study is obviously preliminary in nature, but it is being continued by the junior author at the Bureau of Standards, a thorough investigation of the whole problem being under way.

ACKNOWLEDGMENT

The writers desire to acknowledge the helpful suggestions of Professor Bingham in connection with the inauguration of the work and the preparation of the paper.

Moving Picture Films

In line with the effort of THIS JOURNAL to supply its readers with information in regard to available moving picture films of industrial and educational value, the following list has been

compiled. Data in regard to the source of these films may be obtained from the editorial office.

- Acetylene Flame
- Aids to Cupid (Perfumes)
- Air
- Air Nitrate
- American Roquefort Cheese. Made from Cow's Milk
- Analysis of Motion
- Aqua
- Asbestos for a Thousand Years
- Asphalt Industry
- Asphyxiating Gases
- Automobile Starting and Lighting
- Babcock-Henry Milk Test
- Belt Making and Tanning
- Bleaching
- Cane Sugar
- Cane-Sugar Industry of the United States
- Cane-Sugar Refining
- Carbonic Gas
- Casinghead Gas and Pipe Lines
- Casting Milk Bottles
- Catching and Canning Oregon Salmon
- Cement and Concrete Tests
- Chemical Action
- Chemistry
- Chemistry of Combustion
- Chocolate and Cocoa Industry
- Chu Chu
- Cigars for Kings and Millionaires
- Coal Mining in France
- Cocoa
- Cocoa and Chocolate from Bean to Cup
- Cocoa Industry in Trinidad
- Coconuts and Copra
- Colombia Sugar Plantation
- Concrete Industry
- Conductivity of Heat
- Copra
- Copper Mining, Milling and Smelting
- Copper Smelting
- Cotton Manufacture
- Crystals, Their Making, Habits, and Beauty

- Crystallization
- Cultivating Rubber Plants and Making Rubber Shoes
- Cultivation of Rubber
- Decomposition of Ultra-Rapid Movements
- Delcolight
- "De-Light"
- Demonstration of Inflammability of Coal Dust and Use of Rescue Apparatus
- Dust Explosions in Mills and Elevators
- Dust Explosions in Threshing Machines
- Dynamite-Making
- Earth and Moon
- Earth and the Worlds Beyond
- Electrical Precipitator
- Electrolysis of Metals
- Experiments with Liquid Air
- Experiments with Sulfur
- Expert Classblowing
- Explosive Dusts
- Famous Experiments in Electricity and Magnetism
- Felt
- Fire Prevention
- Flaming Ice
- Formation of Dew
- From Blast Furnace to Finished "National" Pipe
- From Flax to Linen
- From Mine to Molder
- From Pig Iron to Finished Products
- From Pulp to Paper
- From Rubber Tree to Fountain Pen
- From Trap to Can
- From Wheatfield to Oven
- From Wheat to Flour
- Frontiers of a Forbidden Land
- Getting Acquainted with Bacteria
- Glimpses of Making Bricks, Concrete Blocks, and Steel Rails

- Goodbye, Boll Weevil!
- Grape Juice Industry
- Gypsum
- Hang It All (Wall Paper)
- Heat
- How a Blossom Opens
- How Charcoal Is Made
- How Life Begins
- How Movies Move
- How Petroleum Is Produced
- How Plaster Is Obtained
- How the Telephone Talks
- Hydrogen
- Just Kids (Gloves)
- Kelp Industry
- Lead Industry
- Light
- Liquid Air
- Liquid Air and Applications of Intense Cold
- Lubrication
- Made Game
- Magic Clay
- Making a Silk Hat
- Making Brushes
- Making Chocolate
- Making Condensed Milk
- Making Maple Sugar
- Making Natural Color Films
- Making of Fine Tools
- Making of Pure Foods in Battle Creek
- Making of Soap
- Making of White Lead
- Making Rubber Tires
- Making Russian Caviar
- Manufacture and Use of Sulfate of Ammonia
- Manufacture of Adhesives
- Manufacture of Breakfast Food
- Manufacture of Charcoal
- Manufacture of Coke
- Manufacture of Face Brick

- Manufacture of Glue
- Manufacture of Matches
- Manufacture of Steel for Sheets and Plates
- Manufacture of Varnish
- Manufacture of Zinc Oxide
- Manufacturing Paper Money
- Marvels of Crystallization
- Match-Making
- Meat-Packing
- Mechanics of Fluids
- Mechanics of Fluids in Motion
- Mechanics of Solids
- Microscopical View of the Blood Circulation
- Mining and Extraction of Radium from Carnotite Ore
- Modern Metallurgy
- Modern Oil-Refining Plant
- Modern Sugar Refining
- Molecular Mechanics
- Muscle Shoals Nitrate Plant
- Mysteries of Snow
- One of the World's Great Copper Mines
- Origin of Coal
- Oxygen
- Paint and Varnish Making
- Physics Made Amusing
- Pickling Some of the "57"
- Picturesque in American Science
- Picture Story of Tea and Coffee
- Pictures in Chemistry
- Production and Use of Asphalt
- Pure Foods—Oleomargarine
- Rainey's African Hunt
- Romance of a Window
- Romance of Gloversville
- Rope Industry
- Rough Stuff (Carborundum)
- Safety Lessons in a Metallurgical Plant
- Salt Industry
- Science of a Soap Bubble
- Scientific Amusements

Purifying Sodium Hydrosulfite: A Modification of Jellinek's Method^{1,2}

By Walter G. Christiansen and Arthur J. Norton

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AS THE toxicity and sulfur content of arsphenamine prepared by reduction of 3-nitro-4-hydroxyphenyl-arsonic acid with commercial sodium hydrosulfite can be made to vary between wide limits, depending upon the conditions under which the nitro group is reduced,³ and as commercial hydrosulfite usually is of 80 to 87 per cent purity, it became important to determine whether the hydrosulfite itself or the impurities present in commercial samples cause the variations which are obtainable. For this purpose, it was necessary to secure hydrosulfite in a pure form. Jellinek⁴ developed a method of purifying commercial hydrosulfite which gave, in a 50 per cent yield, material analyzing 99.4 per cent $\text{Na}_2\text{S}_2\text{O}_4$; this is the average of a number of experiments. While using Jellinek's method it has been found possible to modify his apparatus and procedure in many ways so that a simpler and more rapid process has been evolved by which pure sodium hydrosulfite may be obtained. After the apparatus has been assembled, it is possible to obtain in 4½ hrs. a 42 per cent yield of hydrosulfite 98.3 per cent pure from commercial material of approximately 85 per cent purity. In outline, the procedure is to saturate an aqueous solution of hydrosulfite with sodium chloride, thereby precipitating $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, which must be dehydrated and dried in order to be stable; all the manipulating must be done *in vacuo* or in an atmosphere of carbon dioxide.

APPARATUS

Carbon dioxide is obtained by running hydrochloric acid (1:2) from an elevated bottle through an intermediate bottle, which serves as a reservoir for CO_2 developed in excess of the amount leaving the generator, onto marble contained in a liter suction flask; this flask, M, carries a siphon to remove spent acid. The gas is washed twice with 10 per cent aqueous sodium bicarbonate and once with water. At this point, a shunt containing a calcium chloride tube is inserted so that dry carbon dioxide can be used after the hydrosulfite has been dried. A T-tube with one arm dipping into a tube of mercury serves as a safety valve.

A is a 600-cc. bottle, the bottom of which has been replaced by a piece of canvas with hardened filter paper on each side; the bottle is firmly cemented into a Büchner funnel with litharge and glycerol. The rubber stopper in A has 3 holes—one for a tube to admit carbon dioxide, another for a tube containing a stopcock, 1, and leading to the bottom of bottle B (750 cc.), and the third for a ½-in. glass tube closed by a rubber stopper; all three tubes extend only slightly below the stopper.

In the following paper an apparatus that has given satisfactory results in purifying sodium hydrosulfite is described, and some changes are made in Jellinek's procedure. One of the features of the apparatus, a combined filtering and stirring device, might be useful in processes other than this. Stable 98.3 per cent pure hydrosulfite is obtained in 42 per cent yields.

The ferricyanide method has been found to be superior to either the copper or silver method for the analysis of hydrosulfite.

B is closed with a rubber stopper through which 4 glass tubes are inserted. One tube, containing a stopcock, 2, connects with the bottom of the Büchner funnel and extends just below the stopper. Another tube, also containing a stopcock, 3, and dipping just

below the stopper, is connected to a water pump which has a mercury manometer attached to it. Of the two remaining tubes, both of which pass to the bottom of B, one is the tube mentioned above connecting with A; the other (¼-in. inside diameter) is joined by a short rubber tube and pinch clamp, 4, to a glass tube extending just below the stopper of bottle C (1 liter).

C, resting on several steam bath rings in a 2-liter beaker, has a 5-hole rubber stopper; one hole is in the center and the others are near the edge. Through one of the outer holes passes the tube connecting with B. Two of the holes are fitted with right-angle tubes extending just below the stopper; one is to admit carbon dioxide, the other, containing a 3-way cock, 5, leads to a 2-liter suction flask and thence to the water pump. The remaining outer hole has a short ½-in. tube closed by a solid rubber stopper. The carbon dioxide tubes of bottles A and C are connected to a 3-way cock, 6. Through the center hole of C there is a short heavy-walled piece of hard rubber tube which extends a little below the stopper and about ½ in. above it; this rubber tube serves as a sleeve for a combined filtering and stirring device.

The filtering and stirring device is constructed by sealing a glass funnel to a long piece of glass tube to which 2 short closed tubes have been sealed on opposite sides about 2 in. above the conical part of the funnel. To the ends of these tubes are attached vertical glass rods, the lower ends of which are flattened and bent so as to act as scoops. These scoops are level with the lower end of the funnel and slightly away from it. The funnel is closed with a Hirsch plate over which a piece of canvas is tightly sewed. A small hole is blown in the upper part of the long glass tube and then the upper end of this tube is sealed off. This device is passed through the hard rubber sleeve, and a snugly fitting glass T-tube, *d*, is slipped onto the upper end of the glass tube and firmly fixed by wiring on rubber tubes so that the side arm is opposite the hole in the long glass tube. The side arm is, or may be, connected to the remaining arm of cock 5. The closed end of the filter-stirrer is joined by a rubber stopper to a pulley which connects with a motor. Over the top of the hard rubber sleeve is a tightly fitting rubber tube which fits the filter-stirrer loosely but which can be made tight by wiring. When stirring is in progress this rubber tube is allowed to be loose around the filter-stirrer and the side arm is disconnected at *e* from the 3-way cock and closed by a glass plug. At all other times the rubber tube is wired tightly and the side arm is connected to the 3-way cock.

PROCEDURE

All solutions, except the one of caustic soda and absolute alcohol which are used in the dehydration and drying, are

¹ Received June 15, 1922.

² This is the eighth of a series of studies on the properties contributing to the toxicity of arsphenamine being made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School. The work is under the general direction of Dr. Reid Hunt.

³ Christiansen, *J. Am. Chem. Soc.*, **43** (1921), 2202; **44** (1922), 847.

⁴ *Z. anorg. Chem.*, **70** (1911), 93.

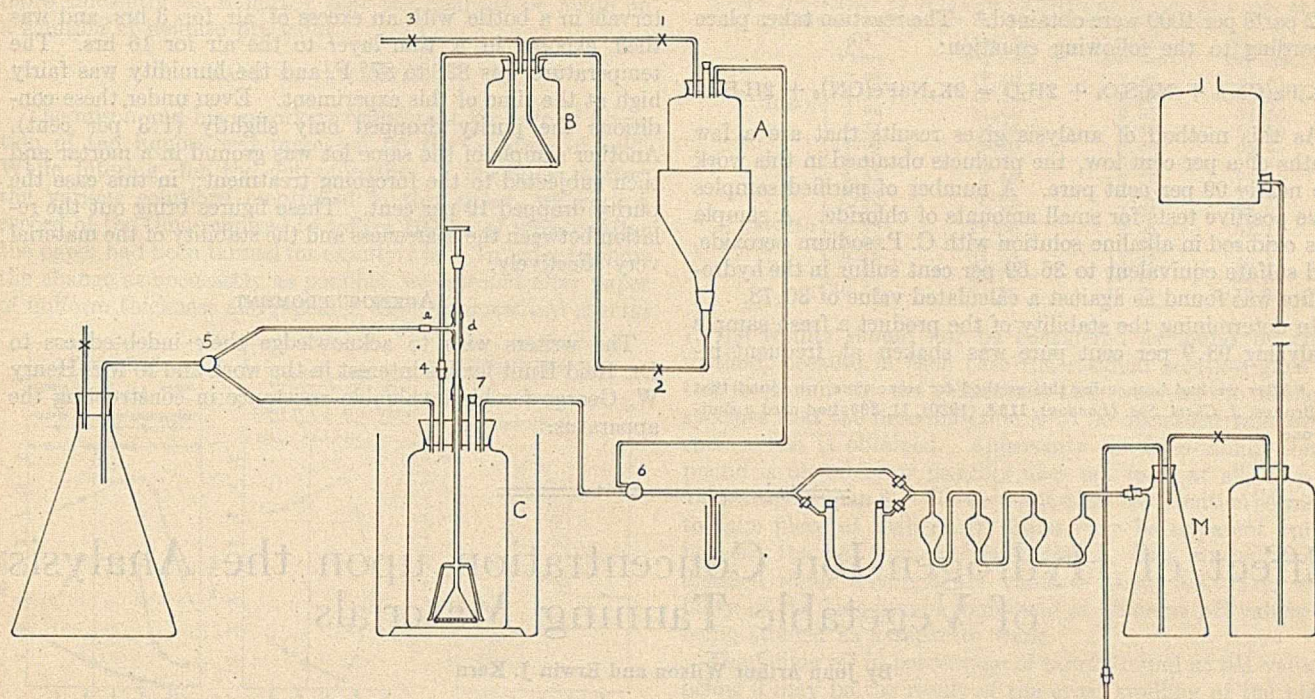


FIG. 1

saturated with washed carbon dioxide, and all pieces of rubber are boiled with alkali and then with water before use. After the apparatus is assembled and made perfectly tight, it is evacuated and filled several times with carbon dioxide; 165 g. of finely ground C. P. sodium chloride are introduced into C through 7, and C is again evacuated and filled with carbon dioxide. To 600 cc. of freshly distilled water, cooled in an Erlenmeyer flask in presence of carbon dioxide, 150 g. commercial hydrosulfite are added, with mechanical stirring to prevent caking. Several grams of Superfiltchar,⁵ which has been kept *in vacuo* over caustic soda and pyrogallol for several days, are added to adsorb any fine material which might pass through the filter. With all the stopcocks closed and with carbon dioxide passing into A, the solution is quietly poured into A, and, after opening 2 and 3, is filtered into B. A perfectly clear, sparkling, yellow filtrate is obtained; the apparatus has been so made that in event of turbidity the filtrate can be blown back into A through 1 by passing carbon dioxide through C into B; but to date this has never been necessary. With only 1 and 4 open and the stirrer in motion, the solution is forced by carbon dioxide from B onto the salt which precipitates $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; the agitation is continued for 30 min.

In the washing, dehydrating, and drying of the precipitate, Jellinek's method⁶ is adhered to with a few changes in technic. As a result of the construction of C it is possible to efficiently agitate during the salting out, washing, and dehydration of the hydrosulfite and to remove the liquor by filtration without disturbing the apparatus. The material is heated during dehydration and drying by filling the beaker with warm water and passing in steam to obtain any desired temperature. The first washing is made with salt solution just under saturation so that any undissolved salt will be removed. The wash solutions are introduced through 7, using a wash bottle the tip of which has holes on the sides instead of the end so that the solution can be blown against the walls of C, thereby washing the solid down. Formation of a coarse product—Jellinek⁶ indicated the importance of

this property in increasing the stability of the material—is favored during the dehydration by vigorous agitation, rapid heating to 60° C., and maintenance of this temperature.

It has been found advantageous to filter to a slightly smaller bulk before dehydrating than Jellinek indicated, so that the walls of C can be rinsed with a little salt solution at the beginning and near the end of the dehydration. After the product has been dried, C is filled with dry carbon dioxide because hydrosulfite rapidly undergoes decomposition in the presence of moisture. In nine consecutive experiments 42 per cent yields of coarse white stable sodium hydrosulfite averaging 98.3 per cent (97.7 to 98.9) pure have been obtained.

In some preliminary experiments the white, hydrated solid underwent extensive decomposition and turned black during the dehydration. This was found to be caused by small amounts of iron in the supposedly C. P. caustic soda added just before the material was heated, the black color resulting from ferrous sulfide. Subsequently, the alkali was made from sodium and distilled water. Similar decompositions took place to a very slight extent when some salt containing traces of iron was used. At another time an attempt was made to use small amounts of litharge-glycerol cement in modifying C. Although only a minute amount of lead was exposed to the vapors in C, enough of it was removed to cause slight darkening of the liquor during dehydration. Evidently great care must be exercised to exclude heavy metals.

ANALYSIS

A satisfactory method of analysis for the purified product was not easily secured; the copper method⁷ gave low results, and the silver method⁸ gave high results. By adding the solid hydrosulfite from a weighing bottle with a small spatula to a stirred solution of a known amount, about 1 g. of C. P. potassium ferricyanide in 50 cc. water containing a little nonacidified ferrous ammonium sulfate solution till the blue color disappears, satisfactory analyses checking

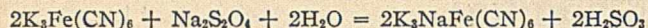
⁵ A high grade of decolorizing carbon.

⁶ Z. anorg. Chem., 70 (1911), 113.

⁷ Helwig, Am. Dyestuff Rep., 7 (1920), 12.

⁸ Smith, J. Am. Chem. Soc., 43 (1921), 1307.

to 2 parts per 1000 were obtained.⁹ The reaction takes place according to the following equation:



As this method of analysis gives results that are a few tenths of a per cent low, the products obtained in this work are nearly 99 per cent pure. A number of purified samples gave positive tests for small amounts of chloride. A sample was oxidized in alkaline solution with C. P. sodium peroxide, and sulfate equivalent to 36.69 per cent sulfur in the hydro-sulfite was found as against a calculated value of 36.78.

In determining the stability of the product a fresh sample analyzing 98.9 per cent pure was shaken at frequent in-

⁹ After we had been using this method for some time, we found that G. Bruhns, *J. Chem. Soc. (London)*, 118A (1920), II, 395, had used a similar one.

tervals in a bottle with an excess of air for 3 hrs. and was then exposed in a thin layer to the air for 16 hrs. The temperature was 82° to 87° F. and the humidity was fairly high at the time of this experiment. Even under these conditions the purity dropped only slightly (1.3 per cent). Another sample of the same lot was ground in a mortar and then subjected to the foregoing treatment; in this case the purity dropped 19 per cent. These figures bring out the relation between the coarseness and the stability of the material very effectively.

ACKNOWLEDGMENT

The writers wish to acknowledge their indebtedness to Dr. Reid Hunt for his interest in the work and to Mr. Henry W. George for his invaluable assistance in constructing the apparatus.

Effect of Hydrogen-Ion Concentration upon the Analysis of Vegetable Tanning Materials¹

By John Arthur Wilson and Erwin J. Kern

LABORATORIES OF A. F. GALLUN & SONS COMPANY, MILWAUKEE, WIS.

AMERICAN LEATHER CHEMISTS ASSOCIATION METHOD

A SERIES of solutions of solid quebracho extract was prepared according to the official method of the American Leather Chemists Association,⁴ except for the addition of hydrochloric acid or sodium hydroxide to produce approximately the desired pH value before making each solution up to the required volume. The pH values were finally determined at 20° C. by means of the hydrogen electrode, and the solutions were analyzed according to the official method. The results, which are shown in Table I and Fig. 1, were calculated on the basis of the original extract, no allowance being made for the added acid or alkali, so that the percentages recorded for nontannin are higher than they should be, but this was done so as to record the more significant values for tannin and insolubles on the basis of the original extract.

In order to show the effect of valency, we ran a second series of determinations, like the first except for the fact that sulfuric acid and lime were used to alter the pH values. The results of these are shown in Table II and Fig. 2.

The solution receiving no addition of acid or alkali had a pH value of 4.60. As the pH value was lowered from this by the addition of either sulfuric or hydrochloric acid, there was an increase in the percentage of insoluble matter found and a corresponding decrease in percentage of tannin found. Sulfuric acid proved slightly more effective than hydrochloric

At a meeting of the Society of Leather Trades' Chemists in London, September 8, 1921, an international commission was appointed, under the chairmanship of H. R. Procter, to consider suggested revisions of the official method of tannin analysis. Among the things which the commission was called upon to investigate was the effect of change of pH value, the importance of which had previously been pointed out by Procter.² Later Thompson, Seshachalam, and Hassan³ made a preliminary study of the effect of adding acetic and hydrochloric acids to extracts of quebracho, mimosa, mangrove, gambier, myrobalans, chestnut and oak wood, and found that the addition of small amounts of acid affected nearly all the determinations made. The present investigation represents an attempt to deal with the subject somewhat more systematically, and was confined to a study of the behavior of quebracho extract at different pH values.

in increasing the percentage of insoluble matter. With increasing pH value, there was first a decrease in the amount of insoluble matter, and the unfiltered solution gradually became more nearly transparent. In the case of NaOH this continued without a break, but with Ca(OH)₂ an abrupt change occurred at the neutral point, and with further rise of pH value the tannin was precipitated in increasing amounts.

The curve for insoluble matter in Fig. 2 furnishes an interesting proof of the accuracy of Procter's limewater method⁵ for determining the percentage of acid in tan liquors.

Since tanning extracts often undergo fermentation during shipment, or upon storing, with a corresponding increase in hydrogen-ion concentration, it is not surprising that analysts sampling a shipment at different times fail to obtain concordant results by the A. L. C. A. method. Since the chief aim of this method is the ability of different analysts to get concordant results, the method would serve its purpose

TABLE I—EFFECT OF HCl OR NaOH UPON THE ANALYSIS OF QUEBRACHO EXTRACT BY THE A. L. C. A. METHOD

	pH Value	Insoluble Per cent	Nontannin Per cent	Tannin Per cent
HCl	1.86	14.72	6.70	61.63
	2.59	12.76	6.63	63.24
	3.60	10.71	6.58	65.09
	3.85	10.06	6.62	65.70
	4.60	8.80	6.62	66.95
	5.60	5.67	6.92	69.96
	5.88	4.15	7.55	71.05
	6.66	3.65	8.00	71.63
	7.29	3.52	8.21	72.15
	7.34	3.50	8.13	72.07
NaOH	7.97	2.55	8.78	72.65
	8.07	2.70	8.58	72.60
	8.89	1.58	17.70	67.80
	9.41	0.98	32.42	58.53
	11.35	0.35	70.55	30.35

¹ Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

² *J. Soc. Leather Trades' Chem.*, 5 (1921), 219.

³ *Ibid.*, 5 (1921), 389.

⁴ *J. Am. Leather Chem. Assoc.*, 16 (1921), 113.

⁵ "Leather Industries Laboratory Book," Spon, London, 1908.

more efficiently by requiring that the analysis be made on a solution of definite pH value.

RATE OF FILTRATION

Thompson and his coworkers found that the rate of filtration of tan liquors was increased by the addition of acid. While filtering, for the determination of insoluble matter, the various solutions mentioned in this paper, we kept a record of the time required to collect 100 cc. of filtrate, after the paper had been tanned for exactly 1 hr. In order to show the change as accurately as possible, we selected filter paper of uniform thickness and repeated each measurement several

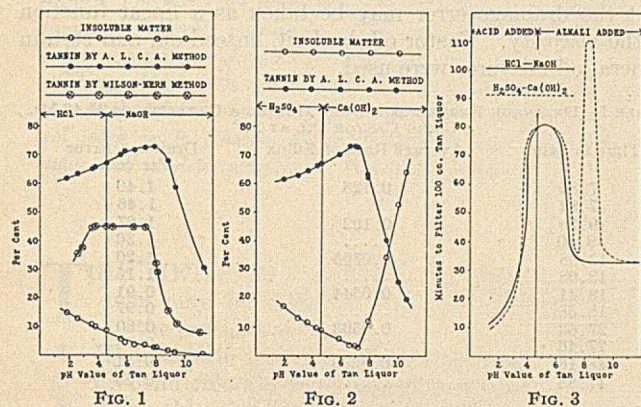


FIG. 1—SHOWING HOW THE ADDITION OF HYDROCHLORIC ACID OR SODIUM HYDROXIDE AFFECTS THE ANALYSIS OF QUEBRACHO EXTRACT

FIG. 2—SHOWING HOW THE ADDITION OF SULFURIC ACID OR CALCIUM HYDROXIDE AFFECTS THE ANALYSIS OF QUEBRACHO EXTRACT

FIG. 3—SHOWING HOW THE RATE OF FILTRATION OF A SOLUTION OF QUEBRACHO EXTRACT IS ALTERED BY THE ADDITION OF ACIDS AND ALKALIS

times. The resulting values are plotted in Fig. 3. It will be of general interest to note that the untreated liquor was one of the most difficult to filter.

The differences in rate of filtration may be ascribed largely to differences in the degree of dispersion of some of the solid matter, which we followed by means of the Tyndall cone. A very fine or very coarse dispersion filtered much more quickly than one of intermediate degree. The effect was very marked in the solutions to which lime was added. With the first appearance of turbidity, after a pH value of 7 was passed, there was a tremendous increase in time required to filter 100 cc., but as the precipitate grew coarser the liquor filtered much more quickly.

WILSON-KERN METHOD

In earlier papers⁶ the authors have shown that the A. L. C. A. method gives values for tannin that are much too high, because of the inclusion of a variable fraction of nontannin that can easily be separated from the hide powder by washing. They proposed a new method for determining the true tanning value of tanning materials that is receiving some attention from the present international commission. In studying the effect of change of pH value upon this method, we prepared a series of liquors from the sample of solid quebracho extract as described in the paper, "The Determination of Tannin,"⁷ except for the addition of HCl or NaOH to give the desired pH values. The results of a series of determinations are given in Table III, and the values for tannin are plotted in Fig. 1 for comparison with those obtained by the A. L. C. A. method.

A practically constant value for tannin is obtained over the wide range of pH values 3.6 to 7.3. Where the falling off in percentage of tannin occurs at pH values higher than

TABLE II—EFFECT OF H₂SO₄ OR Ca(OH)₂ UPON THE ANALYSIS OF QUEBRACHO EXTRACT BY THE A. L. C. A. METHOD

	pH Value	Insoluble Per cent	Nontannin Per cent	Tannin Per cent
H ₂ SO ₄	1.98	17.10	7.97	61.61
	2.97	13.23	7.28	62.69
	3.66	11.65	6.95	64.50
	4.27	9.53	6.60	66.32
	4.60	8.80	6.62	66.95
	5.90	5.77	6.63	70.15
Ca(OH) ₂	6.63	3.42	6.13	73.02
	6.98	3.08	6.80	72.95
	7.17	2.70	7.03	72.90
	7.88	11.65	9.58	62.15
	7.90	11.93	8.45	63.10
	9.15	34.50	13.92	40.28
	9.98	52.75	17.17	25.61
	10.55	63.84	19.98	19.65

7, the results should not be considered as found by this method, because in each case the residual solution gave a test for tannin, by the gelatin-salt test, whereas the method specifies that the determination is to be discarded whenever such a test is obtained. Apparently the hide-tannin compound is unstable, or possibly does not form at all, at pH values higher than 8. The fact that some combination seemed to take place at higher pH values may be apparent only, because the powders, wet with liquor, were washed with distilled water having a pH value of about 5.8. The stability of the hide-tannin compound at different pH values is being studied as a separate work.

The falling off in percentage of tannin found at pH values below 3 may be the result of the great swelling of the hide powder in liquors of low pH value. A complete investigation of this point has not yet been made.

TABLE III—EFFECT OF ADDING HCl OR NaOH UPON THE DETERMINATION OF TANNIN IN QUEBRACHO EXTRACT BY WILSON-KERN METHOD

	pH Value		Gelatin-Salt Test	Tannin Per cent
	Initial	Final		
HCl	1.86	2.57	Negative	...
	2.59	4.20	Negative	35.50
	2.95	4.62	Negative	37.73
	3.60	5.05	Negative	44.35
	3.85	5.35	Negative	44.96
	4.60	5.57	Negative	44.83
	5.03	5.70	Negative	44.87
	6.52	6.50	Negative	44.68
	7.31	7.00	Positive	44.65
	8.04	...	Positive	31.87
NaOH	8.18	...	Positive	29.30
	8.91	...	Positive	15.55
	9.54	...	Positive	10.88
	11.10	9.15	Positive	7.93

¹ Hide powder could not be washed.

² Hydrogen electrode became poisoned very quickly.

The pH values of the liquors were determined both before and after the 6-hr. shaking with hide powder. The curve representing tannin is plotted against the initial pH value of the solutions because not all the final pH values could be determined. When alkali is added to a tan liquor so as to produce a pH value of about 9, there is no difficulty in measuring the pH value immediately after the addition, but after a few hours the determination can no longer be made because the liquor then poisons the hydrogen electrode. This change in tan liquors occurring at a pH value of about 9 has been noted before.⁸

CONCLUSION

The percentage of tannin in quebracho extract indicated by the A. L. C. A. method increases with pH value to a maximum at 8, and then decreases rapidly toward zero. On the other hand, pH value appears to have no effect upon the determination of tannin by the Wilson-Kern method over the range 3.6 to 7.3, but the rate of tanning of hide powder decreases rapidly with increasing pH value above 7.

The rate of filtration of tan liquors is markedly affected by change of pH value, which may be attributed to changing degrees of dispersion of some of the solid matter.

The addition of lime to tan liquors causes a precipitation of tannin, but only at pH values above 7.2.

⁶ THIS JOURNAL, 12 (1920), 465, 1149; 13 (1921), 772.

⁷ *Ibid.*, 13 (1921), 772.

⁸ THIS JOURNAL, 13 (1921), 1025.

The Drainage Error in Measurements of Viscosity by the Capillary Tube Method¹

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IF THE viscometer already described² is used for very viscous materials, there are certain corrections to be considered which are ordinarily not necessary, presuming that a reasonable precision is desired of, say, 0.2 per cent.

A drainage correction arises from the fact that the volume of flow is assumed to be the volume of a certain double cone-shaped bulb which has been calibrated by means of some known liquid. If the unknown liquid does not drain as well as the calibrated liquid, the volume of flow will be too small, and vice versa.

The drainage error may, of course, be decreased to any extent that is desired by simply increasing the time of flow, but it is wasteful to have the time of flow for a single determination consume several hours if an equally good determination can be made in a few minutes by using a more suitable apparatus or previously determined correction terms. Happily, both of these alternatives are open to us. By using the plastometer, no drainage correction is necessary, and with the viscometer simple corrections may be made.

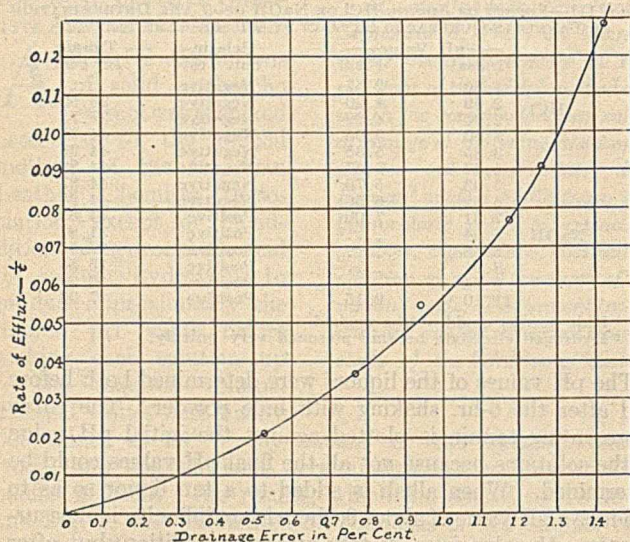


FIG. 1

In our experiment, we have used double cone-shaped bulbs having the following volumes determined by means of mercury—2.50, 3.68, 8.80, 11.46, and 24.42 ml. Liquids of known viscosity were driven under known head through a capillary attached to the lower end of the bulb. The volume of the bulb being known and the volume of efflux found by direct weighing, the drainage error was determined by difference. As an example we give the values obtained for the 24.42 ml. bulb in Table I and Fig. 1. In the figure the drainage error is plotted against the rate of efflux, which is taken as proportional to the reciprocal of the time in minutes ($1/t$). It is seen that in order to determine the viscosity of castor oil at 20° with an accuracy of 0.2 per cent, it is necessary to make the time of flow about 2 hrs. unless a correction is made for drainage error.

¹ Presented before the Division of Physical and Inorganic Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² Bingham, "Fluidity and Plasticity," 1922, p. 76.

Experiments were made to determine how, with a given time of efflux (15 min.), the drainage error varied with the viscosity of the liquid used. Our experiments indicate that the drainage error may be taken as a linear function of the viscosity. Castor oil, lard oil, linseed oil, and certain mineral oil mixtures were used.

TABLE I—DRAINAGE ERROR FOR A BULB HAVING A CAPACITY OF 24.42 ML., USING CASTOR OIL AT 20°

Time in Min.	Average Rate of Efflux $1/t$	Drainage Error Per cent
7.80	0.128	1.40
7.84		1.46
9.79	0.102	1.27
9.80	1.36
13.08	0.0765	1.20
13.08	1.15
18.41	0.0544	0.91
18.38	0.97
27.63	0.0363	0.80
27.46	0.74
48.16	0.0209	0.51
47.88	0.55

As a result, we have prepared Table II to show the drainage corrections for liquids of different viscosities and for different times of efflux. In using the table, suppose that a liquid of approximately 750 centipoises was determined in a time of efflux of 30 min. By interpolation of the table, the error due to faulty drainage is found to be 0.5 per cent. In the formula for viscosity,³ the volume of efflux is 0.5 per cent less than the actual capacity of the bulb; hence we obtain the final simple formula,⁴ $\eta = 1.005 C p t - C' \rho/t$.

If the material used is not a true fluid but partakes of the character of a plastic solid, it is evident that this table of corrections will not apply. Furthermore, a source of difficulty arises in that some liquids do not wet the walls of the bulb uniformly, so that the drainage is uneven.

TABLE II—DRAINAGE CORRECTIONS FOR DIFFERENT VISCOSITIES AND TIMES OF EFFLUX IN PER CENT

Viscosity in Cp.	EFFLUX						
	10 Min.	15 Min.	30 Min.	45 Min.	60 Min.	100 Min.	150 Min.
1000	1.2	1.0	0.7	0.5	0.4	0.3	0.2
500	0.6	0.5	0.3	0.2	0.2	0.1	0.1
100	0.1	0.1	0.1	0.1	0.0	0.0	0.0
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Leaving the question of the drainage error, the question may arise as to whether the heat developed within the capillary, due to the work done in overcoming viscous resistance, is sufficient to make an additional correction desirable.

Take as an example one of our experiments with castor oil at 20°, using a pressure of 214 g. per sq. cm. and a volume of efflux of 7 ml. The work done amounts to 1,470,000 ergs, which is equivalent to 0.035 cal. Assuming a specific heat of 0.48, the elevation of the temperature of the oil on leaving the capillary should have been 0.01°, provided that no heat had been conducted out through the material of the capillary. This would affect the viscosity of the castor oil by only 0.08 per cent, which we must regard as negligible at present.

In plastic flow much higher amounts of energy are absorbed, but the accuracy at present is not better than 0.5 per cent. It will evidently be practicable to make a correction for the heat developed as the necessity arises.

³ Bingham, "Fluidity and Plasticity," 1922, p. 23.

⁴ *Ibid.*, p. 74.

The Determination of Gums in Sugar Products¹

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Sugar boilers and others responsible for the production of refined from raw sugar recognize that different yields and rates of crystallization may be obtained from two raw sugars of similar sucrose, invert sugar and ash content, that have had the same treatment. It is generally conceded that this difference is due to the gums. The gums are presumed to be the strongest molasses formers among the organic nonsugars. This situation is also encountered in the manufacture of raw sugar from the cane.

The problem with which this work is concerned is the selection of a method for determining these gums that could be used for control work or to classify sugar products further than the usual sugar and ash determinations. Our work indicates:

1—Of the various methods proposed for gum determination, the precipitation by ethyl alcohol with hydrochloric acid acidification was found to be the most suitable for a rapid method adapted to control work.

2—The concentration of hydrochloric acid can be varied within rather wide limits without materially affecting the results, but the concentration of the alcohol must be kept within close limits.

3—With suitable precautions, denatured or methyl alcohol can be substituted for the ethyl alcohol.

4—The technic of the method can be simplified, so that its use is not prohibitive for control work.

THE METHODS for determining gum in sugar products may be classified into four groups, according to the precipitant used:

1—Hydrochloric acid-ethyl alcohol methods.²

2—Calcium chloride-ethyl alcohol methods.³

3—Ferric chloride followed by reprecipitation with alcohol.⁴

4—Lead acetate in alcohol methods.⁵

In addition to these there are methods involving dialysis, but they could not be considered as control methods.

We checked representative methods from each group, using black strap molasses for the tests. Both ethyl and methyl alcohol were used. The following average results were obtained:

	METHYL ALCOHOL Per cent	ETHYL ALCOHOL Per cent
HCl-Alcohol (Weichmann).....	2.27	2.53
CaCl ₂ -Alcohol (Bellier).....	7.38	5.74
Fe ₂ Cl ₆ -(Auguet).....	0.68	1.00
Pb(C ₂ H ₃ O ₂) ₂ -Alcohol (Chauvin).....	15.9	19.1

much as three times the alcohol used in an HCl-alcohol precipitation. Compared with the other methods, this method gives abnormally low results.

The Pb(C₂H₃O₂)₂-alcohol method has the very obvious disadvantage that it precipitates many other organic nonsugars in addition to the alcohol-insoluble gums, when applied to a product like black strap. This method involves a lead correction and washing with alcohol and ether. It is slower than the HCl-alcohol method.

REQUIREMENTS OF A METHOD FOR GUM DETERMINATION FOR CONTROL WORK

1—For control work a gum determination should be easily made and should be as rapid as possible.

2—The precipitate obtained in the case of a product which has been defecated probably does not represent entirely the true cane gum present in the cane. This precipitate is thus a more or less indirect measure of the gum or substances that retard crystallization, and only comparative results are obtained. In view of this inability to obtain absolute results, almost any method that will give consistent comparative results and is adapted to rapid and convenient manipulation is justifiable.

3—It is our opinion that no method should be used that throws out large amounts of organic nonsugars other than gums. Since the pure cane gum cannot be isolated by any simple procedure, the alcohol concentration should be such that dextrin will be precipitated. Dextrin is also a gum and retards crystallization.

The most suitable method for control work has been shown to be the HCl-alcohol method. This was studied for the purpose of obtaining such alcohol and acid concentrations that slight changes in the concentration would have little effect on the gum precipitate.

Ethyl alcohol is frequently hard to procure, and for this reason substitutes like methyl and denatured alcohol are desirable. Throughout this work we have compared these with ethyl alcohol.

EFFECT OF SODIUM BENZOATE AS PRESERVATIVE

Five g. of sodium benzoate were added to the stock sirup,⁶ using 10-cc. sirup samples. Analysis before and after addition of the preservative showed the following average results:

Before sodium benzoate	After sodium benzoate
0.0296 g. gums	0.0302 g. gums

There is a slight increase in the gum content after adding the sodium benzoate, but this may be an analytical variation.

⁶ Used in all following determinations except as expressly noted otherwise. 1000 g. 96° raw sugar (gums, 0.14 per cent) and 200 g. black strap molasses (gums 2.53 per cent), with water to 2000 cc. This makes a sirup of 47 to 48 per cent solids.

In the literature the HCl-alcohol method is generally conceded to give the most reliable results. Some of the methods are proposed only on a basis of their results on solutions of gums in water or pure sugar solution. This may help to account for the large variation that we have found.

For our purpose the CaCl₂-alcohol method is objectionable because the precipitation requires 24 hrs. The filtration and washing require more time than the HCl-alcohol method. This is the only case in which the methyl alcohol gives higher results than the ethyl. Possibly CaCl₂·(CH₃OH)_x is formed.

Auguet's Fe₂Cl₆ method from a manipulative viewpoint is the most unsatisfactory of the four. It has these disadvantages: two precipitations and filtrations are involved. The first filtration requires longer than an entire HCl-alcohol gum determination. The gums from the Fe₂Cl₆ precipitation dissolve with difficulty in hot water, and this requires a comparatively large amount of water, which requires as

¹ Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

² L. B. Langguth, Steuerwald, and T. Van der Linden, *Arch. Suikerind.*, **22** (1914), 1033 [*C. A.*, **8** (1914), 3511]; J. J. Hazewinkel, *Ibid.*, **18** (1910), 746 [*C. A.*, **5** (1911), 1850]; *Ibid.*, **19** (1911), 313 [*C. A.*, **5** (1911), 244]; Weichmann, "Sugar Analysis," 3rd ed., p. 134, John Wiley & Sons, Inc., N. Y.; Noel Deerr, "Cane Sugar," **1911**, p. 482.

³ Bellier, *Ann. fals.*, **3** (1910), 528 [*C. A.*, **5** (1911), 928].

⁴ A. Auguet, *Ibid.*, **2** (1909), 136 [*Chem. Zentr.*, **11** (1909), 1011].

⁵ A. C. Chauvin, *Mon. sci.*, [5] **1** (1911), 1, 317 [*C. A.*, **5** (1911), 3353]; *Ann. fals.*, **5** (1912), 27 [*C. A.*, **6** (1911), 1074]. X. Rocques and G. Sellier, *Ann. chem. anal.*, **16** (1911), 218 [*C. A.*, **5** (1911), 3635].

The sirup can be thus kept 4 wks. at ordinary temperatures before any evidences of fermentation appear. Even when bubbles appear there is no perceptible change in the gum content.

EFFECT OF HCl CONCENTRATION ON THE GUM PRECIPITATE

The alcohol concentration was kept constant in these tests while the acid concentration was varied. Ten cc. stock sirup were taken and varying amounts of acid added, but water was added with the acid to make the total added volume 2.5 cc. Then 50 cc. of alcohol (94.5 per cent by volume for the ethyl and 92.7 per cent by weight for the methyl alcohol) were added, and after 30 min. the precipitate was filtered in alundum crucibles, dried 1 hr. at 100° C., weighed, ashed, and reweighed. The gum column in the table represents the net gum content after deducting the ash.

Expt. No.	Ethyl Alcohol			Methyl Alcohol	
	HCl G.	Gums G.	Ash in Gums Pptd. G.	HCl G.	Gums G.
1	0.00	0.1022	0.0472	0.00	0.0987
2	0.02	0.0794	0.0349	0.02	0.0809
3	0.05	0.0364	0.0220	0.05	0.0386
4	0.10	0.0292	0.0213	0.10	0.0283
5	0.15	0.0288	0.0213	0.20	0.0285
6	0.20	0.0288	0.0183	0.30	0.0271
7	0.30	0.0294	0.0105	0.40	0.0264
8	0.40	0.0291	0.0017	0.60	0.0262
9	0.60	0.0279	0.0015	1.00	0.0261
10	1.00	0.0345	0.0014		

These results are shown in Curves I, II, and IV of Fig. 1. The first portion of the gum curve has a very sharp slope, which breaks off sharply. Calcium salts of the various organic acids can be precipitated by alcohol of this concentration, while the free acids cannot. As soon as sufficient HCl has been added to liberate all these acids, the gum precipitate becomes practically constant. After this point is reached the acid concentration may be varied over quite a range without materially affecting the amount of gums obtained. The concentration recommended by Noel Deerr and by Weichmann falls on the flat portion of this curve. It corresponds to a concentration of about 0.27 g. HCl, as plotted on this curve.

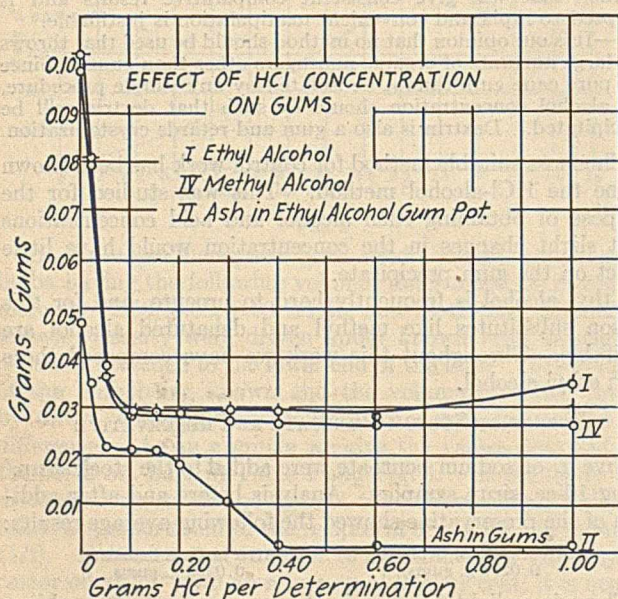


FIG. 1

The combustible matter present in the gum precipitate, and not the ash, determines the amount of gum. It is not necessary to determine this ash to obtain the gums, as is

necessary where the filtration is on filter paper. The ash was determined here only as a matter of information.⁷

EFFECT OF VARYING ALCOHOL CONCENTRATION WITH ACIDITY CONSTANT

The acidity used in these experiments is 1 cc. of concentrated HCl per determination for 100 cc. of alcohol. This concentration permits a considerable variation in the acid measurement without affecting the results. This is a con-

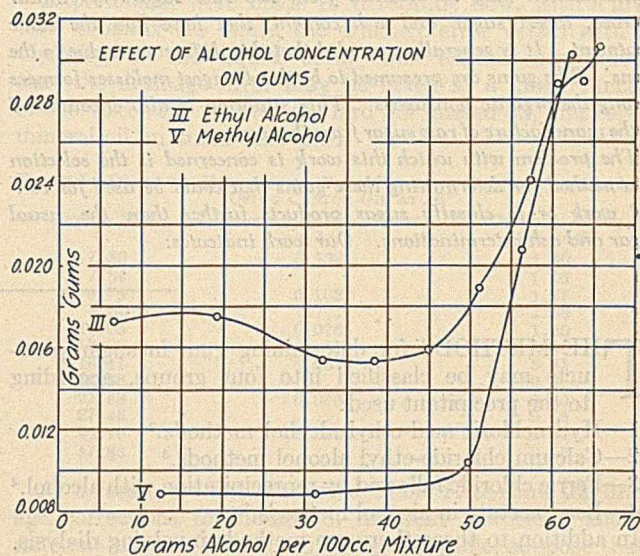


FIG. 2

venient concentration and is the same as is recommended by Noel Deerr and by Weichmann. Ten cc. of sirup were used and 0.5 cc. of concentrated HCl added, and then the desired quantity of alcohol in a volume of 50 cc. Filtration was in alundum crucibles for the ethyl alcohol experiments, and in an asbestos mat Gooch for the methyl alcohol experiments. The precipitate was dried 1 hr. at 100° C., weighed, ashed, and reweighed.

In the ethyl alcohol runs, Expts. 9 and 10 filtered so slowly that the washing was imperfect. In general, the methyl alcohol precipitates settle faster and filter faster than those of the ethyl alcohol.

Expt. No.	G. Alcohol per 100 Cc. Mixture	Gums	Ash in Gum Pptd.
ETHYL ALCOHOL			
1	65.4	0.0307	0.0204
2	63.7	0.0290	0.0187
3	60.5	0.0289	0.0156
4	57.3	0.0242	0.0169
5	51.0	0.0190	0.0036
6	44.6	0.0159	0.0022
7	38.2	0.0154	0.0020
8	31.8	0.0154	0.0031
9	19.1	0.0175	0.0023
10	6.4	0.0172	0.0019
METHYL ALCOHOL			
1	62.2	0.0303
2	59.2	0.0262
3	56.1	0.0208
4	49.6	0.0104
5	31.1	0.0089
6	12.4	0.0087

These data are represented by Curves III and V of Fig. 2. The higher alcohol concentrations are on a rather steep part of the curves. This abrupt drop in the gums is appar-

⁷ The fact that loss on ignition without actual determination of ash is all that is necessary to determine gums is made possible by our use of alundum crucible in place of filter paper commonly recommended. For still more rapid, less precise, work even the loss on ignition might be omitted, if a series of gum determinations were being made on a product with uniform ash character, by taking advantage of the fact, shown on the curves, that above 0.4 g. of HCl per determination, the ash is low and constant. In such a case the ash constancy should be checked occasionally by determining loss on ignition.

ently a dextrin loss. If the alcohol concentrations were carried much higher, there would be danger of throwing out much organic nonsugar and possible sugar. It is evident that the alcohol concentration should be kept within close limits, and as high as the higher concentrations used in these tests.

COMPARISON OF ETHYL, METHYL, AND DENATURED ALCOHOLS

TESTS ON 94° MOLASSES-HOUSE SUGAR—This sugar was made into a 50 per cent sirup and filtered by suction through asbestos. 20 cc. of sirup, 1 cc. of HCl, and 100 cc. of alcohol were used for each determination.

AVERAGE PERCENTAGE OF GUMS

A	B	C
0.252	0.252	0.247

A—Pure ethyl alcohol, 94 per cent by volume.
B—90 per cent ethyl alcohol and 10 per cent methyl alcohol, 92 per cent by weight.
C—Methyl alcohol (commercial), 92 per cent by weight.

These results indicate that for this sugar these alcohols give results that are practically identical.

Another sample of sugar was checked against completely denatured alcohol and the following average results obtained:

Ethyl Alcohol (94 per cent)	Denatured Alcohol
0.266 per cent gums	0.281 per cent

This alcohol was denatured by the following formula (parts by volume): 100, ethyl alcohol; 2, methyl alcohol; 0.25, pyridin; and 0.50, benzene. This denatured alcohol showed 94 per cent by volume.

The results show a slight increase in the case of the denatured alcohol, but the agreement for most purposes is quite satisfactory.

TESTS ON STOCK SIRUP, USING ALCOHOLS DESCRIBED ABOVE—Ten cc. of sirup, 0.5 cc. of concentrated HCl, and 50 cc. of alcohol were used. Series 2 was run with twice the acid concentration used above. The following average results were obtained:

Series	Grams of Gums		
	Ethyl Alcohol	Denatured Alcohol	Methyl Alcohol
1	0.0304	0.0301	0.0259
2	0.0301	0.0280	0.0267

The methyl alcohol gives results that are quite low on a product like black strap. The denatured alcohol is more sensitive to change in acid concentration than either the ethyl or methyl alcohol.

THE TECHNIC OF GUM DETERMINATIONS

FILTRATION OF GUMS—All the methods found in the literature, with the exception of that recommended by Noel Deerr and by Weichmann, are foreign methods, and none of the foreign methods suggest the use of a Gooch crucible. Since the ash in the gums need not be known, only two weighings are necessary when the Gooch crucible is used. This saves two weighings over tared filters, and has the further advantages of greater accuracy and ease of manipulation.

Asbestos mat Gooch crucibles are to be preferred to alundum crucibles chiefly because of the better filtration obtained with the former. Alundum crucibles are also rather difficult to wash properly. Since there is no filtration between weighings, the asbestos mat need not be washed free from fine fibers, thus making mat preparation very simple. There is a loss of only 0.0010 g. between drying and ignition, owing to asbestos and crucible losses for a mat weighing 0.20 to 0.25 g. dry. The corresponding loss for an alundum crucible is at least 0.0020 g.

EFFECT OF TIME OF STANDING AFTER PRECIPITATION ON RATE OF FILTRATION AND WEIGHT OF GUMS OBTAINED—These results were obtained from 10 cc. of stock sirup, 0.5 cc. of concentrated HCl, and 50 cc. of 94 per cent alcohol.

Expt. No.	Time of Standing before Filtration	Time for Filtering and Washing	Gums Obtained Grams
1	0 min.	4 hrs.	0.0282
2	15 min.	8 min.	0.0281
3	30 min.	18 min.	0.0279
4	1 hr.	14 min.	0.0283
5	2.5 hrs.	14 min.	0.0284
6	16 hrs.	15 min.	0.0288

For filtering through asbestos mat crucibles, 15 min. standing is all that is necessary. No serious error is introduced by different times of standing.

TEMPERATURE OF DRYING AND TIME REQUIRED TO REACH CONSTANT WEIGHT—Drying at 90° C. in 30-min. periods comes to constant weight in 90 min. The precipitate goes from 0.0290 to 0.0280 g. from first to last period.

Drying at 100° C.; constant weight in 60 min.; 0.0282 to 0.0280 g.
Drying at 105° C.; constant weight in 30 min.
Drying at 110° C.; constant weight in 30 min.

Using the same gum precipitate, the drying was carried constant at 90° C., then constant at 95° C., etc., with the following results:

90° C. constant at 0.0282 g.;	90 min. required
95° C. constant at 0.0281 g.;	90 min. required
100° C. constant at 0.0277 g.;	60 min. required
105° C. constant at 0.0271 g.;	30 min. required
110° C. constant at 0.0269 g.;	30 min. required

These results show that even a 5° change in drying temperature will cause but little error. The time required to reach constant weight will also vary somewhat with the weight of the precipitate. For this reason it is desirable to dry at least 1 hr. at a temperature of 100° to 105° C.

RECOMMENDED METHOD FOR GUM DETERMINATION

SAMPLE—If the sample is a sirup or juice, dilute to or concentrate to about 50 per cent solids. For work in which only comparative results are desired on products of nearly the same density, this is not necessary but it is desirable. The sample should be free from suspended matter. We find filtering through asbestos or centrifuging fairly satisfactory. Care must be taken that no clarification that has a tendency to remove gums is used. If the gum content is low, use a 20-cc. sample; if high, use a 10-cc. sample. If the density of the sample is not accurately known, it should be weighed to the nearest 0.1 g.

A sugar can be dissolved in an equal weight of water and should usually be filtered. Sodium benzoate satisfactorily keeps sirups for gum analysis.

ACIDITY—Use 0.5 cc. of concentrated HCl for the 10-cc. sample and 1.0 cc. for the 20-cc. sample. Add the acid to the sirup; otherwise, in the case of very low-grade products an unfilterable precipitate may be obtained.

ALCOHOL—Use alcohol at about 93 to 96 per cent by volume. In case methyl or denatured alcohol is used, a large supply should be kept so that the results will be comparable. This old supply should not be entirely used before checking against the new supply on the products usually analyzed. With ethyl alcohol it is only necessary to see that the density is the same. For some products methyl or denatured alcohol will give results nearly the same as the ethyl alcohol, but on other products the results may be lower. Denatured alcohol especially should be watched, as the nature of the substance used for denaturing may be a factor in its behavior as a gum precipitant. Alcohol denatured with methyl alcohol alone is preferable for gum precipitation. All alcohol should be filtered before use.

PRECIPITATION—The precipitation is preferably conducted in 120-cc. Erlenmeyer flasks or in beakers. The alcohol should be added from a rather slow delivery pipet, and the mixture should be well agitated during the precipitation. Use 50 cc. of alcohol for the 10-cc. sample and 100 cc. for the 20-cc. sample. To avoid slow filtration allow the precipitate to stand 15 min. before filtering.

FILTRATION—Use an asbestos mat Gooch crucible. The mat should contain at least 0.20 g. of dry asbestos for a precipitate weighing from 0.2 to 0.5 g. It is unnecessary to wash the mat free from fine fibers or to weigh the crucible before filtering the gums. The flask containing the precipitate should be drained before rinsing, and the rinsings of wash alcohol should not be added until the last drop of the original liquor has passed through the mat. The filtration and washing of precipitates weighing about 0.01 g. ordinarily need not require more than 5 min., and precipitates of about 0.05 g. can be handled in 15 min. Alundum crucibles if used need not be weighed before filtration of the gums.

WASH ALCOHOL—The requirement for the wash alcohol is that it shall be of higher alcohol concentration and of less acidity than the alcohol in the mixture of sirup, alcohol, and acid. This avoids any solvent effect on the precipitate. It is advisable to use the same strength alcohol for washing as was used in precipitating the gums. Occasionally a little acid in the wash alcohol will speed up the filtration.

DRYING—Dry at 100° to 105° C. for 1 hr. For very large precipitates it is well to see whether this is sufficient to give constant weight.

WEIGHING—After drying and ignition the crucible should be cooled in a desiccator and weighed. These weighings should be on a balance accurate to 0.0001 g.

IGNITION—The ignition of the organic matter may be accomplished in a muffle or by a Bunsen flame, and must be continued until all the carbon is consumed. This usually requires 10 to 15 min. The difference between the weight after drying and after ignition represents the dried gums. For very accurate work or where the precipitate weighed is very small, a correction must be applied for the loss in weight of the dried crucible and mat during ignition. For a 14- to 18-g. Gooch crucible with a 0.20 to 0.25 g. asbestos mat, this correction amounts to 0.0010 g. This correction may be determined once for all for any crucible and mat. The mats nearly constant in weight are prepared by using the same volume of a thoroughly shaken stock suspension of asbestos and water.

ACKNOWLEDGMENT

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Color and Ash Absorption by Boneblack and Decolorizing Carbons¹

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THE WIDE interest in decolorizing carbons and the fact that they are frequently offered as substitutes for boneblack in certain lines of work give importance to the comparison of their relative advantages in various technical applications.

Some of the carbons produced in recent years possess a remarkable color-absorbing capacity when applied to sugar solutions, and this has in some cases proved all that was needed to make them of value in some industries, and at the same time has rather diverted attention from their frequent inability to absorb much, if any, ash, which is such an important feature in sugar refining.

ORDINARY PRACTICE

In sugar refining, from 75 to 100 lbs. of boneblack are ordinarily used for the filtration of each 100 lbs. of raw sugar. This boneblack is applied in the filtration of washed sugar and washings, and to sirups from centrifugals at various stages in the process. In this way one-third to one-half of the organic impurities may be removed and one-quarter to one-third of the ash, while about three-quarters of the total color is taken out.

On the other hand, the decolorizing carbons are used in much smaller proportion to sugar, and usually vary from 3 to 10 per cent of the weight of solids in the sugar solution. They remove commonly from about two-thirds to nearly all of the color present without absorbing any notable amount of ash.

For example, in a comparative study of four commercial decolorizing carbons, 250 cc. of bag-filtered, washed sugar solution at 80° C. were added in each case to 25 cc. of the car-

bon, and the whole kept at 80° on the water bath, with frequent stirring, for 40 min., and then filtered. The original liquor had a color of 8, according to an arbitrary scale in which water reads 0 and a rich brown caramel solution reads 100. The four filtrates *a*, *b*, *c*, and *d* read, respectively, 1.5, 0, 3, and 1, showing removal of 81.75, 100, 62.5, and 87.5 per cent. The carbons were then washed and boiled with 10 cc. saturated solution of caustic soda diluted to 75 cc., filtered, and washed free from alkali. Then 80.5 per cent of the original weight of each of these carbons was taken, and to this were added 250 cc. of this liquor darkened with raw sugar washings, the whole heated at 80° C. on the water bath, with frequent stirring, for 40 min., and filtered. The color of this composite liquor was 55, and the filtrates were 10, 8, 32, and 14, respectively. The percentages of color removed were 81.81, 85.50, 41.81, and 74.54. The ash removal was not determined for the first filtration, but by the second filtration practically no ash was absorbed, for, while the original solution contained 0.35 per cent of ash on a dry basis, the amounts found in the filtrates, respectively, were 0.36, 0.37, 0.34, and 0.39 per cent.

EXPERIMENTS TO DETERMINE SEAT OF ASH-ABSORBING POWER

A set of filtrations was conducted, using the main constituents of boneblack separately, and, for comparison, some of the original material at the same time. The original boneblack contained 8.26 per cent carbon, 0.50 per cent insoluble ash, 1.64 per cent calcium sulfate, 0.09 per cent calcium sulfide, 0.17 per cent iron, and 3.89 per cent calcium carbonate. The rest was mainly calcium phosphate. To prepare the samples, 250 g. of high-grade boneblack were digested, heated with about 2 liters of 25 per cent commercial

¹ Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

hydrochloric acid, and the residue washed until it was neutral to litmus paper. The wet carbon and undissolved mineral matter weighed 167 g., and contained 87.95 per cent water, and 12.05 per cent carbon and mineral matter. Another weight of 250 g. of the same boneblack was carefully and thoroughly burned off in the muffle furnace, at a low reddish heat, until all combustible matter was removed. This left 227 g., or 90.80 per cent of the original weight of the char.

For the filtration test, three burets were placed in a double-walled glass box heated by an electric lamp, and 25 g. of the boneblack, for a standard of comparison, were placed in one of the burets above a cotton plug. In the second buret was put burned char weighing 22.9 g., calculated to represent the same original amount of boneblack as in the first buret. For the third tube were set aside 18.1 g. of the wet carbonaceous residue, calculated to contain as much carbon and insoluble ash as 25 g. of the original boneblack. A raw sugar solution at 40° Brix was prepared, and clarified by defecation with infusorial earth and filtering over paper. The original and the burned boneblack were covered with this liquor and allowed to stand 1 hr. at about 75° C., after which the liquor was allowed to percolate slowly through at the rate of 25 cc. per hr. As the wet carbon would have diluted the filtrate unevenly, it was mixed with 100 cc. of the sugar solution and heated near the boiling point for about 10 min., to obtain an even distribution of the 15.9 cc. of contained water with the 100 cc. of liquor. This mixture was poured into the third buret tube, and after standing an hour was drawn off in the same manner as the others. The readings were corrected for the dilution. By this procedure the following results were obtained:

	ORIGINAL SOLUTION	WHOLE BONE-BLACK		BURNED BONE-BLACK		CARBON ¹ FROM BONEBLACK	
		1st 25 Cc.	2nd 25 Cc.	1st 25 Cc.	2nd 25 Cc.	1st 25 Cc.	2nd 25 Cc.
Color	103	4	20	27	60	8	16 ¹
Color absorbed, per cent	...	96.10	80.58	73.80	41.78	92.30	84.50
Ash (on dry substance) per cent	2.914	1.535	2.133	2.235	2.378	2.678	...
Ash absorbed, per cent	...	47.32	26.80	23.30	18.39	8.10	...

¹ Color of liquor supernatant to the carbon. It would no longer percolate through.

Here we see that while the color removal is more vigorous by the carbon than it is by the mineral framework of the boneblack, the burned boneblack far more strikingly absorbs the ash constituents of the sugar solution. This is so very evident that we cannot wonder at the relatively insignificant ash removal by carbons.

The assumption, on the other hand, that the mineral portion exercises the predominating influence in ash absorption, is borne out by the behavior of an artificial boneblack formed by the fixation of carbon on a more or less porous earthy substratum.

ARTIFICIAL CHAR VS. BONEBLACK

In a filtration test arranged much as was the one just described, the artificial char was compared with high-grade boneblack, with the following results:

	ORIGINAL LIQUOR	BONEBLACK		SUBSTITUTE	
		1st 30 Cc.	2nd 30 Cc.	1st 30 Cc.	2nd 30 Cc.
Color	100	2	6	10	24
Color absorbed, per cent	..	98	94	90	76
Ash (on dry substance), per cent	2.81	1.84	..	2.12	..
Ash absorbed, per cent	..	34.52	..	24.60	..

If this hint is followed, we may eventually expect to be able to develop a decolorizing carbonaceous compound, which will not only take up color, but will also absorb ash. When viewed from the financial standpoint of the refiner,

this is an important matter. To demonstrate the point more specifically, reference is made to a certain carbon, prepared from a by-product in manufacture, having good color-absorbing power, but which had no ash-absorbing power.

When 4 g. of this carbon were treated 7 times successively with 100 cc. of washed sugar solution without intermediate washing or revivifying, it was found to be 12 times as effective in color removal as the same weight of boneblack, the boneblack being used but once. The boneblack must be washed and revivified by heat after each use.

A refinery working 225 days a year can count on its boneblack wearing out in about 3 years. As the boneblack makes the cycle of its operations about once in 3 days, in the first year the full char will be used 75 times, in the second year two-thirds of the char will be used 75 times, in the third year one-third of the char will be used 75 times—making 150 times in all, calculated for the full char.

If boneblack can be used 150 times, it will be necessary to use this carbon through 12.5 cycles of 7 mixings with liquor in each cycle to get the same decolorizing effect. As the vegetable carbons are rather soft, they have been found to wear down under the attrition of use, and, as the grains grow smaller, gradually to choke the cloths of the filter press. It seems a fair assumption, from experience in this field, that 18 cycles of this kind would nearly exhaust the utility of most vegetable carbons. In other words, by the time this carbon has done 150 per cent as much decolorizing as an equal weight of boneblack can do in its whole life, the carbon will have been exhausted.

COMPARATIVE COSTS

On a color basis alone, then, it appears that such a carbon must not cost more than 150 per cent as much as char does per pound. The cost of boneblack can be taken at about 5 cents a pound net, as an allowance can be made for old boneblack sold on its phosphoric oxide content. This carbon, then, should not cost over 7.5 cents per lb., on a color absorption basis.

With regard to ash absorption, however, the average raw sugar contains about 0.6 per cent ash, of which the boneblack treatment removes from 0.2 to 0.3 per cent. The carbon failing to do this, the above-mentioned 0.2 per cent of ash holds back about 5 times its weight of sugar from crystallizing, or 1.0 per cent on the weight of raw sugar melted. The 0.4 per cent of ash left after char filtration is ordinarily accompanied by the production of about 4.5 per cent of final molasses. If none of the ash is removed, we might expect to have half again as much molasses; but the carbon removes organic impurities which also have a melassagenic influence, and so it is probably more nearly correct to assume that there will be about one-quarter more molasses with carbon than with boneblack.

Thus, 100 lbs. of raw sugar treated with 80 lbs. of boneblack should produce 93 lbs. of refined sugar at 5.1 cents per lb., or \$4.743, and 4.5 lbs. of molasses at 1 cent, or \$4.788 altogether. The same amount of raw sugar refined with carbon would give about 92 lbs. of sugar (\$4.692) and 5.625 lbs. of molasses at 0.8 cent per lb. (cheaper because of its higher ash content), worth 4.5 cents or \$4.737 altogether, which is 5.1 cents less than when boneblack is used. The cost of the 80 lbs. of char needed for handling 100 lbs. of raw sugar at 5 cents net is \$4.00, and if this can be used in all 150 times, the cost for a single use will be 2.66 cents. Since the boneblack thus effects a saving, compared with carbon, in refining, of nearly twice as much as the boneblack costs, it is evident that such a carbon cannot compete with it at any price.

To offset this, in erecting a plant to use carbon instead of

boneblack, there would be a saving in overhead expenses, and, as revivifying processes develop, it may prove cheaper in revivification than char because of the smaller weight handled, thus diminishing operating expenses also.

The great result to achieve is the production of an ash-

absorbing carbon, and from all present indications it will consist of a porous mineral foundation overlaid with a highly activated carbon, and such a material will have a great advantage if it can be handled in filter presses as the existing carbons are handled.

The Determination of Aluminium as Phosphate^{1,2}

By G. E. F. Lundell and H. B. Knowles

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MANY methods of analysis call for the determination of aluminium by precipitation, and weighing as phosphate, either alone or together with iron and titanium. The calculation of aluminium is ordinarily made on the basis of the composition $AlPO_4$, with corrections, when necessary, for iron and titanium as separately determined and calculated on the basis of the normal phosphates $FePO_4$ and $Ti_3(PO_4)_4$. Most procedures call for precipitation in acid solution, although a few specify an alkaline one; the array of wash solutions is equally broad; hot water, hot or cold ammonium nitrate, and hot dilute acetic acid are all mentioned. In most cases the methods are given with no statement as to their accuracy; in a few instances the methods are rated as of the highest accuracy; while in three researches, at least, attention has been called to the limitations of the phosphate method. One³ states that when aluminium is boiled for 40 min. with an excess of sodium phosphate in acetic acid solution, the phosphate which is obtained approximates the formula $7Al_2O_3 \cdot 6P_2O_5$ more nearly than $Al_2O_3 \cdot P_2O_5$. Another⁴ claims that the phosphate precipitated by boiling a like solution for 5 min. contains P_2O_5 in excess of that called for by the formula $Al_2O_3 \cdot P_2O_5$. The third⁵ points out the difficulty in properly washing the precipitate.

In view of the foregoing facts, it is considered desirable to present the following data which embody tests carried out at this Bureau in order to determine the suitability of the method for work in hand, and which demonstrate that, while the method is quite satisfactory where only small

Determinations of aluminium as phosphate are generally in error. Acceptable determinations are possible when only a few milligrams of aluminium are involved, and high values are the rule when more than 1 to 5 mg. of aluminium are precipitated by ordinary procedures. Immoderate washing of the precipitate or the use of a weak acid wash leads to low values, as does also precipitation with only a moderate excess of the precipitant, or precipitation in alkaline solution. Under these conditions iron behaves like aluminium, while titanium invariably yields low values.

amounts (1 to 5 mg.) of aluminium are involved, it is far from reliable where larger amounts of aluminium are in question, or when iron or titanium or both are also present and precipitated as phosphates.

EXPERIMENTAL

The results of the investigation can best be summarized as in Tables I, II, and III. The aluminium, titanium, and iron solutions were all standardized by proceeding as in the method of W. Blum,⁶ with correction for silica in all cases. The phosphate solutions used for precipitation were standardized gravimetrically as magnesium pyrophosphate. All precipitates were carefully ignited and finally heated to constant weight at approximately 1000° C. In many cases macerated paper was used in an attempt to facilitate the filtering and washing of the precipitate and to obtain a finer grained ignited residue and greater ease in expelling any volatile matter.

In Table I an aluminium chloride solution was used in Expts. 1 to 8 and 15 to 22, and an aluminium nitrate solution in Expts. 9 to 14. The precipitant in Expts. 1 to 8 was sodium ammonium hydrogen phosphate, in Expts. 14, disodium hydrogen phosphate, and in the others, diammonium hydrogen phosphate. Precipitation was in acetic acid solution, except in Expt. 10 where the solution was made just alkaline to methyl orange with ammonia, and in Expt. 11 where an excess of 5 cc. of ammonium hydroxide (sp. gr. 0.90) per 100 cc. was used.

The data of Table I show that all the methods proposed for the determination of aluminium as phosphate are subject to error; those are of the least concern where only small amounts (1 to 5 mg.) are involved. Low values are the rule: (1) when less than five times the theoretical requirement of the precipitant is used; (2) when the precipitation is performed in alkaline solution; (3) when the precipitate is washed immoderately with hot or cold water or ammonium nitrate solution; or (4) when dilute acetic acid is used as a washing medium. High values are invariably obtained with moderate amounts of aluminium when over five times the theoretical requirement of precipitant is employed in acetic acid solution. This holds true regardless of whether the precipitate is washed moderately (with 300 cc. of solution) or until it is free from chlorides with hot water or hot or cold ammonium nitrate solution, or of what ignition temperatures are employed.

There seems to be little hope that a normal phosphate can be obtained by any method. The formula $3Al_2O_3 \cdot$

¹ Received May 22, 1922.

² Published by permission of the Director of the Bureau of Standards.

³ T. M. Drown and Alex. G. McKenna, *Chem. News*, 64 (1891), 194.

⁴ In the "Report of the Committee on Research and Analytical Methods—Phosphate Rock," *THIS JOURNAL*, 3 (1911), 787, the conclusions are given: "In order that the ignited phosphates may contain enough phosphoric acid to form the normal phosphate, it is absolutely necessary that the second precipitation, either in the acetate, Glaser, or thiosulfate method, be made in the presence of an excess of phosphoric acid." "It is impossible to exactly wash out the excess of phosphoric acid, leaving only the normal iron and aluminium phosphates." "It is possible, though hardly practicable, to remove by ignition all excess of phosphoric acid from a precipitate of aluminium phosphate without reducing the normal aluminium phosphate." "It is difficult, and the results are very uncertain at best, to remove the excess of phosphoric acid from a precipitate of iron phosphate without reducing, or, rather, driving off some of the phosphoric acid from the compound." "It is the opinion that any of the methods based on ignition of the phosphate is subject to the above-mentioned errors and uncertainties." These qualifications are not embodied, however, in the final committee report, *THIS JOURNAL*, 7 (1915), 446.

⁵ J. M. Camp, *Iron Age*, 65 (1900), 17, says: "One disadvantage of the phosphate method is that there is no end-point to the washing of the precipitate, it being slightly soluble in the wash water."

⁶ *J. Am. Chem. Soc.*, 33 (1916), 1282.

TABLE I—DETERMINATION OF ALUMINIUM AS PHOSPHATE

EXPR. No.	P ₂ O ₅ Added Theory Al ₂ O ₃ :P ₂ O ₅	AMOUNT OF WASHING MEDIUM ¹	Al ₂ O ₃ Taken G.	Al ₂ O ₃ Found Calcd. on Basis of AlPO ₄ , G. ¹	Error		METHOD
					G.	Per cent	
1	1	500 cc. hot H ₂ O	0.0861	0.0770 ¹	-0.0091	-10.6	"Peters." Blair, "Chemical Analysis of Iron," 8th ed., J. B. Lippincott Co., p. 274. Essentially the same in Ibbotson, "Chemical Analysis of Steel Works Material," p. 104, Longmans Green & Company
2	1	500 cc. cold 2 per cent NH ₄ NO ₃	0.0861	0.0776 ¹	-0.0085	-9.9	
3	3	500 cc. hot H ₂ O	0.0861	0.0846	-0.0015	-1.7	
4	3	500 cc. cold 2 per cent NH ₄ NO ₃	0.0861	0.0851	-0.0010	-1.2	
5	5	500 cc. hot H ₂ O	0.0861	0.0874	+0.0013	+1.5	
6	5	500 cc. cold 2 per cent NH ₄ NO ₃	0.0861	0.0867	+0.0006	+0.6	
7	10	500 cc. hot H ₂ O	0.0861	0.0890	+0.0029	+3.4	
8	10	500 cc. cold 2 per cent NH ₄ NO ₃	0.0861	0.0907	+0.0046	+5.3	
9	10	300 cc. hot 2 per cent Acetic	0.0485	0.0425 ¹	-0.0060	-12.4	"Methods of Chemists of U. S. Steel Corporation for Sampling and Analysis of Ferroalloys, etc.," 1920 ed., p. 42
10	10	300 cc. hot H ₂ O	0.0485	0.0454 ¹	-0.0031	-6.4	
11	10	300 cc. hot H ₂ O	0.0485	0.0367 ¹	-0.0118	-24.3	Ibid., alloy steel, 1921 ed., p. 75
12	1	300 cc. hot 5 per cent NH ₄ NO ₃	0.0485	0.0446	-0.0039	-8.0	
13	5	300 cc. hot 5 per cent NH ₄ NO ₃	0.0485	0.0516	+0.0031	+6.4	Slightly more alkaline than the above
14	20	300 cc. hot 5 per cent NH ₄ NO ₃	0.0485	0.0523	+0.0038	+7.8	
15	10	500 cc. hot 5 per cent NH ₄ NO ₃	0.0471	0.0482	+0.0011	+2.3	Expts. 12 illustrates the effect of insufficient phosphate, and Expts. 14 to 22 embody slight modifications of Expts. 13 and 14
16	10	1000 cc. hot 5 per cent NH ₄ NO ₃	0.0471	0.0459	-0.0012	-2.6	
17	10	2000 cc. hot 5 per cent NH ₄ NO ₃	0.0471	0.0445 ²	-0.0026	-5.5	Expts. 13 and 14 were performed by the method recommended by the Fertilizer Division of the American Chemical Society, THIS JOURNAL, 7 (1915), 446. Scott "Standard Methods of Chemical Analyses," D. Van Nostrand Company, 2nd ed., p. 320
18	10	2000 cc. hot H ₂ O	0.0471	0.0394 ²	-0.0077	-16.4	
19	10	175 cc. hot 5 per cent NH ₄ NO ₃	0.0019	0.0019	±0.0000	0	The washings in Expt. 17 contained only traces of Al ₂ O ₃ , while those of Expt. 18 contained less than 1 mg. of Al ₂ O ₃
20	10	175 cc. hot 5 per cent NH ₄ NO ₃	0.0094	0.0096	+0.0002	+2.1	
21	10	550 cc. hot 5 per cent NH ₄ NO ₃	0.0943	0.0964	+0.0021	+2.2	
22	10	600 cc. hot 5 per cent NH ₄ NO ₃	0.1886	0.1930	+0.0044	+2.3	

¹ Considerable aluminium in filtrate.

² The weighed residue obtained in Expt. 17 gave when analyzed 45.33 per cent Al₂O₃ and 53.88 per cent P₂O₅, while that obtained in Expt. 18 gave 50.16 per cent Al₂O₃ and 48.58 per cent P₂O₅, as against the theoretical values of 41.79 per cent Al₂O₃ and 58.21 per cent P₂O₅ for AlPO₄. These values, in conjunction with the negligible alumina recoveries from the washings, illustrate the progressive hydrolysis of the precipitate and the washing out of phosphoric acid.

4P₂O₅.18H₂O represents very closely the composition of aluminium phosphate precipitates, obtained by the use of an excess of phosphate in either acetic acid or ammoniacal solution, with preliminary drying with blotting paper, final drying in the air, and correction for all impurities. Washing this compound progressively removes phosphorus, with little, if any, aluminium, even after the "AlPO₄" stage has been reached.

Expts. 19 to 22 show that desirable modifications of the official method⁷ consist in precipitating in the presence of macerated paper, and final washing of the phosphate until it is free from chlorides.

TABLE II—BEHAVIOR OF IRON IN THE OFFICIAL METHOD

(Determinations made with a solution of ferric sulfate as in the official method,⁷ except as to varying the amount of diammonium hydrogen phosphate precipitant as noted in Column 1)

EXPR. No.	P ₂ O ₅ Added Theory Al ₂ O ₃ :P ₂ O ₅	Fe ₂ O ₃ Taken G.	Fe ₂ O ₃ Found Calcd. on Basis of FePO ₄ G.	Error—Fe ₂ O ₃	
				G.	Per cent
1	1	0.0530	0.0503	-0.0027	-5.1
2	1	0.0533	0.0503	-0.0030	-5.6
3	5	0.0582	0.0607	+0.0025	+4.3
4	5	0.0505	0.0519	+0.0014	+2.8
5	20	0.0537	0.0565	+0.0028	+5.2
6	20	0.0564	0.0594	+0.0030	+5.3

The data show that iron behaves like aluminium, and that it will increase the errors in any aluminium determinations where both are precipitated and aluminium then obtained by difference after a separate determination of the iron and deduction as calculated FePO₄. For example, in such a procedure a rock containing 10 per cent of Fe₂O₃ and no aluminium would appear to have somewhere in the neighborhood of 0.20 per cent of Al₂O₃ on the basis of Expts. 5 and 6. In the official method, a known amount of iron is added to the solution of the material and a like amount carried through as a blank, which is afterward subtracted together with the theoretical FePO₄ equivalent of the iron in the material as separately determined. As the actual blank is quite small, a more satisfactory procedure would lie in computing the

⁷ Recommended by the Fertilizer Division of the American Chemical Society, THIS JOURNAL, 7 (1915), 446. See Table I, Expts. 13 and 14 of this article.

FePO₄ equivalent of the iron in the material on the basis of the actual performance of the known amount of iron in the blank.

TABLE III—BEHAVIOR OF TITANIUM BY THE OFFICIAL METHOD

(Determinations made by precipitating an acetic acid solution of titanate sulfate as in the official method,⁷ except as to varying the amount of diammonium hydrogen phosphate precipitant, as noted in Column 1)

P ₂ O ₅ Added Theory Al ₂ O ₃ :P ₂ O ₅	TiO ₂ Taken G.	TiO ₂ Found Calcd. on Basis of Ti ₃ (PO ₄) ₄ G.	Error TiO ₂	
			G.	Per cent
1	0.0528	0.0424	-0.0104	-19.7
1	0.0528	0.0422	-0.0106	-20.1
5	0.0528	0.0456	-0.0072	-13.6
5	0.0528	0.0455	-0.0073	-13.8
20	0.0528	0.0485	-0.0043	-8.1
20	0.0528	0.0473	-0.0055	-10.4

The data here show that titanium consistently yields low values in the phosphate method, and that when aluminium is obtained by difference after a separate determination of titanium and deduction as calculated Ti₃(PO₄)₄, small amounts of titanium will offset the normally high values obtained for aluminium, as in Tables I and II, while large amounts of titanium will cause low values. Where titanium is present and ignored, as is usually the case, it will of course add to the high value obtained for aluminium.

The data presented in Tables I, II, and III demonstrate that values for aluminium which are obtained by such methods as that of Peters, and the one recommended by the Fertilizer Division of the AMERICAN CHEMICAL SOCIETY will normally be high in case more than a few milligrams of aluminium are involved; that the values will be higher still when iron is also involved, as in the latter method; and that the values will be lowered by titanium (provided it is considered) in proportion to the amount present.

The degree of Bachelor in Colour Chemistry has been created at the Manchester College of Technology, Manchester, England. Dr. F. M. Rowe, editor of the *Colour Index* now being issued by the Society of Dyers and Colourists, who is in charge of this work, states that students are being encouraged to carry out some of their experiments in a miniature plant, because although the dyestuffs industry is now staffed to capacity with the large numbers who entered it during the war, new research workers will be needed as dye making develops in Great Britain.

Alumina as an Absorbent for Water in Organic Combustions¹

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IN 1912, Johnson² published a note on "Alumina as a Drying Agent," in which he showed that alumina, prepared by heating aluminium hydroxide in a tube at a "low temperature," was as efficient as phosphorus pentoxide for drying purposes. At that time one of us was working on some problems in connection with organic combustions. Since aluminium does not form a stable carbonate, aluminium oxide and hydroxide ought not to absorb carbon dioxide, and therefore the supposition was made that it should be an excellent substitute for anhydrous calcium chloride in the absorption train for organic combustions. Our work, which was begun in 1916, has proved that this supposition is correct. In the meantime, two other articles have appeared dealing with the efficiency of alumina³ in ordinary work as compared with calcium chloride and other drying agents.⁴ After the major portion of our work was finished, it was found that alumina had also been used by Wesson⁵ in the absorption train for combustions, but only to take up the moisture given off from the moist soda lime used for absorbing the carbon dioxide in determining the carbon in the nitrosite of rubber. The hydrogen in this case was not wanted and was not determined, concentrated sulfuric acid being used simply to remove the water formed in the combustion.

PREPARATION OF THE ALUMINA

FROM ALUMINIUM HYDROXIDE—Ten grams of pure aluminium hydroxide were shaken up with 2 g. of purified and ignited asbestos. The asbestos was added to give greater porosity. The mixture was heated in a 7.5 cm. quartz dish over a nonluminous flame 5 cm. high, for 1.5 hrs. During the first half-hour the material lost 3.101 g., the second, 0.068 g., and the third, 0.014 g. On standing over night in a desiccator containing concentrated sulfuric acid, it gained 0.018 g. This mixture gave excellent results.

The aluminium hydroxide must be free from alkali. When mixed with neutral water it should give only the faintest color with phenolphthalein.⁶ The mixture can be used over again simply by heating it once more under the same conditions. It cannot, however, be reheated very often since the asbestos soon crumbles to a powder.

FROM HYDRATED ALUMINIUM CHLORIDE—The alumina as made by the method just outlined tends to pack readily, and then it sometimes requires 3 to 4 hrs. for the complete passage of the carbon dioxide through it. On this account pumice was used in place of the asbestos and the alumina itself prepared in a different way, as follows: 50 g. of hydrated aluminium chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) were dissolved in 100 cc. of warm water in a 11.5-cm. quartz dish and 50 cc. (about 24 g.) of 12-mesh pumice stirred in. It has to be well stirred with a stout glass rod, especially after most of the water has disappeared, since the mixture foams a good deal and tends to form a cake. The particles of pumice should be kept separated as much as possible. The heating and stirring were continued until there was no danger of later fusion of the hydrated salt and agglomeration of the small lumps of impregnated pumice. This material was then transferred to a 7.5-cm. quartz dish and heated in an electric

In this paper the preparation of alumina is described with special reference to its use in the absorption train for organic combustions, its advantages over other absorption agents pointed out, and the results of several analyses given.

muffle furnace to 700° to 750° C. until no more hydrogen chloride was given off. A higher temperature should not be used since alumina when prepared at higher temperatures no longer ab-

sorbs water.⁷ The time of heating can be shortened to 30 to 45 min. if a stream of air is blown or drawn through the heating chamber to remove the gaseous products. At the end of the heating the dish was allowed to cool in a desiccator that had no drying agent in it. If the heating is too long or too high the alumina will no longer cling to the pumice, but will drop off as a fine powder. It will do this to some extent under any conditions.

ALUMINA AS A DRYING AGENT

According to Johnson² the alumina is an excellent drying agent up to the time that it has absorbed about 18 per cent of its weight of water at the ordinary temperature. Fifty grams of hydrated aluminium chloride theoretically yield about 10.7 g. of aluminium oxide, and this amount ought to absorb about 1.92 g. of water under ideal conditions. If we consider the average organic substance as containing about 5 per cent of hydrogen, then a 0.2 g. sample will yield approximately 0.09 g. of water, and on this basis the aluminium oxide theoretically ought to suffice for 21 combustions. In practice we have not used the mixture for more than 4 to 5 combustions.

Since alumina is as efficient a drying agent as phosphorus pentoxide, it must be handled accordingly, even though it gives no outward change in appearance when absorbing moisture.

The material was tested out in a practical way for absorbing the water formed in the combustion of several organic substances. The oxygen for the combustions was purified by passing it through a preheater followed by soda lime and alumina. Blank determinations were run in each case and excellent checks obtained before the substance itself was burned. The carbon dioxide was absorbed by soda lime and this was followed by a second lot of the alumina in order to insure the complete absorption of the moisture from the soda lime. Anthracene was chosen for the first trials on account of its high carbon content. The theoretical percentage of hydrogen in anthracene is 5.66, and the first three results were 5.55, 5.61, and 5.49 per cent. Further results on this and other substances are given below:

SUBSTANCE	Formula	Hydrogen Per cent	Carbon Per cent	REMARKS
Anthracene	$\text{C}_{14}\text{H}_{10}$	Calcd. 5.66	94.34	Alumina - asbestos used
		Found 5.71	94.17	
		5.57	94.36	
Salicylic acid	$\text{C}_7\text{H}_6\text{O}_2$	Calcd. 4.38	60.84	Alumina - pumice used
		Found 4.47	60.77	
		4.38	60.82	
Cane sugar	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	Calcd. 6.46	42.09	Alumina - asbestos used
		Found 6.48	42.05	
		6.46	42.14	

The advantages of alumina over other absorption agents in organic combustions are as follows:

CONCENTRATED SULFURIC ACID—The alumina is a solid and therefore it is easier to handle, and it offers much less resistance to the passage of the gases. Furthermore, less weight can be used.

¹ Dammer, "Handbuch der anorganischen Chemie," 3 (1893), 89.

¹ Received July 31, 1922.

² *J. Am. Chem. Soc.*, 34 (1912), 911.

³ Marden and Elliott, *THIS JOURNAL*, 7 (1915), 320; Dover and Marden, *J. Am. Chem. Soc.*, 39 (1917), 1609.

⁴ Baxter and Warren, *J. Am. Chem. Soc.*, 33 (1911), 340; Baxter and Starkweather, *Ibid.*, 38 (1916), 2038; A. T. McPherson, *Ibid.*, 39 (1917), 1317.

⁵ *THIS JOURNAL*, 6 (1914), 461; 9 (1917), 59.

⁶ Compare the curve in article by Blum, *J. Am. Chem. Soc.*, 35 (1913), 1500.

CALCIUM CHLORIDE—(1) The alumina mixed with the asbestos or the pumice exposes a greater surface. (2) The same bulk weighs less. (3) When it has absorbed water it does not form crystalline hydrates which "freeze" to the walls of the absorption bottle. (4) It contains no basic sub-

stances which introduce an inconstant error, and therefore it need not be saturated with carbon dioxide before using.

PHOSPHORUS PENTOXIDE—The alumina becomes a hydroxide of aluminium, which is a solid and therefore does not clog the apparatus as does the phosphoric acid formed from phosphorus pentoxide.

A Rapid Method of Analysis for Dolomite and Magnesian Limestone¹

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IN THE analysis of dolomite and magnesian limestone for agricultural and commercial uses, a quick, easy, and fairly accurate method of finding the amount of calcium carbonate and magnesium carbonate present is very desirable.

In this paper is given an indirect method which meets those requirements and seems to be generally applicable to that class of stones. The functions concerned are: (1) neutralizing power of the stone as calcium carbonate, A; (2) insoluble residue and ammonium precipitate, B; (3) moisture, M. It does not involve the determination of either calcium or magnesium, and is fully as accurate and somewhat shorter than the usual differential method, which, in addition to the neutralizing power as calcium carbonate, requires the actual determination of calcium.

In the following table a summarization is given of the data obtained on 20 representative samples of magnesian limestones and dolomites:

the percentage combined as $MgCO_3$, we may write the following equations:

$$aX + bY = 100 - (B + M) \quad (1)$$

$$aX + aY = A \quad (2)$$

Solving for Y and getting $BY(MgCO_3)$ we have

$$bY = \left[A - \left(\frac{100 - (B + M)}{a - b} \right) \right] b \quad (3)$$

Substituting for BY, $MgCO_3$, and for $\frac{b}{a-b}$ its value 5.35, we have

$$\left[A - (100 - (B + M)) \right] 5.35 = MgCO_3 \quad (4)$$

Using Equation 4 in connection with the following equation:

$$100 \text{ Per cent} - (B + M) = \text{Per cent } CaCO_3 + \text{Per cent } MgCO_3 \quad (5)$$

which is self-evident, the percentage of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) in the sample can be readily calculated.

A comparison of the figures in Table I for calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) by the indirect and the differential methods shows that they are of about equal accuracy. In connection with this statement it should be noted that the calcium carbonate in the column marked "Differential" was actually determined. The method here given has been checked against the differential method on more than 50 samples of magnesian limestone containing from 3.2 per cent to 42.8 per cent $MgCO_3$ and of varying degrees of impurity. The maximum difference was 0.5 per cent $MgCO_3$. The average was slightly more than 0.1 per cent. This shows as close agreement as could be expected and indicates a reasonably wide applicability of the method.

DETAILS OF THE EXPERIMENTAL PROCEDURE

One-half gram of finely ground stone is put into a wide-mouth flask of 100- to 150-cc. capacity and 25 cc. 0.5 N HCl added, and the sides of the flask washed down with a little water. It is then boiled gently 5 or 10 min., or until decomposition of $CaCO_3$ and $MgCO_3$ is complete. Enough hot water to maintain or slightly increase the volume is used once or twice during the boiling to wash down the sides of the flask. The solution is then cooled and the excess acid neutralized with 0.25 N NaOH, a small drop of methyl orange being used as the indicator, and the first change from pink to yellowish is taken as the end-point. Note exactly the volume of 0.25 N NaOH required to neutralize the excess acid. To the solution add 10 cc. of 10 per cent NH_4Cl solution and two drops of ammonia, heat gently until the

TABLE I

No.	$MgCO_3$		$CaCO_3$		A	$(B + M)$	
	Indirect	Differential	Indirect	Differential			
1	35.80	35.70	48.80	48.80	91.30	15.2	0.20
2	8.99	8.85	87.68	87.82	98.35	3.26	0.07
3	31.80	31.88	63.26	63.05	101.00	4.92	0.02
4	33.76	33.64	57.28	57.30	97.35	8.84	0.12
5	38.80	38.60	49.95	50.00	96.00	11.18	0.07
6	34.50	34.50	56.40	56.30	97.40	8.94	0.11
7	40.70	40.60	56.50	56.50	104.80	2.74	0.06
8	34.80	34.80	50.10	50.04	91.40	14.9	0.20
9	42.30	42.00	54.80	55.04	105.00	2.84	0.06
10	5.08	5.04	89.60	89.60	95.60	5.28	0.07
11	35.30	35.40	62.30	62.05	104.20	2.32	0.08
12	26.50	26.40	70.05	70.06	101.50	3.40	0.05
13	33.70	33.50	59.60	59.70	99.60	6.62	0.08
14	39.05	38.90	49.85	49.90	96.20	10.90	0.20
15	35.80	36.20	54.60	54.04	97.10	9.48	0.12
16	5.10	5.04	92.05	92.10	98.10	2.80	0.05
17	41.50	41.40	55.25	55.25	104.50	3.20	0.05
18	3.20	3.20	89.50	89.50	93.30	7.22	0.08
19	11.80	11.70	79.90	80.00	93.90	8.24	0.06
20	38.00	37.80	60.50	60.55	105.60	1.46	0.04

¹ Assumed except in Nos. 2, 3, and 4.

The figures for $MgCO_3$ in the column marked "Indirect" were calculated from the equation:

$$\left[A - (100 - (B + M)) \right] 5.35 = MgCO_3$$

which expresses the relation of magnesium carbonate ($MgCO_3$) to the neutralizing power of the stone as calcium carbonate, the insoluble residue and ammonium precipitate, and moisture in dolomite and magnesian limestone.

The factor 5.35 is derived as follows: Taking as known quantities $a=2.274$ and $b=1.916$, the factors for converting CO_2 into $CaCO_3$ and $MgCO_3$, respectively, and taking as unknown quantities, X representing the percentage of total CO_2 in the sample combined as $CaCO_3$ and Y representing

¹ Received September 21, 1921. Accepted October 7, 1922. Presented before the Lexington Section of the American Chemical Society, December 15, 1920.

ammonia precipitate flocculates. Filter the precipitate and insoluble residue on a washed, dried, and weighed filter; wash thoroughly with hot water, dry at 100° to 105° C., and weigh. The difference is the weight of insoluble residue and ammonia precipitate.

To the percentage of insoluble residue and ammonia precipitate a small correction for moisture, *M*, must be added. This correction is from 0.02 to 0.05 per cent for pure stones, up to 0.15 per cent and even 0.20 per cent for those containing considerable amounts of insoluble residue.

A clayey insoluble residue contains more moisture than a sandy one, and its character should be noted as a guide to the worker in the assumption of moisture correction.

From the titration calculate the calcium carbonate (CaCO_3) equivalent of the acid neutralized by the stone, as per cent CaCO_3 , *A*. The percentage of insoluble residue and ammonia precipitate, *B*, having been determined, and the moisture, *M*, assumed, we are able to use Equations 4 and 5 as stated above.

The moisture was determined on the samples in Table I subsequent to the assumptions, except in Nos. 2, 3, and 4 as noted, and in no case was the difference more than 0.03 per cent and in a large majority only 0.01 and 0.02 per cent, from which it is evident that, with due regard to the character of the insoluble residue, the moisture may be assumed without material error.

Colloiding Agents for Nitrocellulose^{1,2}

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WHEN colloided straight nitrocellulose powder is exposed to a moist atmosphere, it takes up moisture for two reasons, because of the hygroscopicity of the colloid itself and because of the considerable hygroscopicity of the ether-alcohol that is still retained in the material of the powder grain. Since the moisture so taken up impairs the ballistic properties of the powder, a study of the mechanism of the process by which it is absorbed and of the means by which that process may be regulated or prevented is of obvious interest.

We have shown³ that the absorption of moisture by colloided straight nitrocellulose powder produces precipitation of the nitrocellulose and is accompanied by the production of minute cracks or pores in the surface of the grain. If the powder, after exposure to moisture, is now desiccated, the moisture held in these cracks by capillary action is driven off, the cracks give access to the residual ether-alcohol in the interior of the grain and some of this is also driven off, with the result that the desiccation of the powder actually drives off more volatile matter than the powder had taken up during its exposure to the moist atmosphere. By repeated exposure to moisture and subsequent desiccation, the powder soon reaches a condition of being *perfectly porous*; it no longer contains any ether-alcohol, and the gains and losses on successive exposures and dryings are equal. The amount of moisture which the powder now takes up is a measure of the true hygroscopicity of the ether-alcohol-free material of the powder grain, and, naturally, is considerably less than would be taken up under similar conditions by the original powder grain.

In certain coated or *progressive burning* powders, the exterior of the grain has been toughened and slowed down in its rate of burning by treatment with some colloiding agent.

Certain nonvolatile solvents for nitrocellulose, either incorporated throughout the mass of the grain or applied to the exterior as a surface coating, are used in the manufacture of colloided smokeless powder. Their value lies in the fact that they reduce the amount of volatile solvent needed in the manufacture, and that they influence the rate of burning of the finished powder and determine its attitude toward moisture. The present paper is a report of a study of the solvent action of a number of ureas, urethanes, and sebacic and phthallic esters. Results are such as to permit inferences regarding the relation between structure and solvent action.

Centralite, or *sym*-dimethyl diphenylurea, has been much used for the purpose. Suitable colloiding agents are nonvolatile or high-boiling substances, they are nonhygroscopic and capable of forming with the surface of the powder grain a skin of reduced hygroscopicity which protects the ether-alcohol of the interior

of the grain from taking up the moisture which it would otherwise attract.

In a study of coated powders it has seemed proper to determine the amount of the various colloiding agents necessary for the complete gelatinization of a given amount of nitrocellulose. The results are such as to permit certain generalizations concerning the relation of the structure of the organic compound to its solvent action for nitrocellulose. We find also—a fact which does not seem to have been noted heretofore—that the amount of the colloiding agent necessary for complete gelatinization is in general different when different solvents are used for applying it to the nitrocellulose.

DISCUSSION OF EXPERIMENTS

The experimental procedure was one suggested by Marius Marquoyrol,⁴ Inspector General of Powders of France, who has used it, with alcohol, for studying the action of a large number of colloiding agents on the soluble and insoluble nitrocotton that are used by the French for the manufacture of smokeless powder. We have worked in general with different colloiding agents and have studied the *pyrocellulose* which is standard for United States powder—a nitrocellulose containing 12.60 per cent nitrogen and completely soluble in ether-alcohol. When we have worked with the same materials, our results have been in close agreement with those of M. Marquoyrol for soluble nitrocotton.

Half-gram samples of dry finely pulped pyrocellulose were weighed into 30-cc. beakers, and to each sample a known weight of the colloiding agent previously dissolved in an appropriate amount of solvent (15 to 30 cc.) was added.

⁴ Recently published, Marquoyrol et Florentin, *Mémorial des Poudres*, 18 (1921), 150, 163. These investigators worked at 35° C.

¹ Received June 28, 1922.

² This investigation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance. The author was assisted in this work by Spencer W. Prentiss.

³ Army Ordnance, II, 9. July–August 1921.

The beakers were then suspended in a specially constructed water bath which was maintained at 60° C., and the solvent was evaporated off. During the evaporation each beaker was covered with a watch glass supported on pieces of bent glass rod. It was noticed that the amount of apparent gelatinization increased rapidly during the evaporation of the last portions of the solvent, and that it was increased still further by continued heating for ten minutes or so after all the solvent had disappeared. After the evaporation, the contents of the beakers were examined carefully; some were found to be gelatinized, some not. Other samples were then weighed out and evaporated, with varying amounts of the colloid agent intermediate between the amount which just produced complete gelatinization and the amount which just failed to do so, until the amount necessary for the complete gelatinization of half a gram of pyrocellulose had been determined to the nearest tenth of a gram, and in a few cases nearer than that.

Results, as reported, for the amount of colloid agent necessary for the complete gelatinizing of 100 parts by weight of pyrocellulose, are therefore accurate to the nearest ten parts plus or minus. It is believed that this degree of precision is sufficiently high for ordinary purposes. If greater precision is needed, the experimental procedure that we have used will undoubtedly be adequate.

The first series of experiments was carried out with the colloid agent dissolved in alcohol. In cases where sufficient of the material was available and where the material was soluble in benzene and ligroin, experiments were also carried out with these solvents.

In the case of the liquid colloid agents an excess of the material simply produced a softer and softer jelly. In the case of the solids definite proportions appeared to be necessary for the production of a homogeneous mass; if insufficient was taken, part of the nitrocellulose remained unaffected; if an excess was used, the excess appeared to be deposited as such, as a second phase, and did not amalgamate with the nitrocellulose colloid.

The results are tabulated below.

PARTS OF COLLOIDING AGENT NECESSARY FOR THE COMPLETE GELATINIZATION OF 100 PARTS BY WEIGHT OF PYROCELLULOSE

SUBSTANCE	IN ALCOHOL	IN BENZENE	IN LIGROIN
Methylurea	No action with 100 parts
Ethylideneurea	No action with 100 parts
Sym-dimethylurea	60	70	...
Sym-diethylurea	50	50	...
Unsym-diethylurea	No action with 100 parts
Tetramethylurea	80
Benzylurea	No action with 100 parts
Sym-diphenylurea	No action with 100 parts
Sym-ditolyl (p,p') urea	No action with 100 parts
Unsym-diphenylurea	No action with 100 parts
Triphenylurea	...	35	...
α,α -Diphenyl-p-tolylurea	...	40	...
Tetraphenylurea	No action with 160 parts	30	...
Ethyltriphenylurea	80
Sym-dimethyldiphenylurea	70	26	...
Sym-diethyldiphenylurea	70	30	...
Sym-dibutyldiphenylurea	60	20	...
Unsym-dimethyldiphenylurea	60
Carbamic acid ethyl ester	140	80	...
Methyl carbamic acid ethyl ester	90	60	...
Ethyl carbamic acid ethyl ester	90	60	...
Phenyl carbamic acid ethyl ester	20	90	...
Phenyl carbamic acid phenyl ester	No action with 200 parts
Phenyl carbamic acid benzyl ester	No action with 100 parts
Diphenyl carbamic acid phenyl ester	80	70	...
Methyl sebacate	80	70	105
Ethyl sebacate	80	50	90
Isoamyl sebacate	70	95	90
Methyl phthallate	95	70	115
Ethyl phthallate	95	50	100
Isoamyl phthallate	95	50	80
DNX oil	120	130	330

CONCLUSIONS

In general, the amount of colloid agent necessary for the complete gelatinization of pyrocellulose is greater if the substance is applied by means of its solution in alcohol than

if applied in benzene solution, and is less than if applied in ligroin solution.

Of the alkylated ureas, those in which there is only one alkyl group or in which two alkyl groups are unsymmetrically disposed appear to be without action on pyrocellulose.

Alkylated ureas in which two alkyl groups are symmetrically substituted are excellent solvents, and the property remains even if other aliphatic or aromatic groups are substituted in the molecule. The heavier the alkyl groups, the greater appears to be the gelatinizing power.

Of the aromatic substituted ureas, those in which there are less than three aromatic groups appear to be without action.

In the case of the alkyl esters of sebacic and phthalic acids, the heavier the alkyl group the better, in general, appears to be the gelatinizing action.

Alkyl esters of aliphatic and of aromatic substituted carbamic acid are excellent solvents, while the aromatic esters appear to be without action unless the total number of aromatic groups is equal to three.

Directory of Societies for Chemists

A directory of the names and addresses of the secretaries of the leading chemical societies, and other organizations bordering thereon, is given below in the hope of meeting the needs of those desiring such information:

AMERICAN CERAMIC SOCIETY: Ross C. Purdy, Ohio State University, Columbus, Ohio.

AMERICAN CHEMICAL SOCIETY: Charles L. Parsons, 1709 G St., N. W., Washington, D. C.

AMERICAN ELECTROCHEMICAL SOCIETY: Colin G. Fink, Columbia University, New York, N. Y.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS: John C. Olsen, Polytechnic Institute, Brooklyn, N. Y.

AMERICAN INSTITUTE OF FERTILIZER CHEMISTS: W. J. Gascoyne, Jr., 27 So. Gay St., Baltimore, Md.

AMERICAN LEATHER CHEMISTS ASSOCIATION: H. C. Reed, 22 East 16th St., New York, N. Y.

AMERICAN OIL CHEMISTS SOCIETY: Thomas B. Caldwell, Law & Co., Wilmington, N. C.

AMERICAN PHARMACEUTICAL ASSOCIATION: H. V. Arny, 115 West 68th St., New York, N. Y.

AMERICAN SOCIETY OF BIOLOGICAL CHEMISTS: Victor C. Myers, 308 East 20th St., New York, N. Y.

AMERICAN SOCIETY OF TEXTILE CHEMISTS AND COLORISTS: W. E. Hadley, Clark Thread Co., Newark, N. J.

AMERICAN WATERWORKS ASSOCIATION: John M. Divers, 153 West 71st St., New York, N. Y.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS: R. W. Balcom, Box 290, Penn. Ave. Station, Washington, D. C.

TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY: W. G. MacNaughton, 18 East 41st St., New York, N. Y.

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Photosynthesis and the Possible Use of Solar Energy¹

By H. A. Spoehr

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The purpose of the following brief outline is to show that while the photosynthetic process of the plant is at present the only means we have of utilizing solar energy, this method is so very inefficient and subject to such great uncertainties that it is exceedingly doubtful whether it can be depended upon to maintain our energy requirements. In other words, our civilization is using energy at a prodigious rate, and we would be depending upon the exceedingly inefficient and slow process of photosynthesis to supplant the supplies which have been stored for centuries and are now being depleted. Add to this, that in order to supply food for our increasing population, no encroachment on agricultural industry would be permissible. Theoretical speculations of the nature of what might be accomplished if, for instance, all the arable land were cultivated,

are of no consequence to the problem. Conditions, economic and social, must be faced as they exist. The inertia of our civilization is such that great changes are induced only by the labored movements of evolution or by catastrophe. What part, then, can science and engineering play in the solution of this problem?

First of all, it is the function of scientists to exercise foresight in matters regarding the material welfare of humanity. The experiences of the various scientific bodies called together to cope with the many problems incident to the war, concur in the conclusion that very rarely is necessity the parent of invention where difficult and highly complex problems are concerned. So for this work there will be required an enormous amount of patient labor, which naturally should be begun long before the situation becomes acute.

IT HAS frequently been said of our earth that there are no exports and no imports aside from occasional meteorites.

This is true as far as matter is concerned, but it is not true when energy is considered. Matter and energy are the two fundamental entities in our conceptions of all physical phenomena. As scientific thought progresses, ever-increasing attention is being given to the paramount importance of energy relations in the interpretation of natural phenomena. Matter is of interest to us largely in so far as it exhibits certain properties and undergoes definite changes. In viewing the common materials upon which we depend for the maintenance and propagation of life, it is evident that we are less interested in the matter as such than its ability to undergo certain changes which contribute in one way or another to our life activities. From this practical viewpoint, knowledge of the composition of coal, iron ore, sugar, etc., has its ultimate interest in guiding us in the application of such materials to the manifold needs of our complicated physical and physiological economy.

The eminent physicist Boltzmann pointed out in his classical exposition of the second law of thermodynamics that the struggle for existence is essentially not a fight for the raw materials that are abundant in earth, sky and sea, nor for the energies as such, but for the potential energies as in coal, sugar, and meat. Thus energetics commands the center of attention in the consideration of the chemical phenomena exhibited by the various forms of matter, and matter is but a medium for the manifestation of energy.

If our earth were an isolated system in which there were no imports and no exports, our state of affairs would be very different from that which now presents itself to us. According to our experience, formulated in the laws of thermodynamics, in all naturally occurring transformations there is a tendency to arrive at a condition of stable equilibrium. Thus, the substances on the earth are constantly tending to arrive at a condition of greatest entropy, meaning "rundownness." Most of the metals, for instance, are oxidized to their most stable oxides and converted into other compounds which under existing conditions are extremely stable. Our ores are those stable oxides or salts. Although this condition has not been uniformly attained in the earth, while there are still, for example, natural deposits of metallic copper and silver, yet, unquestionably that is the direction in which the chemical changes are proceeding.

Now most of these substances, before they can be made use of, require certain chemical changes which are a reversal of the

naturally occurring ones. The ores, oxides or salts of the metals, must be reduced to the elemental metals. This, of course, is the reversal of the processes occurring in nature, and to accomplish such a reversal work must be done, energy must be supplied.

If, then, the tendency is to attain the dead level—this state of equilibrium on our earth—what are the agencies or sources of energy that counteract this tendency and make possible the reverse reaction, the pumping of water up-hill, as it were?

In searching for such possible sources of energy which might serve this purpose, we find that a little heat is probably given to the surface of the earth from the interior, another very small amount is the result of certain radioactive chemical changes, the action of the tides contributes some, and a further amount is received from radiation from the stars and moon. But these amounts are quite inadequate and insignificant when compared with the primal source of our energy, the sun. The radiations from the sun constitute our main source of energy. This is our main and most consequential import, the only potent factor which counteracts the tendency of complete running down. It is important not only in such reactions as the smelting of ores, but equally to the life on the planet.

All living things on the earth demand for their maintenance and propagation a continuous supply of energy. The immediate source of this energy for living things is derived from food. All animals, including man, are fundamentally dependent upon plants for their food. Just as the herbivorous land animals are the source of food of the carnivora, the diatoms are the fundamental source of food of the sea. The object of agriculture is essentially to provide man with such materials from which he is able to derive the energy necessary for the maintenance of his bodily activities, his growth and propagation.

MEANING OF "PHOTOSYNTHESIS"

So far as the composition of food material is concerned, there exists a closed cycle. Man feeds on animals, and animals on plants; the plants feed on the carbon dioxide given to the air by the animals as a result of the latter's use of food. Thus the plant reconverts the waste products of animal metabolism into food. The latter process is called *photosynthesis*. The plant absorbs through its leaves the carbon dioxide which is universally present in the atmosphere, and which is formed by the burning of coal, fuel oil, etc., and is also exhaled by animals. By means of the light from the sun the carbon dioxide thus absorbed by the leaves is changed into material such as sugar or wood, which can again

¹ Received October 19, 1922.

be used as food for animals or as fuel. The net result, as far as the changes of materials are concerned in this interrelation of plants and animals, is *nil*. Thus, in brief, a plant yields a certain amount of substance which can be used as food. The food is consumed by man and thus enables him to do some work. Thereby the food material is burned in the body and is exhaled as the gas, carbon dioxide. Or the fuel is burned and the products of combustion escape into the atmosphere.

The fundamentally important point is in relation to the energy changes. The energy expended by the man has been permanently lost to a large extent; similarly, that obtained from fuel. The reconversion of the carbon dioxide into food or fuel material can be accomplished only by the use of a great deal of energy. The cycle is made possible only by the introduction of energy from without. This energy is derived from the sunlight, which the plant, unlike the animal, is able to utilize and convert the waste carbon dioxide again into food or fuel material.

It thus becomes evident that all life on the planet depends upon the energy derived from the sun through the intermediary of the plant—i. e., through the process of photosynthesis. Man-kind lives entirely on the energy derived from the sun through the pursuits of agriculture.

WASTE OF SOLAR ENERGY

But in addition to this, we are squandering the principal of an enormous legacy of solar energy accumulated during the past ages. The plants, which alone are capable of utilizing the enormous floods of solar energy pouring upon the earth, have been at work for many ages prior to man's appearance upon the earth and have, during time which would make the total span of human history appear as but a moment, built the foundations upon which all his present eminence rests. This fossil vegetation, preserved as coal and oil, represents a very small fraction of the energy which has been falling on the earth and which has been conserved for man. It is kindled, its energy liberated and used in a thousand ways, and the rays of sunlight stored beneath the earth for millions of years give birth to a civilization such as the world has never known. It is this source of energy which has made possible the habitation of the temperate zones to the present extent, and on it depend our various modes of rapid transportation and our multifarious industrial activity. What may be called fossil solar energy, coal, made possible the reversal of the natural course by the smelting of ores for the production of metals. In fact, it is solar energy which counteracts the tendency of our earth to attain its maximum entropy.

But this great civilization of coal and steel is at the same time a most squandrous and profligate one; it is using the principal of its legacy in numberless new ways. Modern man's greatness depends upon his being essentially a tool-using animal. To increase the efficiency of one-man power has been his object for centuries. It is the power-driven machine that has done most of his work. But the source of energy which drives these machines is not a steady stream, it is being drawn from the accumulation of centuries. A year's consumption of coal at the present rate represents the accumulation of hundreds of years. The power of man to do work, physical work, the unit one-man power, is now an almost insignificant factor. A return to such a physical standard would almost certainly follow the failure of such sources of energy as man now has at his disposal. The quest of these sources of energy, coal and oil, is at present being pushed with a feverish intensity that has never been known before, and the competition for the possession of these stores recognizes no principles. The destiny of civilization is guided by and reflects the amount of available energy. When coal and oil are exhausted, the daily ration of solar energy will represent almost the entire means of livelihood; our mushroom civilization must pass like the historic empires of the past and we may expect the reappearance in the world once more of galley slaves and serfs.

ENERGY RESOURCES AVAILABLE

And thus the scientific world is awakening to the necessity of taking stock of our available resources of energy. Repeatedly, attention has been called to the inexhaustible floods of solar energy. With cool theoretical nonchalance the untold possibilities of the use of the sun's energy are constantly called to our attention. Yet, the chlorophyllous plant still remains the only converter of solar energy!

The student of photosynthesis cannot, even if he would, escape the practical applications of the problem. It is largely due to the fact that photosynthesis has been dealt with in an academic manner that its fundamental significance has until very recently not been more generally recognized and it has not been possible to enlist the interest and coöperation of workers in the allied sciences. To anyone who has been actively engaged in the investigation of this problem, it must be evident that progress toward its solution would be enormously accelerated by coöperative efforts from different angles.

Recently, interest in the subject has been very greatly stimulated through the realization on the part of industrial scientists that our available supplies of energy are being rapidly depleted.

Our main source of energy is coal, and although it is less than one hundred years since it has been put to extensive use as fuel, the present annual consumption is stupendous—about 650,000,000 tons. Each decade has brought a decided increase in the rate of consumption. While there are, of course, still enormous supplies to draw upon which, considered superficially, might allay all concern, our engineers, most qualified to judge, have repeatedly called attention to the necessity of preparedness on the fuel situation.

A far more serious situation is presented by the petroleum supply. The rapid development of internal-combustion engines of various types has brought about a tremendous demand for liquid fuel. This has increased at such a rate that it can be conservatively stated that the depletion of the petroleum supply in the United States is clearly in sight. A report of the country's foremost oil geologists, under the auspices of the U. S. Geological Survey, states:

The estimated reserves are enough to satisfy the present requirements of the United States for only twenty years, if the oil could be taken out of the ground as fast as it is wanted.

Individual wells will yield oil for more than a quarter of a century, and some of the wells will not have been drilled in 1950. In short, the oil cannot all be discovered, much less taken from the earth, in twenty years. The United States is already absolutely dependent on foreign countries to eke out her own production, and if the foreign oil can be procured, this dependence is sure to grow greater and greater as our own fields wane, except as artificial petroleum may be produced by the distillation of oil shales and coals, or some substitute for petroleum may be discovered.

It is, therefore, not surprising that every available source of energy is being considered to meet the situation which is approaching.

Another very considerable source of energy is that developed from the water powers. Theoretically, this is virtually an inexhaustible supply and one of relatively high efficiency. Mr. Charles P. Steinmitz² has calculated on the basis of collecting every raindrop which falls in the United States and all the power it could produce on its way to the ocean being developed, that there would be possible about three hundred million horse power. This enormous figure represents about the amount received from our present total consumption of coal. Thus, this theoretical hydroelectric power would just about cover our present coal consumption, but leave nothing for future increased needs or to cover other sources of energy now in use. Moreover, this figure for hydroelectric power is purely hypothetical, of which only a small fraction represents that actually

² "The White Revolution," *Survey Graphic*, 1 (1922), 1035.

available, which, when united with other difficulties such as equipment and limitations of distribution, shows very clearly that all the water powers of the country cannot suffice.

The question of liquid fuel is of particular importance in this consideration. The great success of the internal-combustion engines in the automobiles, airplanes, tractors, etc., as well as the many uses of the Diesel engine, has very greatly influenced our economic life, and, as has been stated, it is soon to exhaust our natural resources of liquid fuel. Much attention has, therefore, been given to the production of liquid fuel other than petroleum. Thus far, the investigations along these lines have almost universally led to the opinion that the substance best suited to these needs is alcohol. This is on the basis that alcohol can be produced from vegetable material and is the most direct route from solar energy. It is thus proposed to develop a photosynthetic industry on the basis of agriculture, the products of which are to be converted into alcohol by means of fermentation.

This is, of course, the practical end of the photosynthesis problem. There are so many factors which come into consideration on careful study of the problem in its broadest application, that it is not surprising that some of the most important of these have been entirely disregarded or not given the attention they deserve.

POSSIBILITIES OF PHOTOSYNTHESIS

In considering the sun as a source of energy, two possibilities suggest themselves. The first is a direct utilization of solar energy through some device by means of which the energy could be transformed and stored; the other is by means of the natural process of photosynthesis. Disregarding as inadequate those arrangements that transform solar energy into heat and attempt to use boilers of various kinds, no advance has been made in the direct utilization of solar energy. A transformation of the energy based upon chemical methods has received little attention. The reason for this is that such known photochemical reactions as are endothermic—that is, processes in which energy is stored—are not of a nature to encourage development. The process of photosynthesis in the green plant is such a transformation and storing of energy. Nature has worked out this problem and has done it in a most remarkable manner.

We are therefore still centering our speculations on the plant as a transformer of energy through the production of carbohydrate material. With complete disregard of biological facts, chemists have continued to develop schemes for the employment of the photosynthetic process and to evolve theories of the chemistry of photosynthesis. One of the fundamental fallacies in these speculations may be indicated by a quotation from a recent technical article: "Photosynthesis is simply a manufacture that provides material used in the process of living." It is falsely conceived that this process of manufacture is not a function of the living plant.

There have also been many erroneous and misleading statements regarding the amount of energy radiated from the sun which reaches the surface of the earth. In nearly all the technical discussions on this subject that have appeared recently the calculations are based upon the value of 3 calories per square centimeter per minute. Now this value does not represent the amount of energy which reaches the earth. It is the old value of the solar constant—i. e., the amount of solar energy at the outside of the earth's atmosphere.

The true value of this solar constant is still a subject of some dispute, and it is, in fact, of secondary interest to the immediate problem of the utilization of solar energy on the earth. A great many determinations of the amount of energy received on the earth have been made, and it is certain that a very considerable amount of solar radiation is absorbed in the atmosphere of the earth. For the present purpose, the intensity of solar radiation reaching the earth can be placed at 1.5 calories per square centimeter per minute. On this basis we would receive 5400 large

calories per square meter during six hours. Now one kilogram of coal when burned develops about 8000 large calories; so that six hours of insolation per square meter represents a heat equivalent of 0.675 kilogram of coal, and on an acre, 16.41 tons of coal. This for ninety days of insolation would equal 1476.63 tons.

In order to gain some idea of the degree of efficiency of the photosynthetic process in utilizing solar radiation as expressed in the yield of agricultural products, the heat value of a cereal crop can serve as a comparison. Taking the very large yield of 50 bushels, or 17.619 hectoliters of wheat per acre, and considering this as entirely starch, we get an energy equivalent of 0.623 ton of coal. This last figure of about two-thirds of a ton of coal is to be compared to the 1476 tons, representing the total solar radiation during a period of ninety days, approximately a growing season.

This, then, is the amount of solar energy received at the surface of the earth, and in a practical sense, the amount of this energy that is stored by means of agriculture. It is a very striking fact that the processes of organic nature are exceedingly inefficient and wasteful. This, of course, is so of necessity. Faced with the uncertainties of environmental and climatic conditions, only such processes as are allowed a wide margin of safety are assured the living organism of survival. These figures also indicate that agriculture, as the only photochemical industry, is utilizing but a very small portion of the available energy.

In discussing the possibility of preparing liquid fuel from grain, Boyd³ makes the following statements:

The large amount of motor fuel required seems to exclude the possibility of preparing any considerable percentage of the necessary amount from foodstuffs. In illustration of this statement the following figures are of interest:

	Bushels
Average annual U. S. production of corn 1913-1919	2,740,000,000
Average annual acreage in corn 1913-1919	180,000,000
Alcohol from the corn at 2.75 gallons per bushel	7,500,000,000

The heating value of this amount of alcohol is about equal to that of 5,000,000,000 gal. of gasoline. The production of gasoline in the U. S. during 1920 was very close to this amount, about 4,900,000,000 gal. The average acreage in corn as given above is equal to 166,000 sq. mi., which is more than four times the total area of Ohio. In view of the fact that the possible alcohol production from corn represents close to 60 per cent of the total possible amount of alcohol that could be prepared from all of the starch and sugar containing foodstuffs produced in the United States, and that such a large acreage is required for its production, the possibility of a sufficiently large increase in production of such materials to be diverted to the manufacture of motor fuel seems very unlikely. At any rate, if large quantities of motor fuel are to be prepared from vegetation, another material, if not instead of foodstuffs at least in addition to foodstuffs, must be relied upon as a source.

It seems highly questionable whether the use of the products of photosynthesis offers a rational solution to the problem of industrial energy. It must be borne in mind that the products of photosynthesis are essential to human life as the fundamental source of food. The trend of modern investigation of the chemical, as well as the economic phases of the food problem, strongly supports the dictum that agriculture will always be the basis of food production and that this cannot be supplanted by any artificial method. The materials which are elaborated by plants are directly essential to the well-being of man. Furthermore, any serious disturbance in the way of diverting agricultural products from their use as food to industrial ends would undoubtedly be fraught with profound economic disturbances.

CELLULOSE AS SOURCE OF FUEL

There is one other plant product about which there has been much speculation regarding the possibilities as a source of liquid fuel; that is cellulose. There are so many factors which enter into a rational consideration of the possibilities of producing

³ "Motor Fuel from Vegetation," *THIS JOURNAL*, 13 (1922), 836.

alcohol from cellulose that no adequate analysis of the problem has as yet been attained. These factors embody the biological aspects, the chemical methods, and the economic possibilities. It cannot be claimed that any one of the many compilations and discourses offered since the great interest in this subject has arisen, treat adequately the complexities of the problem. Briefly, the points that demand consideration are the availability of cellulose material in sufficient quantity and the continuous supply thereof, an exact and broad knowledge relative to the chemical processes of converting cellulose to alcohol, and the cost of raw material, manufacture, and transportation, as well as the complexities of labor and influence on other industries. In different sections of the country where different kinds of wood come into consideration there are problems peculiar to each locality.

Much of the speculation as to the use of cellulose for conversion into alcohol is based upon the utilization of waste material in the forests and at the mills. Of the twenty-six billion cubic feet of wood cut annually, the major portion represents accumulated virgin timber, so that this source cannot be considered as a permanent one. To what extent and how soon the depletion of virgin forests will be met by intensive forestry, is a practical question that seems difficult to answer.

These considerations also obtain for the frequently repeated statements of the use of humid tropical regions for growing material from which alcohol could be manufactured. It must be borne in mind that for any such undertaking reliance could not be placed upon extant material, recourse would have to be taken to very extensive cultivation. Moreover, such an undertaking must not interfere with the area now used for the production of foodstuffs.

COMPLEX NATURE OF AGRICULTURAL INDUSTRY

Finally, in advocating the natural photosynthetic process through agricultural industry as the producer of a supply of energy there has been evidenced great neglect of the fact that agriculture is a highly sensitive and complex industry. The fact seems to be too readily forgotten that agriculture deals with biological processes, that solar radiation is but one of many factors influencing the developments of plants, and that in almost every place on the earth where agriculture might be undertaken there is far more light than the plant is capable of utilizing.

The uncertainties of agricultural industry arise from the very complex nature of the biological processes and balances involved in the development of a growing organism. Not only the multiplicity of pests and diseases with which agricultural endeavor must contend, but the relatively sensitive adjustment to climatic environment increases the hazards of this industry enormously. Thus, of course, the growth of plants is not dependent on light only, but on a variety of factors not associated with solar radiation.

The fact that during critical periods in the development of a plant slight changes in climatic conditions during a short time may greatly reduce or entirely destroy a crop, serves to emphasize the hazard of obtaining energy through the intermediary of plants. In agriculture, water supply and temperature are far more variable and determining factors than light intensity. On the proper coordination of these two factors, probably more than any other, depends the success of crop production.

On the other hand, considering alone the solar energy which it is our object to store, there falls on the earth during most of the year a great deal more than any plant is capable of utilizing.

SOLUTION OF THE PROBLEM

Nature has worked out a method of utilizing solar energy. It is the duty of the scientist to learn the precise manner in which this is accomplished. He need not be timid about competing

with nature. He has many cases to his credit of surpassing the processes of nature both in efficiency and reliability. There are many substances now effectively produced artificially which were formerly obtainable only from plants or animals. It is true that in the utilization of radiant energy there are a great many intricate difficulties to be overcome, but to anyone who has given the problem thorough study it must be evident that we are already in possession of much knowledge which can find immediate application to this problem. As the basis of agriculture, the problem of photosynthesis needs development and clarification. As the only known photochemical reaction, proceeding in the visible spectrum, in which there is a large increase in the potential energy of the products, photosynthesis serves as a guide to the utilization of solar energy. Although the chemical reactions constituting the photosynthetic process are of a highly complex and intricate nature, sufficient investigation has been done to justify the conclusion that the problem is amenable to physico-chemical treatment. However, no single academic division of science, such as botany, chemistry, or physics, is of itself sufficiently rich in concepts and methods to attack the problem adequately. The most promising outlook for success in this field would be offered through an organization by which information from the various allied fields can be collected and focused on the chemical and energy changes taking place in the process of photosynthesis. In view of the present academic division of the sciences and the variety of special training which is requisite for such an undertaking, coöperative effort offers the only rational method of advance.

Photosynthesis is essentially a problem of energy transfer. Those aspects of the problem involving the changes of material, the rates of these changes, and the conditions under which they occur, require the methods and conceptions of organic chemistry and physiology. In order to determine the kinetics of these same reactions and the mode of energy transfer, a very different method of experimentation is required. These latter lead directly to the fundamental problems of radiochemistry and require the most advanced methods of physical experimentation.

Has not science here a unique opportunity to lead the way in real coöperation and to demonstrate its true democratic value?

The embryo of a seed, during its first days after sprouting, lives upon material stored for it by the parent, until it gains strength and becomes an independent plant. Throughout nature the young are nurtured and protected until they can care for themselves. So man has had his great patrimony of fuel to help him in his first faltering steps to dominion over his environment. As he grows in intellectual stature, he must meet the problem of physical necessity, a problem of energy pure and simple, ere he can aspire to true independence. The great contribution of the nineteenth century was the establishment of the doctrines of energy. To the twentieth falls the task of freeing us from our economic placenta.

Research on Liquid Carbon Dioxide

The Liquid Carbonic Division of the Compressed Gas Manufacturers' Association announces the establishment of an Industrial Fellowship in the Mellon Institute of Industrial Research of the University of Pittsburgh, for the purpose of classifying, studying, and developing the uses for liquid carbon dioxide. The founding of this fellowship is in accord with the desire of the members of the association to coöperate with users and prospective users of liquid carbon dioxide, with the object of developing efficient means of applying the gas and of obtaining fundamental data bearing on its use in various industries.

In addition to conducting research work, the fellowship will be made a clearing house of information regarding various uses of liquid carbon dioxide, and data will be kept on file for the accommodation of prospective users of this product.

The present incumbent of the Industrial Fellowship is Charles L. Jones, who will be glad to correspond with anyone interested in the use of liquid carbon dioxide in industry.

Progress toward the Artificial Synthesis of Carbohydrates and Proteins¹

By R. W. Thatcher

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WHILE it is not within the lifetime of the present generation that the practices of civilized men will result in critical depletion of the stored energy of the plants of the Carboniferous Era and of the mighty primeval forests of the newly discovered countries of the earth, already there are indications of the approach of that unfortunate time. Before long, as time is counted in history, necessity will compel serious consideration of the problem of replenishment or substitution for the energy stored in plants to supply the needs of mankind. Even now there are signs of approaching difficulties. The demand for foodstuffs for increasing populations, while temporarily halted by the depopulation of the World War and subsequent starvation, will begin anew within a very few years. The inroads of modern necessities upon our rapidly diminishing supplies of timber, and the ravages of insect pests and plant diseases upon economic food and fiber crops, stimulate serious, sober thought in the minds of those who are following the evolutionary development of the earth's inhabitants. The contemplation of the approach of the time when the last ton of coal shall be mined and the last gallon of mineral oil consumed gives to the thoughtful student the same blood-chilling sensation that affects him when he sees through his powerful telescope the cold and barren wastes of the moon.

While these present indications of future dire necessities are not sufficient to cause general gloomy forebodings, they furnish an adequate reason for the utmost interest by chemists in the possibility of a better understanding of how nature has through countless ages stored up the vast reservoirs of solar energy which modern civilization is now so rapidly dissipating. Photosynthesis has come to have an intensely practical, as well as a fascinating theoretical, interest.

RECENT DISCOVERIES

During very recent years certain biochemists have devoted much study to this problem, and, while it is far from being solved, some of its aspects are better understood than they were even five years ago. Exactly how the plant cell accomplishes its total constructive function is as yet a mystery, but some of the steps in the process are now understood and have been artificially duplicated. Several decades ago Emil Fischer and his students accomplished the artificial synthesis of many soluble sugars and of certain polypeptides which closely resemble the natural proteins, but by roundabout processes, and by means of violent chemical reagents, such as could not possibly be conceived to be in any way analogous to those which a plant cell utilizes in its synthetic work. For this plant process it has long been recognized that the gases of the atmosphere are the real initial raw products, and certain fairly simple empirical chemical equations have been cited as representing the steps through which the photosynthetic process goes on; but until very recently attempts to duplicate experimentally and under artificial conditions any of these simple transformations have always failed. Furthermore, while it has been accepted as a fact that chlorophyll-containing plant cells are able to synthesize carbohydrates of all degrees of complexity from the atmospheric gases, until within the past five years it has been supposed that, although the gaseous nitrogen of the air is undoubtedly the ultimate

source of supply of this element, the synthesis of proteins by plants requires the fixation of combined nitrogen in the soil prior to its absorption by the roots of higher plants.

Very recently, however, Benjamin Moore and his associates² have demonstrated that unicellular algae, in the absence of all nitrogen except that in the atmosphere and in the presence of carbon dioxide, can fix nitrogen and grow and form proteins by a process which derives its energy solely from light and is, therefore, photosynthetic. They found also that the rate of this unicellular growth may be accelerated by the presence of oxides of nitrogen such as are present in the atmosphere. Further, Moore has concluded from other experiments³ that green seaweed can and does grow and synthesize both carbohydrates and protein, using only the carbon from bicarbonates of calcium and magnesium present in sea-water and nitrogen from the atmosphere. He explains the failure of fresh water and terrestrial plants to accomplish the same transformations as being due to their inability to establish a satisfactory exchange of alkali material between themselves and their enveloping medium, as do the sea plants.

PHOTOSYNTHESIS OF CARBOHYDRATES

As to the mechanism by which photosynthesis of carbohydrates is accomplished, recent investigations⁴ indicate that under the stimulus of short wave length of light (200 $\mu\mu$) aqueous carbon dioxide can be fairly easily converted into formaldehyde, without the presence of chlorophyll or any other energy-absorbing agent; and that this photosynthesis can be actively photocatalyzed by certain basic colored substances, such as colloidal uranium hydroxide, ferric hydroxide, methyl orange, or malachite green, in the presence of visible light. They also point out that the polymerization of formaldehyde into reducing sugars takes place easily in the presence of light of wave length 290 $\mu\mu$ and that this polymerization can likewise be photocatalyzed by deeply colored alkaline copper solutions. These reactions have been shown to be reversible, depending upon the type of light used and the character of the photocatalyst which is present in the reacting mixtures. Thus, in a system containing reducing sugars, formaldehyde, carbon dioxide, and water, equilibrium is set up between these various components at various points depending on the wave length of the light which falls on the mixture and the nature of the photocatalyst which is present. If ultraviolet light of very short wave length is employed, equilibrium lies far over on the carbon dioxide side; in the presence of a suitable photocatalyst to absorb light of slightly greater wave lengths, formaldehyde is produced in considerable quantities; while in the presence of photocatalysts which absorb light of wave length 290 $\mu\mu$, active polymerization of formaldehyde to reducing sugar goes on, and, in the presence of a photocatalyst which is capable of catalyzing both stages of the reaction, the equilibrium is shifted entirely over to the reducing sugar side. It has been suggested, although not yet experimentally demonstrated, that chlorophyll is an ideal photocatalyst for both stages of the synthesis of soluble sugars from carbon dioxide and water, and the formation of

² *Proc. Roy. Soc. (London)*, **913** (1920), 201.

³ *J. Chem. Soc. (London)*, **119** (1921), 1555.

⁴ *Ibid.*, **119** (1921), 1025.

¹ Received July 24, 1922.

carbohydrates in the growing leaf from very small concentrations of carbon dioxide without the existence of free formaldehyde as an intermediate product is thus explained. If this explanation is finally given successful experimental demonstration, the next step seems fairly obvious—namely, that the reversible changes of reducing sugars to more complex carbohydrates may be likewise photocatalyzed, presumably by light of still greater wave lengths. If this should be found to be true, the entire mechanism of the production of carbohydrates from carbon dioxide and water will be understood, and an ample supply of the photocatalytic chlorophyll, or other plant pigments for artificial synthesis of these important food substances, will be easily available in the noneconomic plants of the country. It would, therefore, seem that the possibility of economic artificial synthesis of one of the important constituents of human food is at least brought much nearer to realization by these recent biochemical researches.

As to the actual part which chlorophyll plays in the photosynthesis of carbohydrates, three possible modes of action are now receiving experimental study. The first of these, which has naturally been longest considered as the probable function of chlorophyll, is that it acts chemically as a catalyst by forming unstable intermediate products with formaldehyde or possibly other simple intermediate compounds of the photosynthetic process. Indeed, several investigators⁵ have shown that chlorophyll actually does form a compound with formaldehyde from which complex the formaldehyde may be either given off or absorbed in order to establish a proper equilibrium in the photosynthetic process, and to afford in the plant a mechanism by which the quantity of free formaldehyde is regulated. In this way the amount present in free form at no time reaches that which would be toxic to the cell protoplasm. The second of these conceptions is that, regardless of the color and of the general chemical reactivity of chlorophyll, the mineral constituent (magnesium) which it contains is held in proper colloidal form to exert a definite catalytic effect upon the photosynthetic process. The third, and most recent, explanation of the mechanism of chlorophyll action is that the pigment acts as a photocatalyst, or light screen, to absorb and transmit the energy from light rays of the proper wave length to accomplish the several steps in the photosynthesis of carbohydrates.

As has been pointed out above, this last conception has very recently been given experimental confirmation, and the artificial synthesis of simple carbohydrates from atmospheric gases under the influence of proper photocatalysts has already been accomplished.

PHOTOSYNTHESIS OF PROTEINS

Not as much progress toward an understanding of the mechanism of the synthesis of proteins by plants, or toward the successful artificial duplication of the process, has yet been made as has in the case of the carbohydrates. It has been shown that the ordinary synthesis of proteins by plants supplied with nitrogen in some oxidized (preferably nitrate) form is not necessarily a photosynthetic process, as it can occur in the dark and in the absence of chlorophyll or any other light-absorbing pigment. However, atmospheric nitrogen cannot be used by plants for this purpose, except in the case of certain bacteria, notably those which live in symbiosis with the legumes in the nodules on the roots of the host plants and other low plants, particularly marine algae. As has been pointed out, it has recently been suggested by Moore that the ability of green algae to synthesize proteins from atmospheric nitrogen, by a process which seems to be photosynthetic—i. e., deriving its energy from solar light—is apparently due to their favorable environment for free exchange of alkali material between their tissues and the surrounding medium, sea water. This indicates that the synthesis of proteins through the nitrogen→ammonia→amino acid→

protein course may yet be understood and possibly artificially duplicated in the near future. Heretofore, it has been supposed that the oxidation of atmospheric nitrogen to nitrate form is a necessary preliminary step to its utilization in the synthesis of proteins, at least by ordinary cell protoplasm. Presumably, the nitrate nitrogen must then be reduced in the plant to nitrite, and then to the ammonia form, in order to enter the amino arrangement which is required for the greater proportion of the protein nitrogen. These preliminary oxidation and reduction changes have heretofore been little understood, but progress toward a satisfactory knowledge of the mechanism of their control is now being made. Artificial syntheses of amino acids by the action of ammonia upon glyoxylic acid and sorbic acid, both of which may be obtained by the oxidation of simple sugars, have been accomplished. The reversible condensation of these amino acids into proteins is readily accomplished in all living protoplasm under the influence of special enzymes which are almost universally present in the cytoplasm.

We are still in the dark as to the mechanism by which this condensation is brought about, but recent investigations have thrown so much light upon the whole photosynthetic process that it seems reasonable to expect that we may soon reach a working understanding of the condensation process, both of the sugar \rightleftharpoons starch and of the amino acid \rightleftharpoons protein transformations. When this result is reached, a long step will have been taken toward the solution of the problem of artificial synthesis of food products, with which to supplement the stored energy of bygone ages that is being so rapidly dissipated by the demands of our modern civilization.

Use of Oxygen in Metallurgical Operations

Use of oxygen in connection with the enrichment of the blast in the blast furnace and in practically all phases of pyro-metallurgical work will furnish the key to success in the further development of such metallurgical operations, according to Dr. F. G. Cottrell, formerly director and now consulting metallurgist of the United States Bureau of Mines, who first directed the Bureau's attention to this subject. Through this enrichment process it is hoped to increase the efficiency of metallurgical operation with a resultant production of metals at lower cost and possibly the use of lower grade ores.

The Bureau of Mines now has outlined plans for two studies which will be carried on simultaneously. The first will cover the present-day processes for the production of oxygen, in order to determine the feasibility of attempting to produce oxygen, or oxygenated air, in such amounts and at such a cost as to permit of its use in metallurgical operations. The second study will be devoted to the feasibility of using oxygen, or oxygenated air, in metallurgical operations.

Because of his interest in this investigation, M. H. Roberts, vice president of the Franklin Railway Supply Co., was asked to select an advisory committee to work with the Bureau of Mines and to act as chairman of this committee. The committee will consist of F. G. Cottrell, director of the Fixed Nitrogen Research Laboratory; W. L. DeBaufre, chairman of the mechanical engineering department of the University of Nebraska; D. A. Lyon, chief metallurgist of the Bureau of Mines; R. B. Moore, chief chemist of the Bureau of Mines; R. C. Tolman, professor of physical chemistry and mathematical physics, California Institute of Technology; J. W. Davis, mechanical engineer of the Bureau of Mines; F. W. Davis, metallurgist of the Bureau of Mines; Frank Hodson, president of the Electric Furnace Construction Company; and P. H. Royster, assistant metallurgist of the Bureau of Mines.

Previous to the war, some work was done in Belgium on the enrichment of the blast with oxygen in connection with the smelting of iron ores in the blast furnace. In the United States, the late J. E. Johnson, Jr., was interested in the possible use of oxygen in metallurgical operations and carried on some experimental work along these lines previous to his death.

On November 3, 1922, Dr. Edgar F. Smith delivered a lecture on Joseph Priestley before the Priestley Club of the University of Pennsylvania. On this occasion various Priestleyana were for the first time exhibited to the public.

⁵ *Proc. Roy. Soc. (London)*, **80B** (1908), 30; **82** (1910), 226.

Manuscript Bibliographies in Chemistry and Chemical Technology

Compiled by Clarence J. West and Callie Hull

RESEARCH INFORMATION SERVICE, NATIONAL RESEARCH COUNCIL, WASHINGTON, D. C.

(Concluded)

Graphite:

H. G. Ferguson, U. S. Geological Survey, Washington, D. C. Entries by author, subject, and locality. Abstracts included in part. Complete to 1919.

See also Refractories (Schurecht).

Grignard Reaction:

C. W. Porter, University of California, Berkeley, Calif. 500 entries. 1900-1921. Many important contributions and some of no value.

Gypsum:

Frank A. Wilder, North Holston, Va. 600 entries by author, title, and subject. Four-fifths complete. To be published in monograph of Iowa Geological Survey.

Heat Transmission:

Heat transmission: evaporating and heating apparatus. W. L. Badger, University of Michigan, Ann Arbor, Mich. 2000 entries, by author and subject. 1850-date. Abstracts included. 25 per cent complete.

Heating Apparatus:

See Heat Transmission (Badger).

Heterogeneous Equilibria:

E. C. McKelvy and L. Yurow. Thousands of entries; by author and subject. Up to 1919. Abstracts and critical comments in many cases. Much data tabulated and plotted. Incomplete, especially for later years. For consultation, write Bureau of Standards, Washington, D. C.

Hydrocyanic Acid:

See Insecticides and Fungicides.

Hydrogen:

Low temperature research; liquefaction of hydrogen and properties of liquid hydrogen. J. C. McLennan, University of Toronto, Toronto, Canada. 1898-1920. Some abstracts included.

Hydrogenation of Oils:

Charles Baskerville. Incomplete. For consultation, write Library, College of the City of New York, New York, N. Y.

Hydrotherapy:

Influence of bathing on metabolism. H. A. Mattill, University of Rochester, Rochester, N. Y. 200 entries, by author. 1890-date. Abstracts usually included. Probably all the important contributions.

Industrial Chemistry:

Industrial inorganic, organic, electro, and combustion chemistry. R. K. Strong, Reed College, Portland, Ore. Entries by subject. 1896-date.

Inorganic Chemistry:

See Industrial Chemistry (Strong).

Insecticides and Fungicides:

J. J. Davis, Purdue University, Lafayette, Ind. 4000 or more entries by subject. 1860-date. Abstracts included in some cases. Fairly complete.

Chemical composition of proprietary insecticides and fungicides and chemical composition and disinfectant action of proprietary disinfectants. J. K. Haywood, Insecticide and Fungicide Board, U. S. Department of Agriculture, Washington, D. C. 9500 entries, by subject. 1910-date. 90 to 95 per cent complete. Cannot be consulted or duplicated, but information will be given state and government scientists in exceptional cases, on understanding that results will not be made public.

Fumigation with hydrocyanic acid gas. E. R. Sasscer and R. S. Woglum. Entries by author. Very complete up to 1920. Abstracts included in a few cases. For consultation, write E. R. Sasscer, Federal Horticultural Board, Washington, D. C.

Lime sulfur as a spray. V. I. Safro. 612 entries, by author. Earliest references up to and including 1911. Abstracts included. Very complete. For consultation, write Department of Entomology, Oregon Agricultural College, Corvallis, Ore.

Miscible oil sprays in combination with other spray materials. Leroy Childs, Hood River, Ore. Well started.

Organic insecticides and fungicides, including hydrocyanic acid, chloropicrin, and others. Clarence J. West, National Research Council, Washington, D. C. 300 entries, by author. Three-fourths complete.

See also Lead Arsenate (Dickey); Poisons (Gray).

Iron:

Effects of sulfur and phosphorus on the properties of iron and steel. 350 entries, by author (35 typewritten pages). For consultation, write joint committee on phosphorus and sulfur in steel, attention of H. L. Whittemore, Bureau of Standards, Washington, D. C.

Iron ores. R. J. Holden, Virginia Polytechnic Institute, Blacksburg, Va. To be published by the Virginia Geological Survey.

Iron ores of the United States. E. C. Harder, 1111 Harrison Bldg., Philadelphia Pa. Entries by author and locality. Moderately complete to 1919, inclusive.

Malleable cast iron. E. S. Davenport. 38 entries, by author. 1914-1922. For consultation, write Eastern Malleable Iron Co., Naugatuck, Conn. Malleable iron. A. E. White, University of Michigan, Ann Arbor, Mich. 83 entries. 1910-1921. Includes most of the pertinent books and articles bearing on the subject.

See also Lead Coatings (Berolzheimer).

Kapok:

Arthur D. Little, Inc., Cambridge, Mass. 22 entries, by author.

Kauri Gum:

Arthur D. Little, Inc., Cambridge, Mass. 14 entries, by author.

Lactose:

Lactose (milk sugar): scientific and industrial. Harper F. Zoller, 3345 Grand River Ave., Detroit, Mich. 44 entries. Up to 1922.

Lead Arsenate:

Corona Chemical Division, Pittsburgh Plate Glass Co., Milwaukee, Wis. 80 entries, by author, title, and subject. 1819-1916. A few abstracts included. 85 per cent complete. For consultation, write C. B. Dickey, Superintendent.

Lead Coatings:

Lead coatings on iron and steel. D. D. Berolzheimer. Entries by author and title. 1904-1914. Thorough for years covered, including a few older references. For consultation, write National Lead Co., 129 York St., Brooklyn, N. Y.

Leather:

Leather and tanning chemistry, tanning materials, etc. J. S. Rogers, Morgantown, N. C. 300-400 entries. 1909-1917. Abstracts included in some cases. Not very complete.

Light:

See Photochemistry.

Lime:

The uses of lime. M. E. Holmes, 918 G St., N. W., Washington, D. C. Several hundred entries, by subject. 1920-date. Very brief abstracts included. Complete.

Low Temperature Carbonization:

The Barrett Co., 40 Rector St., New York, N. Y. 154 entries, by author, subject, and patents. 1873-date. Abstracts included.

Carbonization of coal, particularly low temperature carbonization. Roland P. Soule. 300-400 entries, by subject. 1860-1922. Abstracts included. Very complete on low temperature carbonization and theories of carbonization. For consultation, write Prof. J. J. Morgan, Havemeyer Hall, Columbia University, New York, N. Y.

Lubricating Oils:

See Petroleum (Smith).

Magnesite:

See Refractories (Schurecht).

Maltose:

Maltose in acid-hydrolyzed starch products. L. F. Hoyt, Larkin Co., Inc., Buffalo, N. Y. 66 entries, by author, title, and subject. 1812-1913. Complete as facilities permit.

Marine Borers:

See Wood Preservation (West).

Meat:

Dried meat. Arthur D. Little, Inc., Cambridge, Mass. 22 entries, by author.

Meat packing industry. Library of Congress, Washington, D. C. 150 entries, by author. Up to 1920.

See also Flesh.

Mesothorium:

Herman Schlundt, 303 Hicks Ave., Columbia, Mo. 55 entries, by author. 1907-1920. 85 per cent complete.

Metabolism:

Animal nutrition, calorimetry. H. F. Armsby, State College, Pa. 12,177 entries, by subject mostly, many by author and title. 1870-1922. Abstracts included. Very complete in references to plants—culture, fertilizer, etc., field crops; general science—animal physiology, metabolism; foods, animal—nutritive value, animal products.

Carbohydrate metabolism and physics and chemistry of the blood. E. L. Scott, 437 W. 59th St., New York, N. Y. 3500 entries, by title and subject. From earliest literature to date. Abstracts included in about 50 per cent. 25 per cent complete.

Digestion and assimilation of fat; digestion, fasting, and pathological lipaemia. S. H. Gage, Stimson Hall, Ithaca, N. Y.

Fate of foreign organic compounds in the animal body, and synthesis of amino acids in the body. Carl P. Sherwin, Fordham University, New York, N. Y. 2000 entries. 1912-date.

Influence of mineral waters on metabolism. H. A. Mattill, University of Rochester, Rochester, N. Y. 150 entries, by author. 1890-date. Abstracts usually included. All important contributions.

Metabolism of chickens and nutritive requirements. H. A. Mattill, University of Rochester, Rochester, N. Y. 200 entries, by author. 1890-date. Abstracts included in about one-half the entries. 75 per cent complete.

Metabolism of mineral matter. H. A. Mattill, University of Rochester, Rochester, N. Y. 600 entries, by subject. 1906-date. Abstracts usually included. 90 per cent complete.

Nutrition. J. F. McClendon, 815 Fulton St., S. E., Minneapolis, Minn. More than 1000 entries, by subject. 1918-date. Abstracts included.

Nutrition, bread, and allied topics. C. E. Halstead, Ward Baking Co., New York, N. Y. Entries by author and subject. 1850-date. Abstracts frequently included. 90 per cent complete.

Protein storage in protoplasmic tissue. W. S. Ritchie. Entries by author and title. 1898-1922. Rather complete. For consultation, write C. R. Moulton, 105 Schweitzer Hall, Columbia, Mo.

See also Cholesterol (Arnold); Hydrotherapy (Mattill); Proteins (Mattill).

Metallurgy:

Mining, metallurgy, geology. H. O. Hofman, Massachusetts Institute of Technology, Cambridge, Mass. Hundreds of entries, by author. 1885-1920. All leading articles in periodicals.

Methanol:

Charles Baskerville. Incomplete. For consultation, write Library, College of the City of New York, New York, N. Y.

Mildewproofing:

See Waterproofing (Fenn).

Milk Secretion:

Biochemistry of milk secretion and related nutritional topics. Edward B. Meigs, Dairy Division, Experiment Station, Beltsville, Md. 550 entries, by author. 1850-date. A few abstracts included. No attempt at completeness.

Mineral Matter:

See Metabolism (Mattill).

Mineral Waters:

See Metabolism (Mattill).

Motor Fuels:

Motor fuels and petroleum. E. H. Leslie, University of Michigan, Ann Arbor, Mich. Several thousand entries, by author and subject. Up to date. Abstracts included on many of the cards. Literature and patents are covered thoroughly.

See also Alcohol (Leslie).

Naphthalene:

Homologs of naphthalene. The Barrett Co., 40 Rector St., New York, N. Y. 142 entries, by author and subject. 1869-date. Abstracts included.

Naval Stores:

Naval stores (turpentine and rosin). A. W. Schorger. 5000 entries (572 typewritten pages) by author and subject. Up to 1912. Abstracts included. Every available article read and abstracted. Important articles translated or long abstracts made and deposited in files, with file number given in the bibliography. For consultation write Forest Products Laboratory, Madison, Wis.

Nitric Acid:

See Nitrogen Fixation (Zeisberg).

p-Nitrobenzaldehyde:

C. G. King. 1860-1920. Entries by author and names of compounds. American, English, and German abstract journals covered. For consultation, write Library, University of Pittsburgh, Pittsburgh, Pa.

Nitrogen Fixation:

American Cyanamid Co., 511 Fifth Ave., New York, N. Y. Not complete.

Nitrogen fixation, nitric acid manufacturing, nitric acid concentration. Fred C. Zeisberg, E. I. du Pont de Nemours & Company, Wilmington, Del. 1500 entries, by subject. Abstracts included. All U. S. patents and a number of literature references. 75 per cent complete.

Production of synthetic nitric acid and synthetic ammonia. Engineering Societies Libraries, New York, N. Y. 837 entries. 1788-1917. Abstracts included.

Nitro-o-phthalic Acid:

See Phthalic Acid (Bogert).

Nutrition:

See Metabolism; Proteins (Mattill).

Occupational Diseases:

Occupational diseases in chemical trades. Charles Baskerville. Incomplete. For consultation write Library, College of the City of New York, New York, N. Y.

Oil(s):

See Fats and Oils, Castor Oil, Hydrogenation, Viscosity, Oil Shale, Wood-tar.

Oil Shale:

Oil shale and shale oil. R. H. McKee, E. E. Lyder, and R. T. Goodwin, Department of Chemical Engineering, Columbia University, New York, N. Y. 450 entries, by authors. 1825-July 1921. Abstracts included. Complete as possible. Will appear in AMERICAN CHEMICAL SOCIETY monograph on this subject.

Oil shales. Eliot Blackwelder, 317 Railway Exchange Bldg., Denver, Colo. 125 entries, by author and title. Abstracts in many cases. 60 per cent complete.

Oil Sprays:

See Insecticides and Fungicides (Childs).

Optical Isomerism:

Roy B. Davis, University of the South, Sewanee, Tenn. 2500 entries, by author and subject. Up to 1917.

Organic Chemistry:

See Grignard Reaction (Porter); Industrial Chemistry (Strong); Names of Organic Compounds.

Paper:

See Pulp and Paper (Libby), (West).

Petroleum:

Emulsions in petroleum (lubricating oils). Harrison P. Smith, 615 South Virgil Ave., Los Angeles, Calif. 35 entries, by author and subject. Up to 1920. Abstracts included. Not very complete.

Geology and statistics of petroleum for the United States. G. B. Richardson, U. S. Geological Survey, Washington, D. C. Several hundred entries, by locality. The most important publications since 1900.

Latin-American petroleum. E. W. Shaw, 302 Cosden Bldg., Tulsa, Okla., or 170 Broadway, New York, N. Y. 1000 entries, by author. 90 per cent complete.

Monthly manuscript bibliography of petroleum. E. H. Burroughs, U. S. Bureau of Mines, Washington, D. C. Issued in mimeographed form. Cumulated and published annually as a Bureau bulletin.

Petroleum and natural gas. E. DeGolyer, 65 Broadway, New York, N. Y. 9000 to 10,000 entries, by author and locality. 80 per cent complete.

Petroleum and natural gas: geologic occurrence, statistics and technology. Johnson, Huntley, and Somers, Oil and Gas Bldg., University of Pittsburgh, Pittsburgh, Pa. 7000 entries, by author, subject, and locality. Fairly complete.

Oils from gilsonite. Emmett B. Carmichael, University of Colorado, Boulder, Colo. December 1920-date. Two-thirds complete.

See also Motor Fuels (Leslie); Oil Shale (McKee).

Petrology:

Chemical analyses of igneous rocks. H. S. Washington, Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C. 1913-date. Incomplete. Supplement to U. S. Geological Survey, *Professional Paper* 99.

Chemical composition of igneous rocks. Edward B. Mathews, Johns Hopkins University, Baltimore, Md. 9900 entries, by rock names and silica content. Practically complete to date.

Pharmaceutical Chemistry:

Pharmaceutical chemistry and botany. H. V. Arny. Several thousand entries. 1910-date. Abstracts included. For consultation, write College of Pharmacy, Columbia University, New York, N. Y.

Phenanthrene:

The Barrett Co., 40 Rector St., New York, N. Y. 160 entries, by author, subject, and patents. 1900-date. Abstracts included.

Phenols:

Alkali-insoluble phenols. O. M. Brewster, Pullman, Wash. 88 entries. 1881-1910.

Phosphates:

Acid phosphates and superphosphates. A. Marshall, 3043 St. Paul St., Baltimore, Md. Entries by subject. 1880-date.

Manufacture and uses of dicalcium phosphate. The Grasselli Chemical Co., Cleveland, Ohio. 21 entries. Abstracts included.

Phosphate deposits. Eliot Blackwelder, 317 Railway Exchange Bldg., Denver, Colo. 415 entries by author and title. Many abstracts included. 80 per cent complete.

- Soluble phosphates. Engineering Societies Libraries, New York, N. Y. 52 entries. 1878-1917. Abstracts included.
- The Western phosphate field. G. R. Mansfield, U. S. Geological Survey, Washington, D. C. 160 entries, by author. Many abstracts included. 60 per cent complete. To be published later.
- Phosphoric Acid:**
 Patents on phosphoric acid and its salts. William H. Ross, Bureau of Soils, Washington, D. C. 404 entries, by author, title and patent number. Covers whole period of U. S. Patent Office.
- Phosphoric acid. Engineering Societies Libraries, New York, N. Y. 81 entries. 1876-1918. Abstracts included.
- Phosphorus:**
 Engineering Societies Libraries, New York, N. Y. 83 entries. 1879-1917. Abstracts included.
- Photochemistry:**
 Action of light on organic compounds, visible spectra with few references to ultra-violet spectra. H. M. McLaughlin, Iowa State College, Ames, Iowa. 332 entries, by author and subject. 1850-1921.
- Chemical action of light. Clarence J. West, National Research Council, Washington, D. C. 2000 entries by author. One-half complete.
- Light: theory of photochemistry and biological effects. S. C. Brooks, Hygienic Laboratory, 25th and E Sts., N. W., Washington, D. C. Entries by author and subject. Up to 1918 and occasional later entries. Abstracts usually included. 60 to 70 per cent complete.
- Photosynthesis and allied subjects. H. A. Spöhr, Carmel, Calif. 450 entries, by author. 1797-1922. 95 per cent complete.
- Photography:**
 Physics and chemistry concerned with photography. Research Laboratory, Eastman Kodak Co., Rochester, N. Y. June 1915-date. Printed cards, covering all leading periodicals. Abstracts included.
- Phthalic Acid:**
 Mono-nitro- and monamino-*o*-phthalic acids. M. T. Bogert, Columbia University, New York, N. Y. Over 100 entries, chronological by subject. Up to 1903. Abstracts included. Practically complete.
- Piscatorial Chemistry:**
 Biological, physiological, and technological chemistry of fishes. Harden F. Taylor, Bureau of Fisheries, Washington, D. C. Several hundred entries, by subject. No effort made to include all material found in *Chemical Abstracts*.
- Chemistry of fish flesh. Lloyd H. Almy, Bureau of Chemistry, Washington, D. C. 150 entries. Very complete to 1915. Abstracts included.
- Pitch Coke:**
 Pitch coke for carbon electrodes. The Barrett Co., 40 Rector St., New York, N. Y. 82 entries, by author and subject. 1873-date. Abstracts included.
- Plant Chemistry:**
 Effect of nitrates on plants. H. G. MacMillan, Greeley, Colo. 396 entries, by author. 1882-date. Abstracts included in part.
- Salt absorption and mineral nutrition of plants. R. B. Harvey, University Farm, St. Paul, Minn. 575 entries, by author and subject. Up to date. Abstracts included in many cases. Nearly all references commonly available.
- See also Soils (Eaton); Tobacco (Gross).
- Platinum:**
 Platinum metals. R. Gilchrist, Bureau of Standards, Washington, D. C. 200 to 250 entries, by title. January 1, 1918-date. Brief abstracts in most cases. All references in *Chemical Abstracts* included.
- Poisons:**
 Economic poisons: substances used for the control of insects, fungi, weeds, and rodents. George P. Gray, State Department of Agriculture, Sacramento, Calif. 20,000 entries, by subject. Covers *Chemical Abstracts* 1911-1920; Experiment Station Record, Vols. 13-24.
- Potash:**
 Potash as by-product from blast furnaces and cement mills. Western Precipitation Co., 1016 W. 9th St., Los Angeles, Calif. 100 entries, by author and title. 1904-date. Abstracts included. Complete.
- Potassium Chlorate:**
 Decomposition of potassium chlorate. F. E. Brown and H. M. McLaughlin, Iowa State College, Ames, Iowa. 175 entries, by author, title, and subject. 1840-date. Abstracts included for about one-half. Must not pass out of owner's possession.
- Proteins:**
 Proteins and accessory factors in nutrition. H. A. Mattill, University of Rochester, Rochester, N. Y. 750 entries, by subject. 1912-date. Abstracts usually included. 90 per cent complete.
- Pulp and Paper-Making:**
 C. E. Libby, New York State College of Forestry, Syracuse, N. Y. 800 entries, by author, title, and subject. 1914-date. Very brief abstracts included. Covers four paper trade journals.
- Manufacture, chemical, and physical properties, methods of testing, etc., of pulp and paper. C. J. West, National Research Council, Washington, D. C. 5000 entries, by author, arranged under principal paper-making subjects. One-half complete.
- See also Bagasse (Little); Flax (American Writing Paper Co.).
- Pyrazoline:**
 Pyrazoline derivatives. L. L. Steele, Bureau of Standards, Washington, D. C. 70 entries. Up to and including 1916. Abstracts included. For consultation write either to the Bureau of Standards, Washington, D. C., or Chemical Library, Harvard University, Cambridge, Mass.
- Rare Earths:**
 Rare earths and secondary rare elements. Charles Baskerville. 25,000 entries. Not readily accessible. For consultation, write Library, College of the City of New York, New York, N. Y.
- Refractories:**
 Clay and graphite refractories. H. G. Schurecht, Bureau of Mines, Ceramic Experiment Station, Columbus, Ohio. 75 per cent complete.
- Magnesite and dolomite refractories. H. G. Schurecht, Bureau of Mines, Ceramic Experiment Station, Columbus, Ohio. 300 entries, by author, title, and subject. 1873-1921. Abstracts included. Includes six bibliographies and other references obtained from literature, being fairly complete.
- Resins:**
 See Naval Stores (Schorger); Terpenes (Grotlich).
- Roads:**
 Surface treatment of roads for laying dust. Arthur D. Little, Inc., Cambridge, Mass. 65 entries, by author.
- Rosin:**
 See Naval Stores (Schorger); Terpenes (Grotlich).
- Rubber:**
 Methods of rubber analysis. Frances McGovern, B. F. Goodrich Company, Akron, Ohio. 289 entries, by author and subject. Earliest references to 1920. Abstracts included. Considered complete.
- Rubber insulated cable. Arthur D. Little, Inc., Cambridge, Mass. 15 entries, by author.
- Salt:**
 Salt and salines. W. C. Phelan, The Solvay Process Co., Syracuse, N. Y. Entries by author, title, and locality. Complete to date.
- Salt, sulfur, and salt domes. E. DeGolyer, 65 Broadway, New York, N. Y. 400 to 500 entries, by author and locality. 80 per cent complete.
- Salvarsan:**
 See Arsphenamine (Flick).
- Sand:**
 Glass sands. Charles H. Richardson, Syracuse University, Syracuse, N. Y. 25 additional entries to bibliography published in 1920 in "Glass Sands of Kentucky."
- Sericin:**
 Arthur D. Little, Inc., Cambridge, Mass. 25 entries, by author.
- Smoke:**
 Washing of smelter smoke. F. A. Eustis, 131 State St., Boston, Mass. 330 entries. Up to 1915. For consultation, write to compiler or Library, Harvard University, Cambridge, Mass.
- Soap:**
 Hydrolysis and detergency of soap. L. W. Bosart, Procter and Gamble Co., Ivorydale, Ohio. 80 entries, by title. 1885-1921. Fairly complete.
- Sodium Silicate:**
 William Stericker, Mellon Institute of Industrial Research, Pittsburgh, Pa. 400 entries, by author and subject. 1850-date. Abstracts included.
- Soils:**
 Sulfur content of soils and its relation to plant nutrition. Scott V. Eaton, Department of Botany, University of Chicago, Chicago, Ill. Entries by author and title. 1910-date. Very incomplete.
- Sorrel Reaction:**
 See Cements (Schurecht).
- Specific Heat:**
 Specific heat of the elements, also includes heat of fusion and other energy changes. J. E. Mills, Edgewood Arsenal, Edgewood, Md. Entries by author. Up to 1917.
- Starch:**
 Hydrolysis of starch. Arthur D. Little, Inc., Cambridge, Mass. 133 entries, by author.
- Steel:**
 Boiler tube steel. A. E. White, University of Michigan, Ann Arbor, Mich. 17 entries. 1910-1921. Includes most of the pertinent books and articles bearing on the subject.
- See also Alloys (Estes); Iron (Joint Committee on Phosphorus); Lead Coatings (Berolzheimer).
- Storage Batteries:**
 Storage batteries; lead plate sulfuric acid type. Paul H. Segnitz, Vesta Battery Corporation, 2100 Indiana Ave., Chicago, Ill. In process of compilation.
- Sugar:**
 Determination of sugars by reduction methods. L. F. Hoyt, Larkin Co., Buffalo, N. Y. 50 entries, by author, title, and subject. 1841-1913.

Development of the sugar industry. Lizin A. Becnel, 1510 Arabella St., New Orleans, La. Numerous entries. Covers a period of 170 years. See also Lactose (Zoller); Maltose (Hoyt).

Superphosphate:
See Phosphates (Marshall).

Surface Tension:
Jessie Y. Cann, Smith College, Northampton, Mass. Entries by author. Abstracts included.

Tanning:
See Leather (Rogers); Tannins (Kressmann).

Tannins:
Tannins and the tanning industries. F. W. Kressmann. 3000 entries (316 typewritten pages), by author and subject. Up to 1911. Abstracts included. For consultation, write Forest Products Laboratory, Madison, Wis.

Terpenes:
Terpenes, resins, turpentine, rosin, and their general chemistry. V. E. Grotlisch, Leather and Paper Laboratory, Bureau of Chemistry, Washington, D. C. 500 entries, by title and subject. 1914-date. Abstracts included in some cases. 75 per cent complete.

Textiles:
See Chemistry (Mullin); Waterproofing (Fenn).

Titanium:
J. F. Haskins, Ohio State University, Columbus, Ohio. 1300 entries, by author. 1789 (time of discovery) to 1921. Abstracts included. Nearly complete.

Tobacco:
Chemistry and manufacture of tobacco. Paul Gross, Trinity College, Durham, N. C. Entries by author and subject. 1850-date (in chemistry); 1700-1919 (in manufacture). Abstracts included in a large portion of the chemistry section. Chemistry section about one-half complete.

Turpentine:
See Naval Stores (Schorger); Terpenes (Grotlisch).

Vanilla:
Vanilla extract. Arthur D. Little, Inc., Cambridge, Mass. 17 entries, by author.

Vegetable Oils:
See Fats and Oils (Thurman).

Viscosity:
Viscosimeters and viscosity (on oils). Charles A. Mann, University of Minnesota, Minneapolis, Minn. 200 entries, by author, title, and subject. Up to 1914. Very complete.
Viscosity: (a) General, (b) Rubber solutions. G. D. Kratz, The Falls Rubber Co., Cuyahoga Falls, Ohio. Several hundred entries. 1900-1915. Abstracts in almost all cases.
Viscosity (fluidity, plasticity, lubrication). Eugene C. Bingham, Lafayette College, Easton, Pa. 2000 entries, by author. 1500-1921. Complete as possible.

Vitamins:
Walter H. Eddy, Teachers College, Columbia University, New York, N. Y. 800 entries, by author. 1906-1921. Fairly complete. Partially published in his "Vitamin Manual."
J. F. McClendon, Medical School, University of Minnesota, Minneapolis, Minn.

Volumetric Chemical Analysis:
Volumetric chemical analysis, including colorimetric, gasometric, and epimetric methods. Launcelot W. Andrews, Williamstown, Mass. 17,000 to 20,000 entries, by author, title, and subject. 1847-1914. 1914-date, fragmentary. Brief abstracts included.

Water Glass:
See Sodium Silicate (Stericker).

Waterproofing:
Waterproofing, mildewproofing, and fireproofing of cotton, linen, and burlap fabrics in the heavier weights. Herbert B. Fenn, Metakloth Co., Lodi, N. J. 1868-1920. Abstracts included in some cases. Far from complete.

Water Softening:
See Zeolites (Bartow).

Waters:
Hydrogen-ion concentration of natural waters. F. C. Mortensen, Coe College, Cedar Rapids, Iowa. Abstracts in preparation. Complete.

Wheat:
Wheat milling and baking chemistry and chemical technology. C. H. Bailey, University Farm, St. Paul, Minn. Entries by author and subject. 1900-date. Abstracts included in one-third to one-half of the entries. Nearly complete.

Wood:
The acid hydrolysis of wood. E. C. Sherrard, Forest Products Laboratory, Madison, Wis. 150 entries, by author and subject. 1819-date. Abstracts included. Incomplete. A part is to be published soon in a departmental bulletin.

Wood Preservation:

Wood preservation, with specific reference to protection against marine borers. Clarence J. West, 1000 entries, by author. Two-thirds complete. For consultation, write Committee on Marine Borer Investigation, National Research Council, Washington, D. C.

Wood Tar:

Wood tar and wood-tar oils. The Barrett Co., 40 Rector St., New York, N. Y. 128 entries, by author and subject. 1871-date. Abstracts included.

Zein:

Chemistry of zein. Arthur D. Little, Inc., Cambridge, Mass. 15 entries, by author.

Zeolites:

Use of zeolites in water softening. Edward Bartow and G. C. Baker, State University of Iowa, Iowa City, Iowa. 214 entries, by author. 1907-1921. Abstracts included. Practically complete.

Making Chemistry a White Art

By H. W. Jordan

133 STOLP AVE., SYRACUSE, N. Y.

Advertising is a principle as fundamental as Kekule's benzol ring. It pays to advertise the AMERICAN CHEMICAL SOCIETY in order to destroy the popular notion that a chemist is a bald-headed, black-capped, back-room hermit, whose characteristic pose is that of looking for a precipitate in an old-fashioned, alembic glass retort filled with malt whiskey.

It was pretty generally noised about during 1917 and 1918 that it was a chemist's war. We admitted it. Now that peace rages, there is little said in the newspapers about its being a chemist's peace. Yet so far as peace is permitted to prevail by prime ministers and Congress, it is the peace of the chemist and engineer. Although the mark and rouble have fallen to ultramicroscopic value, and the price of food, fuel, and housing have grown to be measured almost in units of light years, the chemist produces a ton of pig iron with the same weight of coke and the engineer evaporates the same volume of water with a pound of coal as in 1914.

Since these things are so, why not let the public know it?

In arranging programs for this year, Local Sections of the AMERICAN CHEMICAL SOCIETY can do splendid service for the chemical profession by devoting a part of the lectures to subjects of common interest that will draw big general audiences to assemble with our technical selves. We can climb down from our high scientific niche for a noon hour or an evening to tell folks something of our valuable work in the essential industries of iron and steel, sugar, glass, or soap. We can show people the chemical side of laundry processes, of milk and its products, and of city sanitation. These topics, especially if illustrated, will draw scores where units now attend. At the same time, the lectures can be made as instructing to ourselves as though given before the usual section audience of a couple dozen chemical hardy perennials.

Lots of folks live on top of a thick coal vein, but if it doesn't crop out so that they stumble over it and blacken their hands, they never know the coal is there. Our one hundred million Americans live in a daily world of chemistry, yet only a tiny fraction of them realize it. People say, "Oh, he is a chemist, is he?" in much the same tone as they remark, "How natural he looks," at a funeral.

If we would have our achievements properly valued, we need spread them in the show windows to be admired and appreciated. Rotary Clubs, Chambers of Commerce, Commonweal Clubs, Women's Congresses, and dozens more, comb the country every winter for able speakers on any timely subject. If we expose our chemical orators to this raking, some of them will be joyfully gathered in as star attractions before crowds of business men and women. Thus, our profession of chemistry will get some of its share of deserved publicity. Incidentally, chemists will become more effective citizens.

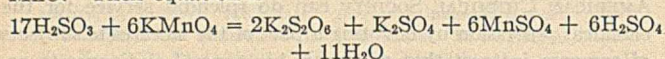
Electrometric Titration of Sulfurous Acid with Permanganate¹

By W. S. Hendrixson and L. M. Verbeck

DEPARTMENT OF CHEMISTRY, GRINNELL COLLEGE, GRINNELL, IOWA

THE PURPOSE of this work was to determine whether sulfurous acid in acid solution is completely oxidized to sulfuric acid by an excess of permanganate, as stated in the literature. If so, the excess of permanganate should be easily and accurately determinable electrometrically with potassium iodide, thus giving a simple method for determining sulfur dioxide, sulfurous acid, or sulfites. The results show that with a small or large excess of permanganate only about 90 per cent is oxidized to sulfuric acid, the remainder of the sulfurous acid probably forming dithionic acid.

The practicability of titrating sulfurous acid with permanganate seems so obvious that it is not surprising that it has been attempted by many chemists, although the results have many times been shown to be too low and discordant. For this fact two causes have been assigned, loss of sulfur dioxide and the incomplete oxidation to sulfuric acid by permanganate whether in excess or not. Nearly forty years ago Honig and Zatzek² stated that permanganate did not oxidize sulfurous acid completely to sulfuric acid in acid solution, but only in neutral or alkaline solution. In titrating sulfurous acid with permanganate Dymond and Hughes³ obtained as the average 88.9 per cent of the oxygen used as compared with theory for complete oxidation. By separate experiments on a large scale they definitely proved the formation of dithionic acid when they at the same time ran permanganate and sulfur dioxide into cold water, keeping the sulfur dioxide in excess. They regarded the formation of the dithionic acid as an essential part of the reaction, and due to a stage in the reaction, namely, the reduction of MnO_2 to MnO . Their equation is



which would require 88.2 per cent of the oxygen required for complete oxidation to sulfuric acid. They say, however, "When a solution of sulfurous acid is poured into an excess of permanganate, only sulfuric acid is formed."

Pinnow⁴ carried out several series of titrations of sulfite with permanganate in parallel with titrations by the iodine method. The oxidation to sulfuric acid was never found to be complete. Temperature, concentration, and acidity had little influence. His results varied from 90.9 per cent in acid to 97.2 in alkaline solution. He also assigned the discrepancy to the formation of varying amounts of dithionate.

Possibly encouraged by the statement quoted from Dymond and Hughes, two papers have appeared which propose the determination of sulfurous acid by oxidation with an excess of permanganate. Milbauer⁵ added a very dilute solution of the sulfurous acid to ten times the permanganate theoretically necessary to oxidize it to sulfuric acid and determined the excess with oxalic acid. Even though the oxidation were complete, it would be difficult to determine the fact by difference in his method, owing to the large magnification of the unavoidable error in determining such a great excess of permanganate. Sweeney, Outcault, and Withrow⁶ added sulfur dioxide or sulfite

to an excess of permanganate and determined the excess colorimetrically. They insist on an excess of permanganate at all times. This permanganate was standardized with specially purified sodium sulfite. However, a later communication⁷ from the same laboratory showed the impossibility of preparing in weighable condition pure sodium sulfite and called in question all determinations of sulfite based on sodium sulfite as a standard.

Though the preponderance of evidence seemed to be against the complete oxidation of sulfurous acid in acid solution by a moderate excess of permanganate, the question seemed to merit a more rigorous test than had apparently been applied to it, and the electrometric method⁸ as applied in the determination of nitrous acid seemed to meet the requirements.

The starting point was a solution of sodium sulfite placed in an atmosphere of hydrogen by use of an apparatus practically the same as that used by Thornton and Chapman.⁹ After standing three or four days it was standardized by the iodine method. In all titrations recently boiled water was used and the titrating vessel was kept full of carbon dioxide. Loss of sulfur dioxide was prevented by use of series of bulbs containing iodine and potassium iodide solutions in the standardizations, potassium permanganate in the titrations with permanganate. On account of the rapid change in the concentration of the sulfite solution it was restandardized by the iodine method on the same days that its concentration was determined with permanganate. Though protected in the apparently perfectly working apparatus which maintained an outward pressure of hydrogen equal to about 20-cm. water pressure, the sulfite solution lost daily about 1 per cent of its reducing power. This would require for the average amount of solution stored the access of about 40 cc. of air daily, which seems impossible, and the facts incline one to the view of Shenefield, Vilbrandt, and Withrow⁷ that the salt suffers autoxidation.

In carrying out the electrometric determinations with permanganate, a weighed amount of this solution was placed in the titration vessel, an amount of dilute, recently boiled and cooled sulfuric acid was added to make the acid concentration about normal at the end of the experiment, and a rapid stream of purified carbon dioxide was run through the solution for several minutes. The current of gas was slowed down, the mechanical stirrer was started and sufficient sulfite solution was run in to use about half of the permanganate in Series 1, nearly all in Series 2, and to the end-point in Series 3. In Series 1 and 2 the excess of permanganate was destroyed by a slight excess of known potassium iodide and then permanganate was run in until the voltage showed the end-point had been reached. The high degree of uniformity attained by essentially the same method in the determination of nitrous acid⁸ was not reached in the titration of sulfurous acid, indicating that the reaction in the latter case is variable, depending upon small differences in conditions that cannot be easily discovered or controlled. Only a few representative determinations are selected for each series. The value of the permanganate was found by sodium oxalate to be $0.05 N \times 1.033$.

¹ Received May 15, 1922.

² *Monatsh.*, **4** (1900), 738.

³ *J. Chem. Soc.*, **7** (1897), 314.

⁴ *Z. anal. Chem.*, **43** (1904), 91.

⁵ *Ibid.*, **48** (1909), 17.

⁶ *THIS JOURNAL*, **9** (1917), 949.

⁷ *Chem. Met. Eng.*, **25** (1921), 953.

⁸ Hendrixson, *J. Am. Chem. Soc.*, **43** (1921), 1309.

⁹ *Ibid.*, **43** (1921), 91.

SERIES 1—TITRATION OF SULFUROUS ACID WITH A LARGE EXCESS OF PERMANGANATE

Detn.	KMnO ₄ Reduced Cc.	Excess KMnO ₄ Cc.	Na ₂ SO ₃ Cc.	H ₂ SO ₄ to 1 Cc.
1	37.61	39.64	24.50	0.00325
2	33.86	41.74	24.95	0.00329
3	51.27	30.88	33.25	0.00326
4	31.28	16.73	20.00	0.00330
AVERAGE...				0.003275

The iodine method may not be perfect, but it is the best we have and is doubtless accurate enough for present purposes. Three determinations in parallel by the iodine method gave 0.00352 sulfurous acid in 1 cc. of the sulfite solution, which means that the permanganate gave only 93 per cent of its value.

SERIES 2—TITRATION OF SULFUROUS ACID WITH A SLIGHT EXCESS OF PERMANGANATE

Detn.	KMnO ₄ Reduced Cc.	Excess KMnO ₄ Cc.	Na ₂ SO ₃ Cc.	H ₂ SO ₄ to 1 Cc.
1	36.39	4.10	24.95	0.00309
2	37.10	2.84	25.00	0.00314
3	53.20	3.39	36.20	0.00311
AVERAGE...				0.003113

The iodine method gave at the same date 0.003476, or the permanganate method gave 89.6 per cent of the sulfurous acid present.

Two titrations as shown in Series 3 were made by running the sulfite solution into acidified permanganate to the end-point, with the result that the percentage of oxidation was found not materially different.

SERIES 3—TITRATION OF SULFUROUS ACID WITH PERMANGANATE TO THE END-POINT

Detn.	KMnO ₄ Reduced Cc.	Na ₂ SO ₃ Used Cc.	H ₂ SO ₄ to 1 Cc.
1	44.72	30.50	0.00311
2	63.18	42.60	0.00314
AVERAGE...			0.003125

The iodine method gave on the same day 0.00340, which is equivalent to 91.9 per cent of the sulfurous acid present.

The conclusion based on our results and the records of the work of others on this subject is that the development of an accurate method for the determination of sulfurous acid with permanganate is impracticable, perhaps impossible.

Some Notes on the Early Indigo Industry in the South¹

By B. B. Ross

ALABAMA POLYTECHNIC INSTITUTE, AUBURN, ALA.

THE INDIGO industry was one of the oldest, and historically one of the most interesting, of the early chemical industries of the southern states. The precise date of the introduction of indigo culture into this country is somewhat uncertain, but it secured a foothold in several of the southern colonies early in the 18th century.

In Louisiana as early as 1720, planters were furnished indigo seed by the Louisiana Company, and in 1723 the South Carolina Colonial Legislature granted a bounty on indigo to stimulate its production.

By 1746 the industry had reached such a flourishing condition that the bounty was repealed, but the British government by Act of Parliament in 1748 authorized the payment of an export bounty of 6 pence per pound on indigo shipped to the mother country.

According to Dr. D. D. Wallace, professor of history and economics in Wofford College, S. C., the establishment of the culture and production of indigo upon a successful and economic basis was due chiefly to the efforts of a woman, Miss Eliza Lucas, daughter of Governor Lucas of Antigua, and who subsequently became the wife of Col. Charles Pinckney. At her home on Ashpoo plantation near Charleston she carried out numerous experiments connected with the growing of indigo and the preparation for the market, and after encountering many difficulties and discouragements her endeavors met with success and gave a marked impetus to the development of the industry in the colony.

Professor Wallace states that the best results were obtained from growing seed imported from Guatemala, though the indigenous indigo was grown to some extent.

The method of preparation of the crude indigo for the market, as given by the same writer, was as follows:

The entire bush was laid in a stout pine or cypress vat about sixteen feet square and two and one-half feet deep, with the

bottom raised about four feet from the ground. This was the *steep*. A quantity of plants held down by sticks, with weights laid upon them, was immersed in water and left to steep for about twelve hours. The foaming and bubbling due to chemical action being finished, the water was let off through a hole near the bottom into another tank or vat, called the *beater*. In this, the indigo water was agitated violently for several hours by means of paddles—a process usually conducted by hand, but by some planters by means of a paddle wheel somewhat like the stern wheel of a river boat. * * * From time to time lime water was added from a tank or barrel which stood beside the beater.

The master indigo-maker decided from specimens dipped up in a saucer when the flakes had reached the proper degree of precipitation, after which the liquid was left to settle. A fine blue silt collected on the bottom. The liquid above was let off through a succession of holes in the side of the beater and the indigo silt scooped up and reduced by pressure to cakes, which were dried under a shed.

The commercial grades of the product were designated, in the order of quality from highest to lowest, as "fine blue," "ordinary blue," "fine purple," etc., while the most inferior quality was known as "ordinary copper."

As a rule in the southern colonies there were two cuttings of indigo each season, the first in May or June, and the second in September.

The amount of indigo exported from South Carolina in 1748 was 134,118 lbs., which increased to 1,150,662 lbs. in 1775. In Louisiana the exports of the province reached a total value of \$100,000 for the year 1769, while in 1775 a single settlement exported 50,000 lbs.

The yield of indigo per acre in the southern colonies ranged from 20 to 100 lbs., the average yield given by one authority being 30 lbs. per acre. The selling price of the product was quoted as ranging from 2½ shillings sterling up to \$1.20 per lb., and under exceptional conditions as high a figure as \$2.25 per lb. was said to have been realized.

The culture and production of indigo in South Carolina, Georgia, and Louisiana, played an important part in the economic and agricultural development of those colonies, and in South Carolina and southeast Georgia the indigo and rice crops were the chief sources of wealth of the large planters near the coast,

¹ From a paper on "Some of the Early Chemical Industries of the South" presented before the Section on History of Chemistry, at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

supplying, as one writer has stated, "the necessary material basis for the rich and cultured low country aristocracy whose influence upon the history of that section has been so powerful."

As a result of the loss of the English export bounty on indigo, and of the invention of the cotton gin, cotton culture after the Revolution rapidly displaced the growing of indigo in South Carolina and Georgia, while in Louisiana sugar soon became a successful rival of indigo.

Still another factor contributing to the downfall of the industry was the supposedly bad effects of the indigo process upon the health of the operatives. A writer of the period, in discussing this feature of the industry, said, "The whole process was of the most disgusting and disagreeable character, and myriads

of flies, generated by it, overspread the whole country. The fetor arising from the putrid weed thrown from the vats was intolerable." Drainage from vats which found its way into streams killed the fish therein and polluted these water courses.

Although the large-scale exportation of indigo ceased before the beginning of the last century, the production of indigo for domestic consumption continued for many years thereafter, and as late as 1845 as much as 35,000 lbs. of indigo were produced in Orangeburg County, South Carolina.

During the Civil War the indigo industry was revived to a certain extent and this important dyestuff was produced in limited quantities to meet the domestic demand.

GRASSELLI MEDAL AWARD

At the meeting of the Society of Chemical Industry at Rumford Hall, New York City, on October 20, 1922, the Grasselli Medal was presented to Mr. Walter H. Fulweiler, chemical engineer of the United Gas Improvement Co., Philadelphia, Pa. This medal is awarded annually by the American Section of the Society of Chemical Industry for the paper presented

before that Section which offers the most useful suggestion in applied chemistry.¹ Mr. Fulweiler is the second recipient of this honor, the first award having been made to Dr. Allen Rogers,² professor of industrial chemistry at Pratt Institute, Brooklyn, N. Y., for his paper on "Industrial Uses for the Shark and Porpoise."

Presentation

By Harlan S. Miner

THE American Section of the Society of Chemical Industry is highly favored in being able to give some tangible recognition to the meritorious papers presented at its meetings. The Grasselli medal and the conditions controlling its award are distinctly American in character. The fact that it is awarded for the paper which, in the opinion of the Medal Committee, offers the most useful suggestions in applied chemistry, makes it peculiarly appropriate in an industrial society. This is only one of many ways in which the donors are advancing the profession of chemistry in the United States.

The Committee of Awards has this year unanimously chosen as the recipient of this honor, Walter Herbert Fulweiler, of Philadelphia, in recognition of the paper which he presented at the March meeting of the Section entitled, "Chemical Problems in the Gas Industry."

The medalist was born in Philadelphia, January 3, 1880, received his preparatory education in the William Penn Charter School, and was graduated from the University of Pennsylvania in 1901, with the degree of B.S. in chemistry.

Having decided to devote his attention to the gas industry, he first accepted a position as chemist at one of the stations of the Philadelphia Gas Works. We next find him as cadet engineer and later as superintendent of manufacture of the Kansas City Gas Company. Returning to Philadelphia in 1907, he entered the Department of Tests of the United Gas Improvement Company, in 1913 becoming chief chemist, and in 1920 chemical engineer for that company.

As might be expected, Mr. Fulweiler's work in connection with the gas industry has been of a very practical nature, and has had a decided economic application, although he has by no means ignored the theoretical or purely scientific side of his subject.



WALTER H. FULWEILER

With an intimate personal knowledge of the industry both from an American and a European point of view, he constructed one of the first waste heat boilers on a water-gas set. Then he assisted in the design and erection of the first American type of vertical retort at Manchester, N. H.

The utilization of some of the ill-smelling by-products of the gas industry is worthy of note in this connection. Our medalist developed and introduced the successful road-binder produced from water-gas known as "Ugite," also the first cold patching material made from tar which is now extensively used in road maintenance. In connection with this work, he invented the "cut back" method

for manufacturing tar products used in the surface treatment of roads, and also devised an apparatus for determining the binding value of pure bitumens in road construction.

The refining of benzol products as recovered from illuminating gas was thoroughly investigated, particularly with reference to the production of toluene. Like many another loyal chemist connected with our "key" industries, he collaborated with the Ordnance Department during the war, studying particularly the manufacture of toluene. In addition to reporting on several methods for the production of this material so urgently needed at that time, he developed and perfected a process for its manufacture by a heat treatment of California distillates, and assisted in the construction and operation of two plants embodying this process—one at Los Angeles and the other at San Francisco, the former having a production of three million gallons a year at the time of the armistice.

Another subject upon which Mr. Fulweiler worked during the war period was the development of a motor fuel for our Air Service, finally producing one as a by-product from the operation

¹ THIS JOURNAL, 11 (1919), 162.

² *Ibid.*, 12 (1920), 1128.

of the toluene process, which under tests at the flying fields enabled the training plane to climb about 5 per cent faster with an economy in fuel consumption of about 8 per cent. This fuel consisted essentially of 60 per cent unsaturated hydrocarbons, 30 per cent benzene, and 10 per cent paraffin hydrocarbons. Refined by a special process, he found by service tests that it was possible to eliminate gumming and corrosion.

In more recent years our medalist has made an extensive study of the petroleum oils used in the gas industry, with special attention to the development of methods for their identification. These researches, which are still in progress, involve the preparation of a large number of hydrocarbons from different series and then the determination of their physical constants, among which are a number of unusual ones, such as magnetic rotation, electrostatic double refraction, and absorption spectra, particularly in the ultraviolet.

An examination of the many articles from Mr. Fulweiler's pen, and published in various journals, indicates still further the great diversity of his researches and developments. A paper on "Physical Theory of Coal Carbonization" as early as 1908 was awarded the Beale Medal by the American Gas Institute. This was followed by "Theory of Flame and Mantle Illuminosity," "Physical Characteristics of Ferric Oxide," "Purification of Water for Gas-Making Purposes," "A Source of Light, Giving a Continuous Spectrum in the Ultraviolet," "The Development of Modern Road Surfaces," "Destructive Action of Motor Traffic on Road Surfaces," and "Refractory Problems in the Gas Industry."

The subjects of wood preserving and of refractories, both vital to the economic success of a gas plant, have received very careful study, as have also the many intricate problems involved in gas purification. In this field researches have been conducted to determine the nature of the sulfur compounds in illuminating gas, and also the chemical reactions involved in the purification by iron oxide and its subsequent revivification.

These and other papers in addition to the one for which this medal is awarded, demonstrate conclusively that the industry which had its inception over a century and a quarter ago in a relatively crude way, now maintains its important position as a result of systematic scientific research and control. Notwithstanding the volumes that have already been written describing the work of the scientists in this and earlier generations, our medalist has found new fields to investigate and with results that have materially advanced the industry in which he has chosen to labor.

We are glad to find a man who will freely impart of the information obtained through his researches and experience and is willing to publish papers which, as our donors suggest, "offer useful suggestions" to his colleagues.

On behalf of the American Section of the Society of Chemical Industry, I am honored in presenting to you—Mr. Fulweiler—this beautiful medal, not so much as an incentive to spur you on to other and increasing activities, for you do not seem to require such a stimulus, but as a token of appreciation from your many

friends in the chemical profession. May you ever see in it an expression of our good will and may it bring you much happiness throughout a long and useful life.

Acceptance

By W. H. Fulweiler

In accepting this beautiful Grasselli medal, I find it difficult properly to express my appreciation of the many complimentary remarks you have made about my work. I am going to refrain from saying the usual things about my unworthiness, as I feel that this would be a reflection of the committee's judgment, and I wish to assure you that I am not unmindful of the honor that has been bestowed on me.

Thirty years ago the gas industry was doomed to early oblivion by the glowing possibilities of electricity. In spite of the tremendous strides of the electrical industry as a competitor, the gas industry to-day employs five times as many men as it did in 1890, its products have ten times their value and the money invested would to-day approximate \$4,000,000,000, which is nearly twenty times that invested in the industry in 1890. If the recent predictions of a prominent statistician regarding the early demise of the industry prove to be as correct as the predictions of 1890, we, in the industry, will have little to worry us.

It is true that the gas industry has lost a considerable portion of its lighting business. This has probably been fortunate, rather than unfortunate, as it has undoubtedly been a strong factor in eliminating the candle-power standards which prevented real progress of the industry for so many years.

The future of our industry, as I see it, is to be the delivery of heat energy in the most convenient, efficient, and economical form. A modern carbureted water-gas plant will deliver in the form of salable gas nearly 70 per cent of the heat energy put into the process.

To-day, a great deal of attention is being given to what is called the complete gasification of coal, as by this means we hope to transform even a greater percentage of heat energy in the fuel into gas. The processes that have been evolved to date yield a gas of much lower heating value from that which we are accustomed, being in the neighborhood of 340 B. t. u. per cu. ft., but it may well be that the heating value of the future will approximate this figure.

Technically, the gas industry is in the position of utilizing in everyday practice some of the most complicated chemical and physical reactions with very vague ideas of the mechanism involved, so that there is a large field for research work in determining the "why" of many of our commercial processes. A good start has been made, but there is a tremendous amount of work yet to be done.

I wish to take this opportunity to express my thanks to the Grasselli Chemical Company for its generosity in providing this medal, to the Committee for their consideration in awarding it to me, and to Dr. Miner for the many nice things he has said in presenting the medal to me.

Duplication of Bibliographic Lists and References

One of the first things a research chemist or chemical engineer does in preparation for work on a new problem is to establish the prior art on the subject. This is so essential that hundreds or even thousands of dollars' worth of time may be spent on the search for pertinent literature in various publications. Often distant libraries have to be visited or books borrowed from them. Not infrequently it is subsequently discovered that a complete bibliography on the subject, which would have saved at least half of the time of the searcher, exists. Quite commonly several individuals or industrial concerns simultaneously prepare reference lists or abstracts on the same subject. One notable instance of this sort of wasteful duplication is the compilation of a complete bibliography on the Grignard reaction by Dr. Henry Gilman in

Iowa and Dr. C. J. West in Massachusetts working in ignorance of one another's interest.

Bibliographies on scientific and technological subjects are constantly being prepared. Some are published. Some remain in manuscript. It is to the advantage of all investigators to be able to locate such reference lists when they need them. The Research Information Service of the National Research Council, Washington, has established a bibliographic section which aims to serve as a clearing house for information about the sources and availability of both published and unpublished lists of references. The catalog of bibliographies already contains thousands of cards. You are urgently invited to avail yourself of this new aid to research and to further its development by reporting bibliographies of your own which you would be willing to have duplicated or to loan under suitable conditions.

Ernest Solvay—An Appreciation

By William H. Nichols

61 BROADWAY, NEW YORK, N. Y.

THE DISTINGUISHED subject of this sketch, an honorary member of this SOCIETY, passed away in his sleep the 26th of May, 1922. It is well for us to pause and take note of some of the salient features of his life, so that those of us who have borne the heat and burden of the day may take renewed courage and pursue our course with determination to the end, and those who are just beginning life may learn what is necessary to attain that success which everyone should strive to achieve.

In an article as brief as this, only certain phases of Mr. Solvay's life and struggles can be considered. It would take a volume to do justice to them all, and to give an adequate idea of the character of the man. He did great things, but what attracts me to him most is not so much what he did, as what he was.

Ernest Solvay was born in the little Brabant town of Rebecq-Rognon, April 16, 1838. His father, a most estimable man, was a refiner of salt on a modest scale. To use Ernest's own words, his "infancy was passed in an atmosphere of chloride of sodium." He had a younger brother, Alfred, of whom he was extremely fond, and who was closely allied to him by bonds of love and mutual understanding during all his early struggles and later successes until called away January 23, 1894. The relations of these brothers were of such an intimate and touching nature that taken alone they will repay a careful study in these days when family affection and loyalty are not too frequently in evidence. After Alfred's death until his own final hour, Ernest's regard for him became a real religion. He would never consent to receive praise unless his brother's name was coupled with his own. Let us, therefore, in speaking of Ernest, remember how much Alfred should be considered as part of him—a loyal co-laborer.

Ernest passed several years at a boarding school in Malonne. He was planning a university course, but a grave malady obliged him to give this up—a bitter disappointment, as we can imagine. So he returned to his native village and kept his father's books. He naturally had considerable leisure, which he employed in reading elementary books on chemistry and physics. He was not long in putting some of his new-found knowledge into practice by making experiments in chemical combinations and reactions.

His uncle, Mr. Semet, was director of a small gas works at Schaarbeek. In 1860, Ernest was called to be his assistant, and here a new life began on a wider plane. He had always been familiar with salt, and now he added a knowledge of the preparation and properties of ammonia. In a year he had discovered and patented in Belgium the reactions now known as the Ammonia-Soda, or Solvay process, utterly unaware of work, without result, by several predecessors. Soon after began that memorable struggle to apply his discovery, which seemed so many times to be at the brink of failure, but which ultimately emerged so magnificent a success, owing to his dauntless courage and faith in himself. We must remember that chemical engineering was not very far advanced in 1861, and this young man was neither a chemist nor an engineer as we understand the terms. That he became both later was much to his credit, and furnishes another instance of the efficiency of hard knocks.

In 1861, a small experimental plant was installed at Schaarbeek. On December 28 of that year, Ernest writes:

Our apparatus is now in order and I believe nothing prevents beginning our experiments. If all goes as I have foreseen, as all

I have been able to try out up till now—apparatus, different combinations—all will go well. As far as I am concerned, however, I do not put too much faith in them and expect to have to make changes, for it would indeed be almost unheard of if everything were to succeed in an undertaking of this importance, and, moreover, entirely new. I have never been in doubt, and at present less than ever, of the success of the apparatus itself, and of the great advantage which there would be in operating on an industrial scale. What I cannot answer for, as indeed no one in my position could, is that I will see all my combinations succeed at the first attempt. I made a summary beforehand of all the difficulties which might arise, and already a certain number of these have been cleared up. No trouble has arisen in so far as my own conceptions are concerned.

Six days later, on January 4, Mr. Solvay wrote:

I believe that I can now tell you something serious, something really certain. If I have ever had the slightest doubt as to the value of my process in so far as its industrial application is concerned, it would now be completely cleared. On Monday, we put all the apparatus in operation, working on 100 kilos of material; everything went perfectly smoothly. All I had foreseen in so far as the ease, the regularity and the practical side of the process were concerned, was far surpassed.

Difficulties arose, and on June 4, 1862, after a shutdown of three weeks given up to repairs and new preparations, Mr. Alfred Solvay wrote:

We began to operate by trying out each apparatus, one at a time; all went well until yesterday. During the night we found that the pump was no longer drawing water. The well was dry, and we had to stop. This is a new delay, but as is always the case it does not come from the process itself! We really have had bad luck with our equipment! And we had had to work like horses day and night!

That same year, the two brothers and their foreman were nearly asphyxiated by an escape of gas, and were only saved by the lucky return of a workman who carried them into the open air. Experiments went on, however. When the trials were considered sufficiently advanced, negotiations were opened up in view of interesting two industrial companies in the enterprise, but without success.

Negotiations were then begun with Mr. Pirmez, and after six months Solvay & Co., with headquarters at Couillet, was founded on December 26, 1863. This was the first step. The second was no less difficult. It lasted until the end of October 1865, when the works were shut down after the most important unit had given way.

The year 1864 was passed in construction work and negotiations of all sorts. Before the end of the year it became necessary to issue a certain amount of new stock to increase the company's capital which was insufficient.

On December 15, 1864, everything was ready to begin work again, and Mr. Solvay wrote:

I spent yesterday and last night at Couillet trying out the new apparatus with water. All the units show leakages but nothing serious***. I am quite satisfied with the general result. When the repairs are completed we will have another trial, and I hope that by New Year we will be able to run the proper raw material through. Our well has not been giving enough water. We will have to run a pipe line to the Sambre which will take about eight days, unless there is an exceptional frost.

Of course there was a frost, but that was only the beginning of new difficulties, and on January 4, 1865, Alfred Solvay wrote:

Ernest arrived and we worked all day Sunday; we did not realize that it was the first of January. A bad leak had just broken out in the distilling apparatus. Everything had been going so smoothly! There had already been a leak, but we had been able to get around this difficulty by not using this particular part of the apparatus. Isn't it rough luck when we had taken such care and gone to such trouble?

Bad luck, however, continued. On June 26, 1865, it was decided to put the works in run again. Mr. Alfred Solvay writes at that date:

We may still have setbacks, but with the changes we have made we have great hope. Let us hope that this time all will go well, and that Ernest will finally be rewarded for so much energy, courage, perseverance, and sacrifice of every sort. Poor boy, he has already suffered a great deal!

In the meantime, the production reached 600 to 800 kilos a day.

Mr. Ernest Solvay writes at this time:

All our efforts have always been aimed at keeping going, if only a few days at a time, on a basis of 2 to 3,000 kilos in order to form a definite opinion of our affair. We always see the promised land in the distance without being able to reach it.

He ended his letter of August 3, 1865, as follows:

The process will win out. Of this I am absolutely certain, but much perseverance must still be applied. Our task is not yet finished. All would go more quickly if we were able to go straight ahead when we see what there is to be done, but we are in a situation which calls for reflection.

The situation which he mentions so delicately was financial.

On June 26, 1865, in the midst of almost insurmountable difficulties, Mr. Ernest Solvay had made an admirable report to Mr. Pirmez, in which he definitely stated his faith in the future of the process, giving as reasons, the enormous production of soda ash in the world, the lowering in the future of the cost of production to the extent necessary to take the place of sulfate of soda in the glass industry, the manufacture of soda crystals and the utilization of residues—in short, a complete program of what was to be realized later. In October a crack appeared in one of the units, but the apparatus was kept going by lowering the pressure and by admitting more gas. Bad luck, however, followed the brothers. A few weeks later the main unit blew up, carrying away, it would seem, their last hopes. They were completely broken down. Ernest felt that he was losing his hold on himself in the midst of so much misfortune; something had to be done. It was in such terms that a member of the family stated the case by letter, for it was in the midst of their family at Rebecq that the two Solvay brothers withdrew to comfort themselves, with their mother who was confident in the efforts of her sons, as all mothers should be, and with their sister. At this time, Mr. Ernest Solvay was married and his wife gave him that wonderful moral support which was to enlighten all his life. The works were shut down under pretext of repairs. The winding up of the affairs of the company was imminent, but this eventuality was avoided, for at this moment the Solvay parents gave

their sons a mark of confidence and abnegation which was to save them. They made a last sacrifice and put 40,000 more francs into the business. The two young men took up the fight anew. In a touching way we are given an opportunity of appreciating the combat which was going on in the mind of the inventor. Mr. Solvay writes:

If I am at times discouraged it is because I feel that I am in vain weighed down under all this burden, because I feel that despite my will power I am losing confidence in my strength—I am afraid to go on for fear of wearing myself out still further.

But this letter closes with a burst of enthusiasm:

I believe that I am capable of making a last effort, and of regaining sufficient energy to forget all, or at least a great deal, and to consider the work that I am about to do as a trial.

Finally on February 18, 1866, Mr. Ernest Solvay ends his letter in these terms:

We reached our 1,000 kilos mark at the end of last week. The product is superb. If we can go on a fortnight in this way, it will be as clear as day that our manufacturing problem is solved, and we must complete it and put ourselves at ease in so far as material is concerned. Let us hope that this time we will have attained success, and been able to prove it. There are so many reasons for desiring this.

Eight days later success was no longer in doubt, and Mr. Solvay writes:

After being so often within an inch, within a hairs-breadth of failure, can I finally succeed in regaining from others and from myself, that moral strength which the entire world seems to refuse me. After all that has happened, this would indeed be a splendid triumph! Let us not speak of it, we are too accustomed to setbacks and deceptions.

On July 1, 1866, at the time when the Austro-German war had just been declared all continued to go well, but then he writes:

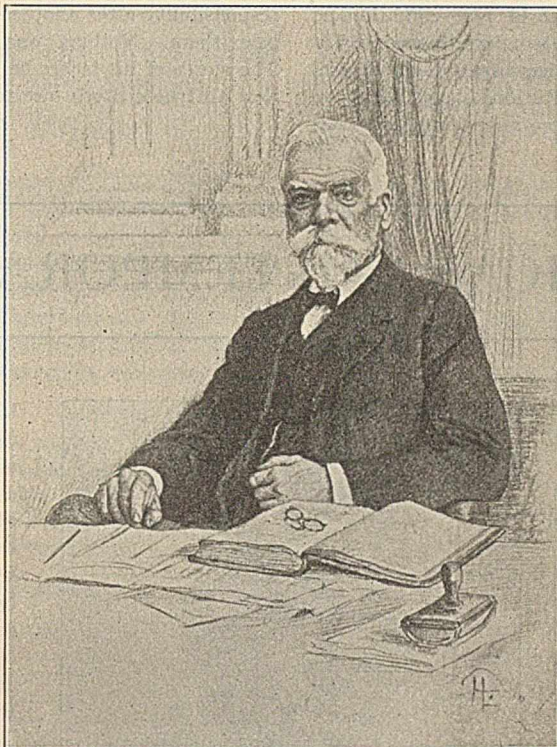
Had it not been for the war we could consider ourselves saved. This is indeed about the last straw.

Eight days later, however, a letter brings out the fact that for three days in succession production had reached 1,300 kilos:

We are working to reach 1,500 or 2,000 kilos. Then only will I believe that we are saved.

A month later, the daily production of 1,500 kilos became a regular thing; all was saved.

Space prevents further quotations. All the world knows what happened after this; plants to utilize the process were constructed in many countries, including our own, and the price of soda the world over came down by leaps and bounds. Neither can we pause to consider the immense influence this had in the whole field of chemical operations. Where others failed, a complete success had been scored. And yet, with all the concrete results, the story shows conclusively that the man was much greater than his works. He succeeded in the face of what seemed insurmountable difficulties, because of his character.



E. Solvay

His character. There is no mystery about that. It shone out in every walk of life, and in every problem that presented itself—simple, courageous, studious, affectionate, honest, and thoroughly human. We find him excelling as an Alpinist, climbing nearly every peak. We find him giving deep thought and study to the amelioration of his fellowmen. We find him, with these dreams and hopes shattered by the World War conditions in 1914 taking the lead in the movement so wonderfully seconded in our own country, to feed and clothe the unhappy people of Belgium. We find him endowing educational institutions of various sorts. We find him always doing good. But we never find him seek-

ing the spotlight. He sought the approval of his own conscience and I am sure he received it. He did not under-rate the value of the encomiums of his fellowmen, but these were a consequence and not an objective.

He lived a happy life, except during those terrible years of the Occupation. As old age came creeping on, he gave up one responsibility after another to those he had so well prepared to bear them. Nothing was forgotten. His life was complete. The words of his father he had made his own: "Work is a debt that all true citizens owe to society."

AMERICAN CONTEMPORARIES

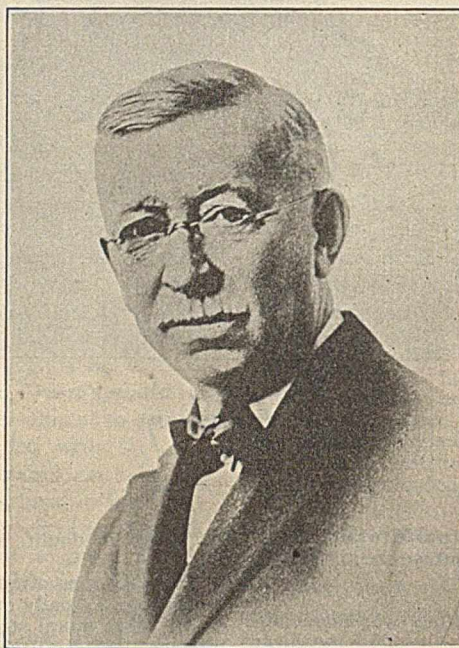
Edgar Fahs Smith

OPENING the door of a quiet study, softly lighted from high windows, walls lined with books and rare prints of eminent chemists of the ages—glimpsing here an ancient lock wrested from the door of Priestley's laboratory in Birmingham as it was destroyed by the mob, there a delicate balance brought by the aged exile to America—one senses contact with a *personality* before one sees, seated at the desk, the quiet figure of the man, Edgar Fahs Smith—teacher, administrator, author, chemist. Human, and of a generous and lovable nature, with a handclasp firm, warm, and sincere, his quiet smile puts one immediately at ease. Sympathy and strength seem to radiate from his person. A most friendly man, he makes friends and keeps them in all parts of the world. Not in a weak optimism, but in virile strength and sound judgment he thinks kindly of human nature.

A son of the soil of Pennsylvania, of pioneer American descent, educationally the product of an old-fashioned college curriculum, broadly trained in the humanities, specializing later in chemistry in a foreign university, a pupil of Wöhler—Dr. Smith's keen and correct appreciation of persons and policies, his power of concentration, of rapid and effective accomplishment of details demanding his attention, the never-flagging energies of his efforts, are qualities that have made him a marked man, and caused his University, his State, and the Nation to press him into services quite foreign to those of his chosen guild—chemistry.

A teacher of chemistry for 44 years, 21 of which were combined with administrative service, first as Vice Provost and then Provost of the University of Pennsylvania, Dr. Smith's career may be summed up as one which for length and richness has seldom, if ever, been equaled in the history of American collegiate education. An enthusiastic, inspiring teacher, an able and efficient administrator, he fairly won the title of the "best beloved college president of his generation."

Dr. Smith is a firm believer in the creed that it is better to wear out than to rust out, and his intense industry and



EDGAR FAHS SMITH

happy disposition furnish a living example of the joy of work. Gifted with rare ability as an investigator, his contributions in chemistry have made his name familiar to students of science throughout the world. More than 200 scientific papers have been published by him, as well as numerous books on chemistry. His monumental work on "Electro-Analysis" has reached six editions and has been translated into French, German, Italian, and Russian. Tungsten, molybdenum, columbium, tantalum, the separation of rare earths, and the constitution of complex inorganic acids, have particularly engaged his attention. His work in the field of atomic weights is characterized by marked originality.

In his valuable contributions to the field of historical chemistry, Dr. Smith has accomplished that rare thing—the imparting of literary charm to a scientific subject. Opening a door more than a century old, he has let us peep at the babyhood of American chemistry. In his biographies of Robert

Hare, James Cutbush, James Woodhouse, in "Priestley in America," and in "Chemistry in America" he has put flesh on the skeletons of pioneers in the science, making them living, breathing personalities, depicting their struggles and achievements in a manner inspiring to patriotic Americans of the present generation.

Other pages list the honors and rewards which have come to this man of many-sided interests. Thrice elected to the office of President of the AMERICAN CHEMICAL SOCIETY, his administrations have been characterized by untiring work for the protection of American chemical industries that America may be free from foreign domination, by aiming to build up American chemical literature, by urging a broader education for chemists as a proper foundation upon which to build for research, and by emphasizing the study of what American chemistry has done that American work, already large, may be appreciated.

Service, yes, in the highest sense of the word—service to mankind—so runs the record of Edgar Fahs Smith.

SCIENTIFIC SOCIETIES

Standard Methods for the Sampling and Analysis of Commercial Soaps and Soap Products¹

The *Committee on Methods of Analysis and Specifications of Commercial Soaps and Soap Products* of the *Division of Industrial Chemists and Chemical Engineers* of the AMERICAN CHEMICAL SOCIETY has given careful consideration to criticisms of its previous report² and has also cooperated with the Soap Committee of the American Specialty Manufacturers' Association and with the Technical Committee on Soaps of the U. S. Government, with the result that the following report was unanimously adopted April 3, 1922.

ARCHIBALD CAMPBELL, *Chairman*, The Globe Soap Co., Cincinnati, Ohio.
 C. P. LONG, The Globe Soap Co., Cincinnati, Ohio. J. R. POWELL, Armour Soap Wks., Chicago, Ill.
 PERCY H. WALKER, Bureau of Standards, Washington, D. C. R. E. DIVINE, Armour Soap Wks., Chicago, Ill.

APPLICABILITY OF THE METHODS

It is admitted that the methods of sampling may not in all cases yield samples that are truly representative of the whole lot, but any method that would do so would be so cumbersome and expensive as to defeat its own purpose.³ The methods given do not favor either buyer or seller, and are believed to be as accurate as the economic considerations warrant, and if mutually agreed upon should be satisfactory to all interested parties.

The methods of test differ somewhat in form, and in some cases in substance, from those given in the previous report, because the committee has attempted to cover methods that would be of importance in commercial transactions rather than methods that would be mainly of theoretical interest and only applicable in special cases. As presented, the methods of sampling and testing can be directly applied to commercial transactions, and it may be of interest to state that the methods prescribed in the specifications for various soap products recommended as U. S. Government Standards by the Federal Specifications Board are essentially the same as these.

A—SAMPLING

The seller shall have the option of being represented at the time of sampling and when he so requests shall be furnished with a duplicate sample.

I. CAKE SOAPS, FLAKE AND POWDERED SOAP PRODUCTS, WHEN PACKED IN CANS OR CARTONS—One cake (can or carton) shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 lbs. In the case of smaller containers, a cake (can or carton) shall be taken at random from each lot of containers totaling not more than 5000 lbs. The total sample shall in all cases consist of not less than three cakes (cans or cartons) taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs.

Wrap the individual cakes (cans or cartons) tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector shall accurately weigh each wrapped cake (can or

carton), record its weight and the date of weighing on the wrapper, place the wrapped cakes (cans or cartons) in an airtight container which should be nearly filled, and seal, mark, and send to the laboratory for test. Samples should be kept cool until tested.

II. FLAKE AND POWDERED SOAP PRODUCTS WHEN IN BULK—A grab sample of not less than $\frac{1}{2}$ lb. shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 100 lbs. In case of smaller containers, a grab sample of not less than $\frac{1}{2}$ lb. shall be taken at random from each lot of containers totaling not more than 10,000 lbs. The total samples shall in all cases consist of not less than three grab portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs. The inspector shall rapidly mix the sample, place in an airtight container, which shall be filled, and seal, mark, accurately weigh, record its weight and date of weighing on the package, and send to the laboratory for test. Samples should be kept cool until tested.

III. LIQUID SOAP—A sample of not less than $\frac{1}{2}$ pt. shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 10 gal. each. In case of smaller containers, a sample of not less than $\frac{1}{2}$ pt. shall be taken at random from each lot of containers totaling not more than 1000 gal. The total sample shall in all cases consist of not less than three portions of $\frac{1}{2}$ pt. each taken at random from separate containers. Before drawing the sample from the container selected, the contents of the container shall be thoroughly agitated. The inspector shall thoroughly mix the samples drawn, place in clean, dry cans or bottles, which shall be completely filled and securely stoppered with clean corks or caps; seal, mark, and send to the laboratory for test.

IV. PASTE SOAP PRODUCTS—(1) *When packed in cans or cartons of 5 lbs. or less.* One can or carton shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 lbs. In case of smaller containers, a can or carton shall be taken at random from each lot of containers totaling not more than 5000 lbs. The total sample shall in all cases consist of not less than 3 cans or cartons taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs. Wrap, seal, mark, and send to laboratory for test.

(2) *When packed in bulk.* Take a trial sample at random of not less than $\frac{1}{2}$ lb. from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 lbs. In case of smaller containers a trial sample shall be taken at random from each lot of containers totaling not more than 5000 lbs. The total sample shall in all cases consist of not less than 3 half-pound portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 10 lbs., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 10 lbs. The inspector shall promptly place the combined sample in a clean, dry, air- and watertight container, which shall be filled, and seal, mark, and send to the laboratory for test.

¹ Approved by the Supervisory Committee on Standard Methods of Analysis, American Chemical Society, July 29, 1922.

² THIS JOURNAL, 11 (1919), 785.

³ Sampling and testing small shipments is more or less impracticable, as the expense is in most cases greater than any differences that might be involved.

B—PREPARATION OF SAMPLES

I. CAKE SOAP—In case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. When the sample is large, each cake may be quartered and one-quarter of each cake run through the chopper. With samples that cannot be handled as above, select a cake of average weight, quarter it by cutting at right angles in the center and shave equally from all freshly cut surfaces sufficient soap for analysis. Mix and weigh out all portions for analysis promptly. Preserve the remainder in an airtight container in a cool place.

II. POWDERED AND CHIP SOAPS—Rapidly disintegrate and mix the sample; if desired, quarter down to about 1 lb. and weigh out all portions for analysis at once. Unused portions of the sample for analysis shall be preserved in an airtight container in a cool place.

III. LIQUID SOAP—No preparation of the sample, other than thorough mixing, is necessary unless it is received during very cold weather, when it should be allowed to stand at least 1 hr. after it has warmed up to room temperature (20° to 30° C.) before it is noted whether it forms a satisfactory lather.

IV. PASTE SOAP PRODUCTS—Mix thoroughly by kneading and quarter down to about 1 lb. Weigh out all portions for analysis promptly and preserve remainder in an airtight container in a cool place.

C—METHODS OF ANALYSIS

When a determination shows nonconformity with the specifications, a duplicate shall be run.

I. MATTER VOLATILE AT 105° C.—Weigh 5 g. of the sample in a porcelain or glass dish about 6 to 7 cm. in diameter and 4 cm. deep, dry to constant weight in an inert atmosphere at a temperature not exceeding 105° C.

II. TOTAL MATTER INSOLUBLE IN ALCOHOL. FREE ALKALI OR FREE ACID—(1) *Matter insoluble in alcohol.* Digest hot a 10-g. sample with 200 cc. of freshly boiled ethyl alcohol neutral to phenolphthalein (94 per cent or higher). Filter through a counterpoised filter paper neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper, or in the crucible, with hot neutral alcohol until free from soap. Dry the filter paper, or crucible, and residue at 100° to 105° C. for 3 hrs., cool, and weigh the total matter insoluble in alcohol.⁴

(2) *Free alkali or free acid.* Titrate the filtrate from the above, using phenolphthalein as indicator, with standard acid or alkali solution, and calculate the alkalinity to sodium hydroxide (or potassium hydroxide), or acidity to oleic acid.

(3) *Matter insoluble in water.* Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue, extract it with water at 60° C., and wash the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing.) Dry the filter and residue at 100° to 105° C. for 3 hrs., cool, and weigh matter insoluble in water. The nature of this matter may be determined by further examination.

(4) *Total alkalinity of matter insoluble in alcohol.* (*Alkaline salts.*) Titrate the filtrate from the determination of matter insoluble in water with standard acid, using methyl orange as indicator. Calculate the alkalinity to sodium oxide (Na₂O),

⁴ The matter insoluble in alcohol will contain most of the alkaline salts, such as carbonates, borates, silicates, phosphates and sulfates, as well as starch, and may be used for the approximate determination of these constituents. These salts are not entirely insoluble in alcohol, so for accurate determinations separate portions of the soap should be used.

For determination of carbonates see C—XI; phosphates, C—XII; sulfates, C—XIII; silicates, C—XX; borax, C—IX; starch, C—XIV(4).

and, if desired, to any other basis agreed upon by the parties interested.

III. COMBINED ALKALI. TOTAL ANHYDROUS SOAP—Dissolve 5 to 10 g. of the sample, depending upon the anhydrous soap content, in 100 cc. of water in a 250-cc. Erlenmeyer flask. When solution is complete, add dilute sulfuric acid in slight excess, insert a small funnel in the neck of the flask, and heat the flask at a temperature not exceeding 60° C. until the fatty acids separate as a clear layer. Transfer to a separatory funnel, draw off the acid layer into a second separatory funnel and shake the acid aqueous liquid with two 20-cc. portions of ethyl ether. Dissolve the fatty acids in the ether used for washing the aqueous liquid and shake with 10-cc. portions of water until they are no longer acid to methyl orange. Unite the water portions used for washing and shake with 20 cc. of ether. Wash this ether until the wash water is neutral to methyl orange. Save the acid water for chloride determination. Unite the ether solutions (if necessary, filter, washing the paper with ether) in a suitable weighed vessel, add 100 cc. of neutral alcohol free from carbon dioxide, add phenolphthalein and titrate to exact neutrality with standard sodium hydroxide solution. Evaporate off the alcohol, dry to constant weight as in the determination of matter volatile at 105° C. and calculate the percentage of soda soap. This soap naturally includes any mineral oil and neutral fat, which, if determined separately, must be deducted from the result to obtain the true soap. Calculate the combined sodium oxide (Na₂O) and deduct from the weight of soda soap to give the anhydrides. If the original soap was potash soap, proper calculation must be made to reduce to potassium oxide (K₂O), or the titration made directly with standard potassium hydroxide solution. In case the soap shows an excess of free acid, proper corrections must be made in calculating the combined alkali in the original soap.⁵ (See determination of rosin.) With soaps containing a large amount of soluble silicates and soap products containing a high percentage of finely divided material insoluble in water, the foregoing procedure cannot be applied as given. In such cases the filtrate obtained in the determination of total matter insoluble in alcohol can be used after neutralizing any free acid or alkali. Evaporate off the alcohol on a steam bath, take up in water and proceed as above.

With soap products containing a high percentage of matter insoluble in alcohol where approximate results will suffice, such as may be the case with cleansers, soap powders, scouring compounds, pastes, etc., and where agreed upon by the parties interested, the alcoholic solution, obtained after filtering off and washing the matter insoluble in alcohol, may be evaporated directly in a weighed vessel, dried at 105° C. to constant weight, and the result reported as soap.

IV. CHLORIDE—Neutralize with chlorine-free alkali the acid water obtained in paragraph C—III. Titrate with standard silver nitrate solution, using potassium chromate as indicator, and calculate the result to sodium chloride or potassium chloride as the character of the soap indicates.

In case the total anhydrous soap is not to be determined it will be more convenient to use the following method.⁶ Dissolve 5 g. of the sample in 300 cc. of water, boiling if necessary to effect solution. Add an excess of neutral, chlorine-free magnesium nitrate solution (about 25 cc. of a 20 per cent Mg(NO₃)₂·6H₂O solution). Without cooling or filtering, titrate with standard silver nitrate solution, using potassium chromate as indicator.

V. UNSAPONIFIED AND UNSAPONIFIABLE MATTER—Weigh 5 g. of the soap into a beaker and dissolve in about 100 cc. of 50 per cent alcohol on the steam bath. If the sample has been found to contain free fatty acid, add just enough aqueous alkali to neutralize this. Evaporate off the bulk of the alcohol, take up

⁵ A blank test should be made on the sodium or potassium hydroxide solution for neutral salts and the proper corrections made if necessary.

⁶ H. C. Bennett, THIS JOURNAL, 13 (1921), 813.

with about 200 cc. of hot water and transfer to a separatory funnel of about 500-cc. capacity, designated as No. 1. When cool, rinse out the beaker with about 50 cc. of ether and add it to the soap solution. Shake thoroughly for one minute. By the addition of small amounts of alcohol (5-cc. portions and the total not to exceed 25 cc.), a clear and rapid separation of the aqueous and ether layers is effected. After adding each alcohol portion, the separatory funnel is not shaken but merely given a whirling movement. Draw off the aqueous portion into another separatory funnel, designated as No. 2. Wash the ether solution with 10-cc. portions of water until this water is no longer alkaline to phenolphthalein. Add all these washings to Funnel No. 2 and extract this solution with 20-cc. portions of ether until the ether is absolutely colorless (3 or 4 extractions should be sufficient). Combine these ether extracts in a third separatory funnel (No. 3) and wash with 10-cc. portions of water until the water is no longer alkaline to phenolphthalein. Now add the ether in Funnel 3 to that in Funnel 1, a small amount of ether being used to rinse out Funnel 3. Wash the ether solution with 20 cc. of 10 per cent hydrochloric acid solution and then successively with 20-cc. portions of water until the water is no longer acid to methyl orange. Filter the ether solution through a dry filter paper into a weighed beaker or flask. Evaporate or distil off the ether on the steam bath, dry as under the determination of matter volatile at 105° C. and weigh the residue, then heat with alcohol and, when cool, neutralize with standard alkali, using phenolphthalein. Deduct any appreciable amount of fatty acid found by this titration from the weight of the residue. This residue consists of the unsaponifiable matter and any neutral fat that may have been present in the soap. In case it is desired to separate these, thoroughly saponify the residue with alcoholic alkali and repeat the foregoing procedure. The residue obtained is unsaponifiable matter only.

VI. ROSIN—*Wolff's method*.⁷ Dissolve 5 g. of the sample in 100 to 200 cc. of hot water, add a slight excess of dilute sulfuric acid, heat until the fatty acids collect in a clear layer, cool to room temperature, extract with a small portion of ether, draw off the water layer and wash the ether solution with water until free from mineral acid. Transfer to a 200-cc. Erlenmeyer flask, evaporate off the ether and dry 1 hr. at 105° C., cool and dissolve in 20 cc. of absolute alcohol. Then add 10 cc. of a solution of one volume of concentrated sulfuric acid (sp. gr. 1.84) and 4 volumes of absolute alcohol, and boil on the steam bath for 4 min. under a reflux condenser. Remove from steam bath, add to the liquid about 5 times its volume of 7 to 10 per cent sodium chloride solution, and extract with ether. Shake out the aqueous portion 2 or 3 times with ether. Unite the ether solutions and wash with sodium chloride solution until the washings are neutral to methyl orange. Add 30 cc. neutral alcohol, and titrate the rosin acids with standard sodium hydroxide solution, using phenolphthalein as indicator. Calculate to rosin or rosin soap, as desired (1 cc. normal alkali = 0.346 g. rosin or 0.377 g. rosin soda soap). If the true fatty acid soap is desired, subtract the rosin soap from the total anhydrous soap obtained under C-III.

VII. TITER TEST—(1) *Preparation of total fatty matter (fatty and rosin acids and unsaponified matter)*. Dissolve about 50 g. of soap in 500 cc. of hot water, add 100 cc. of 30 per cent sulfuric acid, heat until the fatty matter collects in a clear layer, siphon off the acid layer and wash the fatty matter free from sulfuric acid with hot water. Decant the fatty matter into a dry beaker, filter, using a hot-water funnel, or placing both funnel and receiving beaker in a water-jacketed oven, and dry for 20 min. at the temperature of boiling water.

When other determinations are to be made on the total fatty matter, and volatile and readily oxidizable fatty acids are present, the following method should be used: Dissolve about 50 g. of

the soap in 300 cc. of hot water, transfer to a separatory funnel, add 150 cc. of approximately 2 *N* sulfuric acid, cool somewhat, add 120 cc. of ether, shake, draw off the acid layer, and wash the ether layer free from acid with a strong salt (NaCl) solution. Then draw off the aqueous layer as completely as possible, transfer the ether layer to a flask (it is not necessary to transfer quantitatively), add 20 to 30 g. of anhydrous sodium sulfate, stopper the flask, shake, and let stand at a temperature below 25° C. until the ethereal liquid becomes perfectly clear, showing that all water has been taken up by the sodium sulfate. Filter through a dry paper into another Erlenmeyer flask, and completely evaporate off the ether by passing through the flask a current of dry air and heating the flask to a temperature not above 50° C.

(2) *Determination*.⁸ (a) *Thermometer*. The thermometer shall be a standard titer thermometer graduated at zero and in tenth degrees from 10° to 65° C., and certified by the U. S. Bureau of Standards.

(b) *Procedure*. Transfer the fatty acids prepared as under VII(1), when cooled somewhat, to a titer tube 25 mm. by 100 mm. placed in a 16-oz. salt-mouth bottle of clear glass 70 mm. by 150 mm., fitted with a cork that is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly (about 100 r. p. m.) until the mercury remains stationary for 30 sec. Allow the thermometer to hang quietly with the bulb in the center of the tube and report the highest point to which the mercury rises as the titer of the fatty acids. The titer should be made in a room at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

VIII. ACID NUMBER OF FATTY ACIDS—(1) *Preparation of fatty acids*. Follow procedure given under C-VII.

(2) *Determination*. In a 250-cc. Erlenmeyer flask dissolve 2 g. of the fatty acids, accurately weighed, in 20 to 30 cc. of neutral 95 per cent ethyl alcohol. Titrate with standard alkali, using phenolphthalein as indicator. Calculate the acid number (mg. of KOH per g. of fatty acids).

IX. BORAX DETERMINATION⁹—Weigh 10 g. of the soap (or 5 g. if more than 5 per cent of borax is present) into a platinum dish and add 2.15 g. of fusion mixture (consisting of 200 g. sodium carbonate, 15 g. silica in fine powder). To this mixture add 15 cc. of alcohol, mix with the aid of a glass rod and, after washing the rod with a little alcohol, evaporate the mass to dryness on the water bath. Ignite until the combustible material is destroyed, cover the dish with a piece of platinum foil and fuse. Completely disintegrate the fusion by boiling with water and transfer the solution to a 250-cc. round-bottom flask. Acidify with 20 cc. of dilute hydrochloric acid (1:1), heat nearly to boiling, and add a moderate excess of dry precipitated calcium carbonate. Connect with a reflux condenser and boil vigorously for 10 min. Filter out the precipitate through a folded filter, washing several times with hot water, but keeping the total volume of liquid below 100 cc.

Return the filtrate to the flask, add a pinch of calcium carbonate and again boil under a reflux condenser. Remove the flame and connect the top of the condenser with a water pump. Apply the suction until the boiling has nearly ceased. Cool to ordinary temperature, add 50 cc. of neutral glycerol and titrate the solution with 0.1 *N* sodium hydroxide, free from carbonate, using phenolphthalein as indicator. After the end-point is reached add 10 cc. more of glycerol and again titrate. Repeat this process until the addition of glycerol causes no further action on the end-point. The number of cubic centimeters required multiplied by 0.00955 will give the equivalent of borax (Na₂B₄O₇·10H₂O) present in the solution.

⁸ "Methods of Analysis of Assoc. Official Agr. Chem.," 1920, 242. Fat Analysis Committee Method, THIS JOURNAL, 11 (1919), 1163.

⁹ Poetschke, *Ibid.*, 5 (1913), 645.

⁷ *Chem.-Ztg.*, 38 (1917), 369, 382, 430; C. A., 8 (1914), 2495.

X. DETERMINATION OF SILICA PRESENT AS ALKALINE SILICATES—When the material contains no mineral matter that is insoluble in water, ignite a sample of the soap containing not to exceed 0.2 g. of silica in a platinum dish at a low temperature. When charred, extract the soluble salts with water, return the paper and charred residue to the dish and complete the ignition. Unite the residue in the dish and the water extract, carefully acidify with hydrochloric acid, finally adding the equivalent of from 5 to 10 cc. strong hydrochloric acid in excess. The dish or casserole containing the solution should be covered with a watch glass while adding acid so as to avoid loss by spray.

When the material contains mineral matter insoluble in water, or a determination of highest accuracy is not necessary, take a portion of the solution after titrating the matter insoluble in alcohol C-II(4) containing not more than 0.2 g. silica and add 5 to 10 cc. strong hydrochloric acid.

Evaporate the acidified solution (washing off and removing the cover glass if used) to dryness on steam bath or hot plate at a temperature not exceeding 200° C. Cool, moisten with concentrated hydrochloric acid, let stand 5 to 10 min., breaking up all lumps with a stirring rod. Add about 25 cc. of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

Evaporate the filtrate to dryness and repeat the above treatment, filtering on a second paper. Carefully ignite the two papers and contents in a weighed platinum crucible, first at a low temperature until the paper is consumed, but finally heating to constant weight over the blast lamp; cool in a desiccator before weighing. If extreme accuracy is desired, moisten the contents of the crucible with water, add 10 cc. hydrofluoric acid and 4 drops of strong sulfuric acid, evaporate to dryness over a low flame, ignite at the temperature of the blast lamp for about 2 min., cool in a desiccator and weigh. The difference between this weight and the previous weight is the weight of the silica (SiO₂).¹⁰

To calculate sodium silicate (Na₂Si₂O₅) multiply weight of SiO₂ by 1.26.

XI. DETERMINATION OF CARBON DIOXIDE (CARBONATES)—For most determinations the dry matter insoluble in alcohol as obtained in C-II(1) will be suitable for this determination. In some cases it might be desired to run the test directly on an original sample of the soap. This should always be done when the highest accuracy is required. Any reliable absorption method for determining carbon dioxide may be used.¹¹

The following is a method which has proved satisfactory:

A 250-cc. Erlenmeyer flask is placed on a gauze over a burner. The flask is equipped with a 2-hole rubber stopper, through one opening of which is a 10-in. reflux condenser and through the other a thistle tube equipped at the outer end with a 3-way stopcock. The lower end of the thistle tube is drawn to a small point, which is placed very close to the bottom of the flask. To the straightaway end of the stopcock is attached a small funnel for the introduction of acid to the flask. The other opening of the stopcock is attached to receive air from a purifying train consisting of a wash bottle containing concentrated sulfuric acid and a second at the outer end of the train containing a 50 per cent solution of potassium hydroxide. The top of the reflux condenser is attached first to a drying wash bottle containing concentrated sulfuric acid, and then to a weighed absorbing train consisting of a suitable potash bulb charged with 50 per cent potassium hydroxide, and a second containing concentrated sulfuric acid. This train is attached to a protective U-tube containing calcium chloride. The U-tube is attached to an aspirator.

¹⁰ "The Analysis of Silicate and Carbonate Rocks," by W. F. Hillebrand, *U. S. Geol. Survey, Bull.* 700, 102.

¹¹ "Methods of Analysis of Assoc. Official Agr. Chem.," 1920, 277, *Bur. Chem., Bull.* 107, 169.

Procedure. Set up the apparatus, leaving out the weighed train, and aspirate with a slow stream of the dry carbon-dioxide-free air until the apparatus is freed from carbon dioxide. Insert the train and continue the aspiration for 1/2 hr. Check the weight of the train to determine if the air is passing through too fast, or if the system is free from carbon dioxide. The system must be free from leaks. Weigh out 1 or 2 g. of the sample into the Erlenmeyer flask, cover with 20 cc. freshly boiled distilled water, close the apparatus with the train in place. Add 20 cc. dilute hydrochloric acid (1:1) through the funnel very slowly, with no heat being applied to the flask. The rate of adding acid should be carefully controlled so that the gas does not pass through the train too rapidly. As soon as the acid is added, start aspiration gently. When the absorption begins to stop the gas flow, start heating gently and continue until the contents of the flask have boiled 15 to 20 min. Stop heating and continue aspirating until the flask has cooled down. Remove the train and weigh. Calculate increase of weight as carbon dioxide. Carbon dioxide multiplied by 2.41 equals sodium carbonate.

XII. DETERMINATION OF PHOSPHATES¹²—If a qualitative test has shown the presence of phosphates and their determination is desired, the matter insoluble in alcohol C-II(1) or the ash from the incineration of an original sample can be used. An original sample should always be used when the highest accuracy is desired.

(1) *Reagents.* (a) *Molybdate solution.* Dissolve 100 g. of molybdic acid in dilute ammonium hydroxide [144 cc. of ammonium hydroxide (sp. gr. 0.90) and 271 cc. of water]; pour this solution slowly and with constant stirring into dilute nitric acid [489 cc. of nitric acid (sp. gr. 1.42) and 1148 cc. of water]. Keep the mixture in a warm place for several days or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered vessels.

(b) *Ammonium nitrate solution.* Dissolve 200 g. of commercial ammonium nitrate, phosphate-free, in water, and dilute to 2 liters.

(c) *Magnesia mixture.* Dissolve 110 g. of crystallized magnesium chloride (MgCl₂·6H₂O) in water, add 280 g. of ammonium chloride, 261 cc. of ammonium hydroxide (sp. gr. 0.90), and dilute to 2 liters.

(d) *Dilute ammonium hydroxide for washing.* Dilute 100 cc. of ammonium hydroxide (sp. gr. 0.90) to 1 liter.

(2) *Determination.* Weigh out a 2-g. sample of the alcohol-insoluble or ash, and proceed as in C-X for removal of silica, saving the filtrate. Make up to 250 cc., concentrating if necessary. Take an aliquot corresponding to 0.50 g. or 1 g., neutralize with ammonium hydroxide, and clear with a few drops of nitric acid. Add about 15 g. of dry ammonium nitrate or a solution containing that amount. To the hot solution add 70 cc. of the molybdate solution for every decigram of phosphoric acid (P₂O₅) present. Digest at about 65° C. for an hour, and determine if the phosphoric acid has been completely precipitated by the addition of more molybdate solution to the clear supernatant liquid. Filter and wash with cold water or, preferably, ammonium nitrate solution. Dissolve the precipitate on the filter with ammonium hydroxide and hot water, and wash into a beaker to a bulk of not more than 100 cc. Nearly neutralize with hydrochloric acid, cool, and from a buret add slowly (about 1 drop per sec.), stirring vigorously, 15 cc. of magnesia mixture for each decigram of phosphoric acid (P₂O₅) present. After 15 min. add 12 cc. of ammonium hydroxide (sp. gr. 0.90). Let stand till the supernatant liquid is clear (2 hrs. is usually enough), filter, wash with the dilute ammonium hydroxide until the washings are nearly free from chlorides, ignite to whiteness or to a grayish white, weigh, and calculate to phosphoric acid (P₂O₅), or alkaline phosphate known to be present.

¹² "Methods of Analysis of Assoc. Official Agr. Chem.," 1920, 1.

XIII. DETERMINATION OF SULFATES—For most determinations the matter insoluble in alcohol obtained under C-II may suffice. If a determination of the highest accuracy is desired, ignite a 10-g. sample of the soap and use the ash from the ignition. Digest with 100 cc. of water, cover with a watch glass, and neutralize carefully with hydrochloric acid. When neutralized, add 5 cc. excess of hydrochloric acid, filter, and wash the residue thoroughly.¹³ Make up the filtrate to 250 cc. in a beaker, and boil. To the boiling solution add 15 to 20 cc. 10 per cent barium chloride solution slowly drop by drop from a pipet. Continue boiling until the precipitate is well formed, or digest on a steam bath over night. Set aside over night or for a few hours, filter through a prepared Gooch crucible, ignite gently, and weigh as barium sulfate. Calculate to sodium sulfate, or the alkaline sulfate known to be present.

XIV. DETERMINATION OF GLYCEROL, SUGAR, AND STARCH—
(1) *Determination of glycerol in the absence of sugar.*

SOLUTIONS REQUIRED
Potassium Dichromate, 74.552 g. per liter
Sodium Thiosulfate, 0.1 N
Potassium Iodide, 10 per cent

Dissolve an accurately weighed sample of the soap¹⁴ equivalent to not more than 3.0 g. of glycerol in 200 cc. of hot water in a 600-cc. beaker. Decompose with 25 cc. sulfuric acid (1:4). If alcohol is present, volatilize it by boiling for 20 to 30 min. Cool, remove, and rinse the cake of fatty acids, transfer the acid water and rinsings to a 500-cc. graduated flask, add about 0.25 g. silver sulfate to precipitate traces of chlorides and soluble fatty acids. Make up to volume and mix contents thoroughly.

Transfer a filtered, accurately measured 50-cc. aliquot of the above to a 400-cc. beaker, to this add 75 cc. accurately measured potassium dichromate solution, followed by 25 cc. of sulfuric acid (sp. gr. 1.84). Cover with a watch glass, and oxidize by heating in a steam bath for 3 hrs. Conduct a blank in like manner but using 100 cc. of water, 25 cc. of sulfuric acid (sp. gr. 1.84), and 25 cc. accurately measured potassium dichromate.

Cool and make up the solution to 1000 cc. in graduated flasks. The excess of potassium dichromate is determined by taking 50 cc. aliquot of the above, adding 50 cc. of water, 20 cc. of 10 per cent potassium iodide solution, and titrating the liberated iodine with 0.1 N thiosulfate, using starch solution as indicator.

Calculate the percentage of glycerol (1 cc. of the potassium dichromate solution equals 0.0100 g. of glycerol).

(2) *Determination of sugar.*¹⁵ Dissolve 10 g. of the soap in 200 cc. of hot water in a 600-cc. beaker. Decompose with 25 cc. of sulfuric acid (1:4), boil gently for 20 min. to invert the cane sugar completely. Cool, remove, and rinse the cake of fatty acids. Extract the acid liquid with 25 cc. of ether. Transfer the acid liquid to a 500-cc. graduated flask, make up to volume and mix thoroughly. Determine invert sugar in 50 cc. of this solution by the Munson-Walker Method.¹⁶ To calculate sugar (sucrose) multiply the amount of invert sugar found by 0.95.

(3) *Determination of glycerol in the presence of sugars.*¹⁷ Proceed as above under (1), taking a sample so that the sum of the glycerol and sugar is not more than 3.0 g.¹⁸ The solution must be boiled in all cases at least 20 min. to insure complete inversion

¹³ Evaporation to dryness is unnecessary unless gelatinous silica should have separated, and should never be performed on a bath heated by gas. See Hillebrand, *U. S. Geol. Survey, Bull.* 700, 232.

¹⁴ If starch is present, it will be necessary to remove the matter insoluble in water as described under this determination [C-II (1) and (3)]. Combine the alcohol and water solutions, evaporate off the alcohol, and proceed.

¹⁵ If starch is present, see footnotes 13 and 18, and determination of starch XIV(4).

¹⁶ *J. Am. Chem. Soc.*, 28 (1906), 663; *Bur. Chem., Bull.* 107; "Methods of Analysis of Assoc. Official Agr. Chem.," 1920, 78.

¹⁷ Hoyt and Pemberton, *THIS JOURNAL*, 14 (1922), 54; Correction, 14 (1922), 340.

¹⁸ See footnote 13, if starch is present.

of cane sugar. Determine the amount of potassium dichromate solution required to oxidize both the sugar and glycerol. Determine also the sugar by the method given in (2).

Calculate the percentage of glycerol after deducting the amount of potassium dichromate required by the sugar.

1 cc. potassium dichromate equals 0.0100 g. glycerol.

1 cc. potassium dichromate equals 0.01142 g. invert sugar.

(4) *Determination of starch.*¹⁹ Separate the matter insoluble in water as under C-II(3), using a sample of soap that will give not more than 3 g. of starch. Transfer the insoluble matter, without drying, to a beaker and heat for 2½ hrs. with 200 cc. of water and 20 cc. of hydrochloric acid (sp. gr. 1.125) in a flask provided with a reflux condenser. Cool, and nearly neutralize with sodium hydroxide. Complete the volume to 250 cc., filter, and determine the reducing sugars by the gravimetric method as given under method for the determination of sugar.

Calculate the amount of dextrose (*d*-glucose) equivalent to the cuprous oxide obtained. This multiplied by 0.90 equals the amount of starch.

XV. VOLATILE HYDROCARBON—Weigh not less than 250 g. of the sample into a flask of about 5-liter capacity, which is so placed on a gauze that it can be heated. Add 2 to 3 liters of distilled water. Place a 2-holed rubber stopper in the flask, through one hole of which is inserted a copper or brass tube extending into the flask and terminating in a small circular ring of the tubing, bent so that the ring is in a horizontal position. Numerous small holes are drilled in the upper side of this ring and the end of the tube is sealed. This ring should be near the bottom of the flask.

Through the other hole of the stopper is inserted a glass tube provided with a trap of suitable form, the upper end of which is bent so as to be connected with a plain Liebig condenser. The end of the condenser tube is bent so as to extend into a buret graduated to 0.1 cc.

Introduce steam (free from oil) into the flask through the brass tube and collect the distillate in the buret. When the buret becomes full, draw off the water by opening the stopcock. The foam which forms in the flask may be controlled by momentarily shutting off the steam and by regulating heat applied to the flask.²⁰

Read from time to time the amount of hydrocarbon distillate which collects on the top of the water in the buret, and when there is no further increase in this distillate the operation is finished. Allow the buret to stand over night, tightly stoppered, and then, after reading the amount of distillate, draw off the water as carefully as possible. Determine the specific gravity of the distillate, and calculate the weight and percentage in the original sample.

¹⁹ "Methods of Analysis of Assoc. Official Agr. Chem.," 1920, 95; *Bur. Chem., Bull.* 107, 53.

²⁰ Some find it an advantage to add 200 to 300 g. calcium chloride to the flask containing the soap solution, to prevent foaming.

Editors of Journal of Physical Chemistry

The following have been elected editors of the *Journal of Physical Chemistry* under the coöperative agreement published on page 91 of Proceedings of the AMERICAN CHEMICAL SOCIETY, for October 1922.

CHEMICAL SOCIETY OF LONDON: Prof. T. M. Lowry, Prof. J. W. McBain, and Prof. J. C. Phillip.

FARADAY SOCIETY: Prof. F. G. Donnan.

AMERICAN CHEMICAL SOCIETY: Dr. A. L. Day, Prof. G. A. Hulett, Dr. Irving Langmuir, and Prof. W. L. Miller.

The editor-in-chief will be elected by this board.

Report of the Viscosity Committee of the Cellulose Division¹

To the Cellulose Division of the American Chemical Society:

Your special committee on viscosity determination, appointed at the Rochester meeting, begs to present the following report. Your committee has carefully considered the possibility of standardizing a method for determining the viscosity of cellulose ester solutions in order to obtain a uniform standard for specifying this property, particularly in the buying, selling, and using of such solutions.

Early in June 1921, a questionnaire was sent out to the larger manufacturers and users of cellulose ester solutions in the United States, telling them what the committee planned to do and asking if their cooperation could be counted on. Although two replied that they were not interested, sixteen assured the committee of their cooperation. That there was an obvious need for the work that the committee planned to do, was indicated by the fact that most of the replies used such expressions as "We recognize the value of such a standard and we will be greatly interested in the work of your committee;" "We are heartily in favor of the movement and will gladly cooperate with you;" "Think it desirable that one standard method be adopted;" "We are thoroughly in favor of standardizing a method for use in determining the viscosity of nitrocellulose solutions."

These replies also showed that of the sixteen concerns sending favorable replies nine used the falling ball method and a number of these used it exclusively. Two concerns used the MacMichael viscometer, but no other method was used by more than one concern. In other words, the falling ball method was in most common use, and therefore the logical thing to do seemed to be to standardize the conditions of this method.

On sending out a second questionnaire inquiring about eleven variable conditions in this method, only one was the same in any two laboratories and that one was uniform in all of the nine from whom replies were received. In considering these various conditions, it was recognized that in the strictly scientific sense it is not possible to measure "viscosity" by the falling ball method, since cellulose ester solutions are not true viscous liquids but really plastic materials in which the consistency depends on the so-called yield value or force required to start the mass flowing and also on the mobility or ease of flowing after it has once started. The committee does not feel, however, that this distinction is of importance in a method for general practical use, provided only that it is realized that the property being measured is not true viscosity. The main object is to standardize the method so that different users will use identical conditions, and therefore of necessity obtain close agreement in measuring the *apparent* viscosity of a given solution.

It is hoped that the suggested method will be adopted for regular factory use by most, if not all, of the manufacturers and users of cellulose ester solutions. This is the more necessary because in using different rates of shear the *apparent* viscosity may conceivably vary within very wide limits. If it is not possible for a given manufacturer to adopt this method, it is suggested that the manufacturer or user determine the ratio between his particular apparatus and the standard apparatus for solutions of widely different *apparent* viscosity and then

¹ This report of the Viscosity Committee of the Cellulose Division was presented at the Pittsburgh meeting and is being published in accordance with a vote of the Division. In its present form it is only tentative and it is hoped that all those interested will forward their suggestions and criticisms to the chairman of the committee, G. J. Esselen, Jr., 248 Boylston St., Boston 17, Mass. Some suggestions have already reached the committee and these will be taken into consideration in preparing the final report.

It is further to be hoped that laboratories having occasion to determine the viscosity of cellulose ester solutions will cooperate with the committee to the extent of giving the proposed method a thorough trial, in order that any weaknesses may be shown up and corrected.

write his specifications in accordance with the standard apparatus.

The proposed method consists, in brief, of allowing a 0.635 cm. ($\frac{1}{4}$ in.) steel ball to fall through the solution of which the viscosity is to be measured, the solution being contained in a cylindrical glass tube. The time in seconds which is required for the ball to pass between two marks 25.4 cm. (10 in.) apart is the viscosity in seconds. The apparatus should conform to the following specifications:

	Centimeters	Inches
Height of tube.....	At least 33	13
Inside diameter.....	3.5	$1\frac{1}{8}$
Distance between marks.....	25.4	10
Distance from top of tube to upper mark.....	5	2
Distance from lower mark to bottom of solution.....	At least 2.5	1
Height of liquid above upper mark.....	2.5	1
Diameter of ball.....	0.635	$\frac{1}{4}$
Temperature of solution to be maintained by a water jacket within.....	$\pm 0.5^\circ \text{C.}$	
Material of ball.....	Steel	

Delivery of ball—The ball is to be released at the top of a small glass tube 4.5 cm. ($1\frac{3}{4}$ in.) long, the lower end of which shall dip into the solution 0.6 cm. ($\frac{1}{4}$ in.). The small glass tube through which the ball is to be delivered shall be of such an inside diameter that the ball will just slip through without binding. This delivery tube shall be maintained in a vertical position by passing it through the center of a stopper which fits the top of the wider tube containing the solution.

Measurement of time of fall—The time shall preferably be measured with a stop watch, tested and found accurate to 0.2 sec.

The committee recognizes and wishes to call attention to the fact that there are advantages in reporting viscosity measurements in terms of centipoise units, since the results obtained at one time will then always be comparable with those obtained later, even if changes have in the meantime been made in the details of the viscometer. In the case of the falling ball method, the formula for this conversion is $V = K(S - S')T$, where

V = the viscosity in centipoises
 S = the density of the ball
 S' = the density of the liquid
 T = the time of the fall in seconds
 K = a constant for the apparatus

The constant K for every apparatus is best obtained by standardizing against a liquid of known viscosity, and for this purpose castor oil is very satisfactory. The Bureau of Standards will determine the viscosity of a sample of castor oil at any one temperature for \$2.00. The density of castor oil can be obtained from the tables in the literature within the limits of accuracy of the method. The time of fall for a large ball in castor oil is so short that it cannot be accurately measured, and for this reason it is probably best to use $\frac{1}{8}$ -in. steel balls rather than the larger ones which are to be regularly used. The ratio between $\frac{1}{8}$ -in. steel balls and $\frac{1}{4}$ -in. steel balls is approximately 3 : 1. It should be noted again that the value thus calculated does not, strictly speaking, represent viscosity, since cellulose ester solutions are not true viscous liquids; but the results will be of value in a practical way.

It is recommended (1) that, if the method as specified meets with the approval of the members of the Division, it be submitted for further approval to the Supervisory Committee on Standard Methods of Analysis of the AMERICAN CHEMICAL SOCIETY, (2) that, subject to this approval, a vote be passed designating this method as "The Tentative Standard Method of the Cellulose Division, AMERICAN CHEMICAL SOCIETY, for Determining the Viscosity of Cellulose Ester Solutions by Means of a Falling Ball," and (3) that this report be published in *The Journal of Industrial and Engineering Chemistry*.

It is further recommended that arrangements be made to have the method tried out in a number of laboratories to determine how closely different manipulators will check one another on

the same example, a further report to be made at the next meeting on this phase of the matter. If the method proves reliable in practice, the word "Tentative" can then be dropped from the title and the method finally adopted as "Standard."

The committee wishes to acknowledge the valuable suggestions given by Mr. Winslow H. Herschel, of the Bureau of Standards, and by the various manufacturing firms who have been kind enough to give the committee information regarding the methods in use by them for determining viscosity.

GUSTAVUS J. ESSELEN, JR., *Chairman*
C. P. BEISTLE
EUGENE C. BINGHAM
HAMILTON BRADSHAW
W. J. WAITE

American Institute of Chemical Engineers

The 15th Annual Meeting of the American Institute of Chemical Engineers will be held at Richmond, Va., on December 6 to 9, 1922.

Reports for the year of the various committees and officers will be rendered and new officers elected for the coming year.

The program of papers will include the following, most of which are included in a symposium on "Materials of Construction:"

Wood. J. V. N. DORR.
Oil Substitution Products. W. B. PRATT.
Chemical Stoneware. P. C. KINGSBURY.
Use of Propane for Refrigeration. H. D. EDWARDS.
Effect of Rate of Flow on Absorption of Gases. WALLACE B. VAN ARSDEL.
Resistance of Packing to Fluid Flow. F. C. BLAKE.
Absorption and Scrubbing Tower Design. R. T. HASLAM.
Methods of Attacking Evaporation Problems. H. K. MOORE.
Asbestos Protected Metal. J. H. YOUNG.
Volume Changes in Portland Cement Structures. A. H. WHITE.

Opportunity will be offered for visiting the following plants in Richmond and vicinity: The Richmond Chemical Works, a subsidiary of the Virginia-Carolina Chemical Co., acid, phosphate, and fertilizer manufacturers; plants of R. J. Reynolds Tobacco Co., and Larus & Brother Co., manufacturers of chewing tobacco, cigarettes, and smoking tobacco; Richmond Cedar Works, the largest wood works in the world; Atlantic Varnish Works; Richmond Forgings Corporation; American Glass Works; Richmond Guano Co.; Albemarle Paper Manufacturing Co.; C. F. Sauer Co.; Southern Manufacturing Co.

The Hotel Jefferson will be convention headquarters.

The membership of the Local Committee is as follows:

W. T. DABNEY, Business Manager of the Chamber of Commerce, *Chairman*.
JOHN G. ARMISTEAD, Lefebvre-Armistead Co., Merchandise Brokers.
GEORGE H. NASH, Virginia-Carolina Chemical Co.
JULIUS B. WEEMS, Chief of the Department of Chemistry, State Department of Agriculture.
J. B. ROBB, Robb & Arnold, Analytical Chemists.
HENRY FROEHLING, Froehling & Robertson, Analytical Chemists.
SAMEUL H. SHEIB, Froehling & Robertson.

Calendar of Meetings

- American Association of Textile Chemists and Colorists—1st Annual Meeting, New York City, December 2, 1922.
American Institute of Chemical Engineers—Richmond, Va., December 6 to 9, 1922.
American Ceramic Society—Annual Meeting, Pittsburgh, Pa., February 12 to 17, 1923.
American Chemical Society—65th Meeting, New Haven, Conn., April 2 to 7, 1923.
American Electrochemical Society—43rd Semiannual Meeting, New York City, May 3 to 5, 1923.

Papers for Program of Industrial Division

In order that more time can be given to the presentation and discussion of papers delivered before the Division of Industrial and Engineering Chemistry of the AMERICAN CHEMICAL SOCIETY, it has been decided to ask all who plan to give papers before this Division to submit completed manuscripts not later than March 1 to the Secretary of the Division. The manuscripts will then be sent to reviewers just as articles now submitted to any of the journals of the SOCIETY are treated. Upon favorable recommendation of the reviewers and the officers of the Division, the papers will be included in the final program of the Division.

It has been keenly felt for some time that something must be done to raise the standard of some of the papers that have been given before the Division. In some cases old material has been redescribed under a new heading, which often was misleading. No doubt the new method will reduce the number of papers to be presented at any one meeting, but it is felt that a few genuinely good papers followed by a sufficient time for discussion will be what most chemists desire. At Pittsburgh there were so many papers on the program that a time limit of seven minutes was allotted with three minutes for discussion. This time proved to be so short that a speaker could not present the paper in the best manner, and the period for discussion was so short that there was practically no attempt on the part of members to discuss the subject.

Since the spring meeting occurs at New Haven, April 2 to 7, inclusive, it is necessary for members of the SOCIETY who are planning to present papers before this Division to send their papers on or before March 1 to the Secretary of the Division.

ERLE M. BILLINGS, *Secretary*

KODAK PARK
ROCHESTER, N. Y.

American Electrochemical Society Spring Meeting Announcement

The 43rd General Meeting of the Society will be held in New York City, with headquarters at the Commodore Hotel. The meeting will take place May 3, 4, and 5, 1923.

A committee, consisting of Irving Fellner, *Chairman*, H. B. Coho, and Chas. F. Roth, has already started making arrangements for the accommodation and comfort of members and their guests. The large local membership, the accessibility of New York from all points, and the interesting symposia in course of preparation are but a few of the reasons why this meeting should be one that will break all previous attendance records.

Dr. F. M. Becket is making extensive arrangements for a symposium on the "Rarer Metals" which is bound to give rise to interesting and enthusiastic discussions. This symposium will include papers on "The Production and Application of the Rarer Metals," such as vanadium, tungsten, cobalt, molybdenum, zirconium, cerium, uranium, tantalum, calcium, magnesium, and others.

Another symposium, on "Electrode Potentials," in charge of Dr. Wm. G. Horsch, will take place at this meeting and will include studies on reversible electromotive force, overvoltage, ion activities, electro-titration, and pH determinations.

Members submitting manuscripts for this meeting of the Society are kindly requested to forward two copies of their manuscripts to the Secretary by January 15, 1923, and not later than February 1, 1923, as this is the closing date for accepting papers.



The 1922 Meeting of the Association of Official Agricultural Chemists

After an interval of several years, the Association of Official Agricultural Chemists returned to the Raleigh Hotel, Washington, D. C., for its 38th Annual Meeting, November 15 to 17. There were more than 350 members and visitors present. The usual reports of referees, associate referees, and committees were presented.

Honorable Henry C. Wallace, Secretary of Agriculture, welcomed the chemists to Washington in behalf of the Department of Agriculture. He stressed the importance of coordinating the work of the various branches of the Government, using as illustrations the different activities of his own department in grain and cotton, and pointed out the great opportunities that such coordination will unfold for the chemist.

On Thursday, the regular sessions were interrupted sufficiently long to listen to some special addresses. First came a concise but live talk by the president, F. P. Veitch, on "Opportunities and Responsibilities of the Association of Official Agricultural Chemists." He urged the members to advise the secretary of any proposed outside activity which would come in any way within the field of the association so that steps might be taken to coordinate the various efforts and avoid duplication of work. He stressed the importance of promoting uniformity in methods, the interchange of ideas, of at least one representative from each member organization attending the annual meetings of the society, and recommended that the association revert to its former practice of printing the full report of the annual meetings, including all discussions. In addition to work on methods and their application, the president urged the members to take a larger directing part in all scientific service relating to agriculture and to give all the information they have to give when service, private or public, involving chemistry is performed.

Then came an address by Dr. Harvey W. Wiley, honorary president—the man who has the rare distinction of never having missed a meeting of the association. This is a happy circumstance for those attending these conventions, since his address is always regarded as the bright spot of the meeting. Always timely in his remarks, it being Cancer Week, he discussed the

cancer question. He regarded it as peculiarly appropriate to address chemists on this subject since one of the remedial agents for cancer has been provided by the action of chemists. He spoke in scathing terms of the misleading advertisements for cancer that are being broadcasted, considering them one of the greatest enemies of cancer cures. Commenting upon the remarkable change that has taken place in our ideas of the nature of matter, our present-day belief that all matter is alike—that all the electrons in the nucleus are the same wherever they exist—in his inimitable manner he compared the history of the atom to the history of humanity, likening the protons to men and the electrons to women. In conclusion he said that the unknown will always offer endless fields and opportunities for investigation, and that there is no end to the good which this association can accomplish—it is boundless in its activities and in its field of endeavor. He urged chemists to cultivate the true scientific spirit, never to be satisfied, but to keep on with perfect humility even in the attainment of great progress.

Senator E. F. Ladd of North Dakota, many years actively engaged in association work, first as referee, then as a member or chairman of various important committees, and at one time president, next addressed the convention. He seemed happy to be in a gathering of chemists and declared that he felt more at home with them than he has ever felt among politicians. He believes that there is no greater field than that of chemistry and that the future holds even greater possibilities for the chemist. National laws, in regard to paint, varnish, and textile, will probably be enacted at an early session of Congress. Such laws will throw added responsibility upon our regulatory officials and will open new fields of endeavor both for the regulatory and research worker. These laws will be for the best interest of the people and, in the end, for the manufacturers themselves. Need for reform in expert testimony was emphasized, and chemists were urged not to allow the lawyer to determine what they shall give as evidence. Very often the chemist allows the attorney to shape the answer so that it suits the attorney's ideas and thus the chemist only presents a half-proof, which frequently leads to wrong decisions. He urged chemists to insist that they formulate their own questions and their own answers in court cases, and called attention to the importance of the



Tenschert & Flack

service which the association could render in this respect. The Senator paid special tribute to Dr. Wiley as the guiding spirit of the association and said that he had come before the association to meet the chemists with whom he had been associated in the past, and to show his good will and respect for the great calling of chemistry.

So much interest was manifested in the Drug Section that the program, instead of occupying half a day as scheduled, continued for more than one and one-half days. In all, eighteen reports and papers were presented. Methods were adopted as official for the examination of arsphenamine and nearsphenamine. This is the first time the association has had official methods for these substances. Very notable action was taken when the association went on record as recommending that the methods for the assay of physostigma and its preparations and fluid extract of hyoscyamus be submitted to the chairman of the revision committee of the United States Pharmacopeia, and that these methods remain tentative until such time as they appear in the Pharmacopeia. Mr. Julius Hortvet presented a special paper on sublimation, which evoked considerable comment. The method he outlined gives promise of being adaptable to quantitative work and also of having wide industrial application, especially in the purification of chemicals.

The referee's report upon the preparation of neutral ammonium citrate terminates the work upon this important subject which has been before the association continuously for a period of many years. To those interested in the use of this solution the settling of this question is of the most importance, since it places a reliable colorimetric method of determination, based on physico-chemical principles, in the hands of every chemist. A special paper on the utilization by crops of potash absorbed by gels probably indicates a new phase of potash availability which may have a direct bearing upon methods used in the analysis of commercial fertilizers and potash materials.

The Committee on Editing Methods of Analysis was instructed to revise the methods of the association so that they can be voted upon at the 1923 meeting, the 1923 changes incorporated therein, the revision completed, and the book of methods available for distribution by July 1, 1924. It was further voted that a

chapter on the analysis of liming materials be prepared for insertion in the Methods, and that so far as possible the methods which are already official be adopted after adapting them to the determination of liming materials as such. This compilation is to be completed and published as a part of the 1922 proceedings. The present official method for citrate-insoluble phosphoric acid in fertilizers was modified so as to be applicable to precipitated phosphates, the change consisting in the reduction of the charge from 2 g. to 1 g. The Wagner method was adopted as official for the determination of available phosphoric acid in basic slag phosphates. This is the first time that there has been an official method for this determination.

The Committee on Definition of Terms and Interpretation of Results on Fertilizers presented a list of subjects for consideration and study prior to the adoption of definitions and rulings thereon.

The chairman of the Board of Editors briefly outlined the difficulties and complications which the board has encountered, and made the highly gratifying announcement that the society is now up to date in the publication of its proceedings.

A number of resolutions were adopted, of which the following is especially noteworthy:

Resolved, That this Association go on record as heartily endorsing the campaign recently inaugurated by the American Chemical Society to educate the American people to a better understanding of chemistry, its possibilities, and applications to everyday life.

The following officers were appointed for the ensuing year:

Honorary President: HARVEY W. WILEY.
President: A. J. PATTEN.
Vice President: R. E. DOOLITTLE.
Secretary-Treasurer: W. W. SKINNER.

Additional members of the Executive Committee are E. M. Bailey, P. B. Dunbar, R. W. Balcom, J. B. Weems, and J. W. Kellogg.

The names of members of committees, referees, and associate referees for the year 1923 may be secured through the secretary. The full proceedings will be printed in the *Journal of the Association of Official Agricultural Chemists*.

NOTES AND CORRESPONDENCE

An Appreciation

Editor of the Journal of Industrial and Engineering Chemistry:

On the eve of my return from New York to England, I cannot refrain from asking you to allow me, through the columns of your well-known journal, to express my thanks to all who have helped to make my visit to the United States a continuous round of pleasure, instruction, and interest. I leave more than ever impressed with the great work which is being done for the American nation by the profession and industry of chemistry, with the value of so great an organization as the AMERICAN CHEMICAL SOCIETY in the consolidation of chemical interests and the direction of their influence upon the national life; and especially with your organization, both through state action and through private and industrial enterprise, for the prosecution of research—the secret and foundation of all real progress.

To yourself, sir, and to your colleague, Dr. Charles L. Parsons, I am indebted for a welcome to Washington which I shall never forget, and for an opportunity of meeting a gathering of distinguished American scientists whom it was indeed an honor and a pleasure to know. I return, as all my fellow-delegates do, overwhelmed with the memory of American friendship and hospitality. The fundamental unity of the English-speaking race is no longer to us a mere theory but a potent reality for us and for the world, and I trust and believe that the only rivalry England and America will ever know is the rivalry as to which shall best serve the welfare and progress of mankind.

With real gratitude for all the kindness I have received on this side and with the heartiest wishes for the prosperity of your work.

F. E. HAMER
Editor, The Chemical Age

NEW YORK CITY
October 27, 1922

The Paint Industry

Editor of the Journal of Industrial and Engineering Chemistry:

To your September issue, p. 775, Dr. A. H. Sabin contributes a brief review of the progress of the paint industry, which parallels the famous chapter on "Snakes in Ireland." Dr. Sabin writes "little can be said of progress in the paint industry," and then proceeds to describe the manufacture of Titanox, its properties and qualities, with an equivocal glance at light-resistant lithopone and a recognition of Perilla Oil.

The impression left by this statement is certainly not favorable to the industry. It is hardly to be expected that in an industry so long established new materials should be discovered daily, but progress in any industry certainly does not consist merely of the introduction of new materials; rather it consists in improvements in methods and processes, in increased knowledge of materials, in better laboratory control, in better technology.

In all these fields the paint and varnish industry has made consistent progress, not only in the past year, but during a number of years past. The practical chemist, once a *rara avis*, is now an important factor in most plants. The research laboratory, once unknown in this field, is now an established feature of the larger organizations, and all of these are correlated through the Federation of Production Clubs, the Scientific Section of

the Educational Bureau, and Committee D-1 of the American Society for Testing Materials.

Not only has great progress been made in the standardization of specifications for materials and products—e. g., the specifications of the Interdepartmental Committee of the Government at Washington, and the standard specifications of the A. S. T. M.—but considerable progress has been made in elucidation of the physical and physico-chemical laws underlying paint problems, together with means for measurement and numerical expression of properties and qualities.

As to lithopone, it is a fact familiar to all paint manufacturers that practically all the standard brands show decided improvement in light-resistance as well as in physical uniformity, while at least one and possibly others are—as pigments in oil—practically light-proof. Their use in exterior paints is constantly increasing, and, in contradiction to the opinion quoted by Dr. Sabin, it is the general opinion that this use will expand indefinitely.

In a long-established industry progress is commonly manifested in details rather than in revolutionary changes, and in these details both the paint and the varnish industry show encouraging progress. A reference to your own files during the past year will amply demonstrate this assertion.

G. B. HECKEL, *Secretary*

PAINT MANUFACTURERS' ASSOCIATION
OF THE UNITED STATES
PHILADELPHIA, PA.
October 9, 1922

Editor of the Journal of Industrial and Engineering Chemistry:

Mr. Heckel's criticism is that of a hopeful optimist; but the review was an attempt to tell of facts as they are, and not what we hoped for. I, myself, know little about lithopone, for example; but I had the separate and agreeing opinions of several of the largest makers of that substance, and of chemists of paint companies that use it. I know it does not agree with the advertisements. I appreciate the value of the work done by Dr. Bingham, Mr. Green, and others, but it seems incomplete, and special mention may be deferred until some practical results are shown. If there has been any important progress in varnish making during the year, none of the makers whom I have been able to consult have heard of it. There is no use in taking space for telling of things that are not yet done.

A. H. SABIN

NATIONAL LEAD COMPANY
NEW YORK, N. Y.
October 20, 1922

A Mistaken Rumor

A rumor is spreading in this country that the International Research Council, which is represented in America by the National Research Council, took action at its meeting in Brussels last July excluding Germans and Austrians from its meetings and from meetings of the various international unions affiliated with it for a period of twelve years. No such action was proposed or taken. No German or Austrian organizations have as yet been admitted to the International Research Council but their admission is probably a matter of the near future. [VERNON KELLOGG, *Permanent Secretary*.]

A New Method of Color Measurement for Oils

Editor of the Journal of Industrial and Engineering Chemistry:

I cannot refrain from writing to straighten out, and in some cases contradict a number of statements regarding Lovibond's tintometer contained in an article headed "A New Method of Color Measurement for Oils" in your issue of April 1922, page 269.

It is evident from the start that the writers are not themselves well acquainted with Lovibond's system or Lovibond's Color Laws.

In the foreword it is implied that Lovibond's method is not consistent if we give the word "consistent" its dictionary meaning of "not contradictory," then most certainly Lovibond's method *is* consistent, as with proper precautions for the initial measurement it can be relied upon and be reproduced with accuracy in any country.

It is also stated to be unsatisfactory for three reasons. I will take them in order and as lettered:

1—WIDE SEPARATION OF THE SQUARES OF LIGHT. The wide separation of the fields is found by some color workers to be a great help, and after twenty-five years of color work, I am not at all certain it is not the correct method; but as, on the other hand, some persons have found difficulty in their readings by this method, in the newest instruments it has been abandoned and the two fields are now side by side. As yet no optical device has been approved by the Tintometer Laboratory workers as giving true and reliable color readings.

2—MATCHING OILS ABOVE 500 COLOR. Mr. Lovibond himself, as long ago as in 1901, begged chemists testing oils for color not to measure them in too great a color depth. He advised a small cell or thin film but the commercial man would not hear of it and adopted 18 in. and 5 $\frac{1}{4}$ in. as their standard cells.

3—COLORS NOT ADDITIVE. If your writers will refer to page 8 of Mr. Lovibond's book, "Light and Color Theories," they will find the answer to (3) in Law 9. "Every definite substance has its own specific rate of color development for regularly increasing thicknesses." This law, which is one upon which the whole science of color measurement hangs, has been overlooked throughout the paper before us.

We would like to add here that it is quite easy to determine the actual amount of coloring matter removed by fuller's earth under definite conditions by means of the tintometer. The use of the Lovibond scale for oils was first suggested by Mr. Lovibond himself, in connection with Sir Boverton Redwood. The cell then advised was $\frac{1}{16}$ in. strata thickness; the oil trade, however, preferred the longer length of 5 $\frac{1}{4}$ in., which was too great a length as, of course, the longer the length of cell the deeper is the color to be matched by the standard glasses.

The color of a solution always changes very gradually by means of a sufficiently large number of graduated cells, the color absorption curves can be accurately established, and the exact point where one color dies out and the other appears can be ascertained. Here again I would refer to "Light and Color Theories," page 33 and plate 5.

Mr. Lovibond proved many years ago that percentage dilution and cell dilution by varying thickness gave concordant results.

It would be interesting to know what is meant by "colors between 3 or 4 and 200" and "above 400°." It is impossible for any color observer to read with accuracy at such a depth as 200, or for the glass standards themselves to be made. The best way is to adopt the use of a thin film of the substance to be measured.

The relationship between the true Lovibond scale and the arbitrary scale can always be found with a little careful work.

Lovibond curves are, of course, not additive in one sense on account of the before-mentioned Law 9, but the colors themselves are additive.

With reference to the "True color" scale mentioned, it would be interesting to learn on what this scale is based and why it is "True," also of what the standards themselves consist.

THE TINTOMETER, LTD.
SALISBURY, ENGLAND
June 10, 1922

F. E. BAKER

Editor of the Journal of Industrial and Engineering Chemistry:

The writers had no intention of casting any reflection upon the admirable work of Lovibond and his associates on color. They have read his book on "Light and Color Theories," and feel that Mr. Baker, if he had read our articles more carefully, would have noted a reference to many points on which he asks for information. We have carefully stated, mathematically and otherwise—although possibly in a different form—the fundamental laws of color measurement, which we are said to have overlooked.

As stated, the scope of our work was to develop a method for use in the petroleum industry, where, besides other methods, the Lovibond amber-colored glasses are now employed. Two years' personal work in both laboratory and plant, as well as conferences with other oil chemists, convinced us of many disadvantages in using the Lovibond amber-colored glasses. These disadvantages are carefully noted in our article, and it may again be emphasized that it is practically impossible to check readings by this system with dark stocks, with which our work was largely concerned, and as a consequence of this disadvantage, the yield of filtered oils often varies by many hundreds of gallons with resulting uncertainty in filtering processes.

That some form of accurate color measurement is greatly needed, is evident by the vast amount of research now under way by various oil chemists.

In our foreword, "consistent" was used in another equally rigid dictionary meaning of "uniform," as evidence of our attempt to find a method and apparatus which would measure the color of all petroleum oils from the lightest to the darkest. As stated, with the present Lovibond amber glasses, for dark oils it is imperative that these be diluted with water-white kerosene or other solvent to permit them to be matched in the tintometer. Furthermore, the values so obtained on dilution bear no definite relation to the colors of lighter undiluted oils.

Regarding "wide separation of light squares," the writers believe that most color experts will agree that close juxtaposition of color squares is a great aid in matching. Mr. Baker admits a difference of opinions, yet states that no optical device has been approved by his laboratory. Other methods have, however, been found.

In matching oils above 500 color, we are in apparent agreement with Lovibond's original suggestion of measuring oils in thin films. We have devised such thin films and applied them successfully to the problem in hand.

In our adaptation of thin films, according to Mr. Baker, we also check Lovibond's original observation regarding the relation between percentage dilution and cell dilution by varying thickness.

Again referring to our article, by "colors between 3 or 4 and 200," is meant the color of the Lovibond amber glasses. Use of any tri- or multi-colored standards would obviously be impracticable in an oil-testing laboratory where speed and simplicity of recording data are both imperative. Mr. Baker again agrees with our data in saying that it is better to measure thin films than to use a dark color glass.

Our "True color," as stated, means a figure proportional to the amount of coloring matter present in the oil. The relation between the Lovibond color and True color is clearly explained in detail and given in tabular form where the relation between N. P. A. colors, Lovibond colors (Series 500), and True color

values is stated. Detailed curves, Plate VIII and Plate IX, also give plotted data showing these relationships. Reference to these plates indicates that Lovibond color and True color are the same up to 50°, but deviate above this point. In fact, we refer to standardizing our oil standard, L. S., against a 50 Lovibond glass.

In conclusion, it may be stated that we do not claim any new system, but rather an adaptation of the laws and facts of color measurement to a method for measuring the true colors of petroleum oil from the lightest to the darkest, using specially constructed thin films for measuring the darker oils. Research and plant work, involving oil varying in amount from 1 cc. to 8000 gal., has been covered, and data obtained on a laboratory scale have been checked absolutely in the plant, all being based on our True color method. Plant control was compared, incidentally, by both Lovibond and True colors.

It is regretted that Mr. Baker interpreted our article as reflecting on Lovibond's basic laws, and pioneer work in this field. A more careful perusal of our description and data indicates the various points involved.

LEON W. PARSONS

RESEARCH LABORATORY OF APPLIED CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
October 30, 1922

The Plant Manager and the Chemist

Editor of the Journal of Industrial and Engineering Chemistry:

Mr. Griffin's comment in the October issue of *THIS JOURNAL*, on the article entitled, "The Plant Manager and the Chemist," embodies several points of extreme interest to both the chemist and the plant manager.

Mr. Griffin maintains that the chemist who does not require authority to secure the coöperative development of his ideas would be discredited for holding a subordinate position. This is admittedly true, but it is equally true that the chemist does not wish to stay in a subordinate position, nor is it to the advantage of the plant to keep him in such a place.

Mr. Griffin's comment that he has seen many plant managers who are out of place, is undoubtedly true, as many men in this position have the position for reasons other than their adaptability to it, the position being given to them for a great many reasons that are present in all industrial plants. Invariably, however, the plant manager has to engage the chemists for the plant, and for this reason the chemist must, until there is some other way of selecting plant managers, accept them as such.

It is to be remembered that the average plant chemist, in comparison with the plant manager, is a new-comer, most managers only attaining their position after long experience in their particular branch of manufacture. The technical man must learn to take advantage of the experience accumulated by the men who have long been connected with the industry and must be guided in his work largely by such experience.

Many men engage themselves as chemists who believe that they are in direct line for executive positions and that these positions should come quickly. If the advances do not realize with speed, then many chemists feel that their case is not treated fairly and that the profession as a whole is not properly recognized. I believe in the natural evolution of an industrial chemist, which is to become a manager of the industry. I do not mean the plant manager alone, but there is no reason why he should not manage the whole of the undertaking. His training should fit him to be a keen, observing man of business.

There are plenty of illustrations where this has been the result with chemists who were fitted to their work and who wanted to get the most out of it. It is a fact that many chemists are offered

the pay of ordinary employees when their training warrants a very much better return. There is not at this time any way of correcting this difficulty. It is certain, however, that a chemist cannot be good in his work and be hired for a niggardly sum for long, so that a chemist making a good showing is bound to have the returns somewhere near what they should be.

Many managers expect more from inexperienced chemists than it would be possible for experienced men to deliver, and I believe that this condition will continue until the trained chemist is more fully established in industrial plants. Then there will be a medium of understanding with the chemist, plant manager, and the embryo chemist looking for honors in production.

I acknowledge the fact that the chemists as a whole are constant and hardworking, but I am of the opinion that there are a vast number of men in the profession who are indifferent to the fine points in it and who are as a result injuring high-grade chemists. The title of chemist should indicate that the holder is a person of considerable mental attainments.

It was farthest from my intentions not to show a "kindly sympathetic spirit of encouragement." Chemists should assume greater responsibility and interest in the manufacture than they do at present, as the future of any industrial firm should lie in the improvement of its products through the intelligent application of technical ideas.

GEORGE L. O'BRIEN

O'BRIEN VARNISH COMPANY
SOUTH BEND, IND.
November 9, 1922

"America First"

Editor of the Journal of Industrial and Engineering Chemistry:

Two very different tendencies have grown in the world during and since the war. During the war, more than a dozen nations fought together in close coöperation under a single command. American soldiers used French airplanes and French artillery. Without them the contribution of America to the war would have been almost negligible. Thousands of Americans worked for the Government on the "dollar-a-year" basis and most of these were not profiteers. The American people ate corn bread and curtailed their use of sugar, that the people of England and France might not starve. Fighting against us were four other nations, equally united. On both sides workmen forgot their grievances and worked for the common cause, and in return received more consideration and more adequate pay.

Since the war, nationalistic and capitalistic tendencies have become more pronounced and more harmful than ever before. "America First" has become so exactly like "Deutschland über Alles" that it is hard to distinguish the spirit of the two slogans, though *both* slogans are also used in the sense of a patriotic international rivalry with no thought of injury to others. Instead of establishing national boundaries on economic principles and for the common welfare, the lines were placed largely for strategic reasons, as though war were to be the common and normal condition of the world.

All Europe was preparing for decades for the catastrophe of 1914. Instead of realizing that every nation was responsible in part for the conditions that had arisen, and uniting now in their common misery to repair the injury that has been done, too many statesmen are intent on some selfish aim for their own people, apparently indifferent to the injury they are doing to other nations. Frenchmen insist that Germany alone was responsible for the war and fought to destroy France and secure dominion over Europe and ultimately over the world. Germans are equally insistent that they fought a defensive war against an overwhelming combination. The intellectual leaders of

France refuse to have any intercourse or acquaintance with the intellectual leaders of Germany, and suspicion and hatred grow fast on both sides. French statesmen insist on the full payment of the so-called reparations, which are really, in part, indemnities to provide pensions in France and England. They seem to be rather glad that this insistence is bringing economic ruin to Germany, and to forget that it may make further payments impossible for years to come. And it is not certain that Germans and especially German capitalists are doing all that they might to comply with the terms of the treaty.

Before the war, it was customary to travel all over Western Europe without a passport. Now, following the example set by America, expensive visés are required, passports are examined at every boundary, and customs examinations are a nightmare to travelers. An exaggerated spirit of nationalism holds sway everywhere.

No one who has visited Europe recently and who has seen at all below the surface will claim that the picture is too dark. Indeed, one prominent German chemist with whom I talked this summer sees starvation and cannibalism coming to Germany as they have come to Russia. And no one seems to see any way out.

Yet, the way is clear before us if the nations could only take the lessons of history and apply them. It is only a little more than fifty years since Prussia and Bavaria fought each other, but very soon afterwards Bismarck had welded Prussia, Bavaria, and the other German states into a unified empire,—with the fatal mistake, however, that the unification grew out of successful wars and was essentially military at its foundations. Instead of being a federation of states with equal rights, the Prussian State was dominant. In 1914 some Germans—though by no means all—wished to build an enlarged Germany and make their empire dominant in Europe. Instead of an empire of that sort, it should be clear to every one that further wars between France and Germany must bring a hundred- or a thousand-fold greater loss to each than the small gain which might possibly come to the victor in the strife. Switzerland is a federal state, including Frenchmen, Germans, and Italians. The only reasons

why France and Germany may not also form a federal state seem to be their larger size and the animosities which have grown from centuries of intermittent wars. These obstacles are doubtless too great to be overcome at once, but France and Germany should certainly find some practicable way to cooperate in the restoration of the devastated areas on a basis that will not bring financial ruin to Germany or make necessary the maintenance of a large and expensive army in France.

It will be asked why such questions should be discussed in a chemical journal. Because the chemists and other scientific men may, if they will, contribute very much toward a better understanding between France and Germany. The International Union of Pure and Applied Chemistry excludes Germans and Austrians from membership, apparently on the basis that the allies were on so much higher a plane during the war that they are unwilling to associate with them. Have the events of the last four years demonstrated that Frenchmen and Englishmen and Americans are so far less selfish than Germans and Austrians in their national ambitions that they can afford to take a "holier-than-thou" attitude? And, even if we still believe that some Germans were very wrong in their Pan-Germanism, is there more hope that the Germany of the future will become a safe member of international society if she is ostracized than there would be if we met her scientific men on the basis of equality and friendly cooperation?

When the French soldiers came to the Rhine they found the German children starving, and they fed them. The French *poilus* and the German common people learned a lesson in human brotherhood which will not soon be forgotten. It has long been the custom of the scientific men of the world to work together in friendly rivalry, and to share their discoveries freely with each other. Is it not possible, now, for the chemists of the world to meet together once more and to contribute their share toward the establishment of genuine peace among the nations?

W. A. NOYES

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
November 1, 1922

Frank Sherman Washburn

A man of broad, driving interest was Frank Sherman Washburn—a man of personal power, who never knew when to stop. From the beginning of his career he drove himself to the limit of his physical endurance, and up to the time of his death, on October 9, he continued driving himself. Even in periods of rest he held himself to a rigid schedule in everything.

The American Cyanamid Company stands as a memorial to the force of his character and his ability to associate able men with him in his enterprises. Never overbearing, yet always forceful, he made associations with men of the highest type in carrying through his many ideas. As a tribute to his ability as an organizer, he was appointed to carry through the immense government fixed nitrogen project at Muscle Shoals, and, working against the almost insurmountable difficulties of the war-time pressure, he had this plant producing fixed nitrogen within a year from the signing of the contract. The feat was accomplished



FRANK SHERMAN WASHBURN

only with the utmost sacrifice of his personal energy. Never a moment of time was wasted and never a bit of his limitless supply of energy was allowed to be misdirected. Probably the strain of the investigation of his conduct of this project, which followed the war, had more to do with the final failure of his physique than any other one thing.

As a friend and companion, few could equal him. His broad interest in affairs and the immense fund of information in his well-ordered mind made him a delightful talker; yet as a listener he had a most charming deference to the opinions of others. His character may well be read in the characters of those with whom he associated. His hobbies, if such a dynamic person may be considered to have hobbies, were education and boating. His educational work included the chairmanship of the drive for an endowment for Cornell University, of which he was trustee for many years. On his infrequent boating trips he always played with the same whole-hearted energy that he displayed in his business.

It will be long before another comes to fill his place.

The Nobel Prize in Chemistry for 1921 has been awarded to Frederick Soddy, professor of inorganic and physical chemistry at the University of Oxford. Professor Soddy was from 1900 to 1902 demonstrator in chemistry at McGill University, Montreal. The prize for 1922 has been awarded to Francis William Aston, research fellow at Trinity College, Cambridge. Dr. Aston recently delivered a very interesting series of lectures on isotopes in this country.

WASHINGTON NOTES

As usual, the past month brought to Washington several conventions of interest to the chemist. From October 25 to 28 the Optical Society of America held its 7th annual convention and exhibit of optical instruments at the Bureau of Standards. Then came the meeting of the Association of Feed Control Officials, at the Raleigh Hotel on November 13 and 14. The dominant note sounded at this meeting was uniformity as to labels and application blanks. Some twenty-one states were represented, and the opinion was practically unanimous that the types of uniform labels and registration blanks submitted could, with few exceptions, be accepted in all the states having feed control laws. This action has been taken after several years' efforts on the part of the officials of the association. Other important business accomplished was the adoption as official of tentative standards on crude fiber, standard middlings, flour middlings, and red dog flour. Next came the annual meeting of the Association of Official Agricultural Chemists, reported elsewhere in THIS JOURNAL. That convention had scarcely completed its deliberations when the American Society of Milling and Baking Technology convened at the Raleigh Hotel and voted to amalgamate with the American Association of Cereal Chemists. The officers of the society were reelected, and it was decided to maintain the present organization until the American Association of Cereal Chemists meets next June and acts upon the resolution to combine. And now, as we go to press, the Association of Land Grant Colleges is about to hold its 36th annual convention at the New Willard Hotel.

TARIFF DEVELOPMENTS

Every effort is being made by the Government to facilitate the operation of the 1922 Tariff Act. An Executive Order has been issued declaring that all requests for action or relief under the Tariff Act shall be filed with the Tariff Commission. The latter, in turn, has issued regulations stressing the importance of the following points: Applications for investigation are not required to be in any special form. All that is necessary is a simple statement of the relief sought and the grounds therefor. No investigation will be ordered except for good and sufficient reason. The commission will not confine itself to the issues presented but will modify them as seems best. All evidence presented will be subject to verification.

Assistant Secretary of the Treasury Clifford has issued a formula to guide appraising officers in assessing duties on non-competitive coal-tar products. This is in contradistinction to American valuation which is to be applied to duties on competitive coal-tar products. It is hoped that the application of this formula will result in uniform tariff duties at all ports.

Meantime a conference of representatives of the Tariff Commission, the Bureau of Standards, and the Customs Division of the Treasury Department, was held in New York, November 2 and 3, to discuss the administration of the coal-tar provisions of the new tariff law. Another conference is scheduled for early in December, and it is probable that similar conferences will be held from time to time. Just now these representatives are most concerned with plans for determining the standard strength of dyes in commercial use prior to July 1, 1914, and securing domestic samples for comparative purposes.

The flexible section of the McCumber-Fordney Tariff Act has been in operation since November 9, and about fifteen applications for revisions of duty on chemical products have been received by the Tariff Commission, some asking for increases in duty and others for decreases. One case of chemicals is now before the commissioners for action, and it is probable that by the time THIS JOURNAL issues a preliminary investigation will have been ordered. This will be the first chemical case to be investigated under the new law.

CONFERENCE ON LUBRICATING OILS

Proposed changes in the classification of lubricating oil specifications were discussed at a joint meeting of the Interdepartmental Petroleum Specifications Committee, the Advisory Board to the Committee, the Lubricants Division of the Society of Automotive Engineers, and the Technical Advisory Committee of the American Petroleum Institute, held in Washington, D. C., on November 13.

Separate schemes for classification were presented by representatives of the Society of Automotive Engineers and by the Navy Department. After considerable discussion, it was brought out that a difference exists between turbine oils for land service

and turbine oils for marine service; also that, for turbine oils with paraffin base and asphalt base, lubricants seem to have the same effective viscosity at about 130° F.

A special committee was appointed to consider a list of descriptive names to be used for lubricating oils in the Federal specifications, for explanatory purposes only, and this committee reported a majority opinion that four names should be used together with descriptive numbers: light oil, to cover S. A. E. Nos. 15 and 20; medium oil to cover Nos. 30 and 40; heavy oil to cover No. 50; extra heavy oil to cover Nos. 60, 80, 95, and 115. This majority report was accepted. A minority report, which follows the present classification adopted by the Navy Department, was also submitted.

The conference recommended the measurement of viscosities of oils up to 500 series at 100° F., 600 series and higher at 210° F.

It was further decided to request the Interdepartmental Committee to omit requirement for organic acidity from all motor oil specifications; to make investigations into the relation between acidity, emulsion tests, and service tests, and into the relation between oxidation and evaporation and service tests.

The conference also discussed color, carbon residue, and pour-test requirements for lubricating oils and the fire point for mineral seal oil. The Interdepartmental Committee is considering taking all these proposals, and will take decisive action at a later meeting.

AGRICULTURAL RESEARCH JOURNAL TO RESUME

The United States Department of Agriculture, in cooperation with the Association of Land Grant Colleges, will resume the publication of *The Journal of Agricultural Research*, which, with a number of other publications issued by executive branches of the Government, was discontinued over a year ago. The first issue is expected to appear January 6, 1923.

This journal was established in 1913 for the purpose of segregating and rendering more generally available to agricultural specialists the reports of important discoveries or other original investigations of interest to agriculture.

WASHINGTON CHEMICAL SOCIETY OFFICERS

The Washington Section of the AMERICAN CHEMICAL SOCIETY on November 9 elected the following officers for 1923:

President: W. M. CLARK.

Secretary: J. B. REED.

Treasurer: H. W. HOUGHTON.

Councilors: W. D. COLLINS, R. B. SOSMAN, W. W. SKINNER, F. C. COOK AND R. C. WELLS.

Executive Committee: L. H. ADAMS, R. O. E. DAVIS, V. K. CHESNUT, C. W. BACON, A. SEIDELL, E. T. WHERRY, AND F. W. SMITHER.

INTERDEPARTMENTAL PATENT BOARD AT WASHINGTON

By Executive Order an Interdepartmental Patent Board has been created consisting of the following members:

DR. ANDREW STEWART, Department of the Interior, *Chairman*.

LT. COL. JOSEPH I. McMULLEN, War Department, *Secretary*.

DR. F. G. COTTRELL, Department of Agriculture.

MR. HARRY E. KNIGHT, Department of Justice.

DR. S. W. STRATTON, Department of Commerce.

The researches which the board will conduct relate to the status of inventions and patents of employees of the Government as well as to the administration of patents and patent rights owned by the Government. The board is assembling data preliminary to recommending to the President, for his consideration and approval, a policy to be followed by the Government in the premises, the need for such a policy having been made increasingly manifest during the past several years.

The board will also act as a center for the dissemination of information among the several governmental departments and other units relating to patents and patent rights owned by the Government.

The President has announced that the resignation of Dr. George Otis Smith as director of the United States Geological Survey is of a temporary nature, and that he will be reappointed to his former position when his work with the Federal Coal Fact Finding Commission has been completed.

Frederick S. Dickson, former chief of the dye and chemical control section of the Treasury Department, has been retained by the State Department in an advisory capacity.

November 18, 1922

PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

INTERNATIONAL CONGRESS OF COMBUSTIBLE LIQUIDS

The importance of combustible liquids in the life of a country was demonstrated by the necessities of war. When Germany was cut off from oil supplies because of the blockade, she directed her research to the transformation of coal into combustible liquids, and—thanks to the success of these investigations—she was able to keep her airplanes, automobiles, and tanks supplied.

In France, the consumption of combustible liquids is 8,000,000 hectoliters a year. At the International Congress and Exposition of Combustible Liquids, held at Paris in the early part of October, under the presidency of Mr. Sabatier, an inventory was made of all the possible resources of combustible liquids and their utilization.

As Mr. Berthelot said in the opening conference, humanity is acting in regard to combustibles like a son who is squandering the family fortune. We waste without thought that which is not inexhaustible; and, as Sir William Pope suggested a year ago, ought we not to hunt for combustibles in the vegetable products which have made available through photosynthesis, resources which will exist as long as the sun lights the world; and should not the efforts of chemistry be directed toward searching for an imitation of the mechanism of the vegetable world? Water, oxygen, carbon dioxide are able by a catalytic process to produce carbohydrates, and from them the oily materials of which combustion closes the cycle.

The Congress was divided into six Sections:

SECTION OF PETROLEUM—Here the methods of exploitation by subterranean drainage were studied—such as are in practice at Pechelbronn, under the direction of Mr. de Chambrier. The members of the Congress were able to visit this exploitation.

I would also call attention to the process described by Mr. Maihle, which consists of transforming solid hydrocarbons or those with a high boiling point to liquid hydrocarbons that are very volatile. The method of "cracking" of Burton, used in the United States, gives efficiencies of 30 to 40 per cent, but has the inconvenience of operating under pressure.

The catalytic decomposition of these hydrocarbons can be effected in the presence of catalysts, such as copper or iron. The products obtained vary from a gas with calorific value of 15,000 calories, to an oil boiling at a maximum of 200° C.

The hydrogenation processes were likewise studied, and especially the Bergius process, which hydrogenizes, at a pressure of 200 atmospheres and 400° C., the formerly nonutilizable residues, such as the heavy oils, tars, asphalts; even coal has been hydrogenated to give useful hydrocarbons.

All the hydrogenation processes should be carefully perfected, for they are very often applicable only in very narrow limits of temperature. This fact has, moreover, already been pointed out by Sabatier—it is possible at high temperatures to obtain a product that is incompletely hydrogenated, while at a lower temperature a completely hydrogenated product is obtained. An example of this is naphthalene, which at 200° C. gives a tetrahydride, and at 175° C. gives the decahydride, the pressures being identical.

The methods of using the petroleum and the processes of lubrication were also discussed.

SECTION OF SCHISTS—The geographic distribution of schists, both in France and in the surrounding countries, was discussed, as well as the models of furnaces for their distillation.

SECTION OF LIGNITES AND PEATS—Statistics on the resources of lignite and peat were furnished, and the methods of their utilization. The total production of lignite in France in 1920 was 960,000 tons. The French lignites give a minimum of 15 per cent crude oil, of which 25 per cent of light oil, such as benzol, can be extracted.

SECTION OF BENZOLS AND TARS—The production of benzol in each country was considered, as well as the low temperature distillation of coal. The methods for recovery of the by-products, especially the removal of benzene, in the small gas factories so numerous in France were discussed, also the hydrogenation of tar products, and the by-products of the manufacture of cyclohexanol and tetralin.

A Committee on International Terminology has been formed, composed of a representative of each country, to make more

uniform the use of terms which often give rise to confusion—for example, the words "benzene," "benzol," "benzine," often used interchangeably.

SECTION OF ALCOHOL—France is, indeed, an agricultural country, a great producer of alcohol, and she should find in this alcohol a valuable fuel. I mentioned once before the "Concours du Carburant National," and the results which it has accomplished.

Aside from the alcohol produced from beets and artichokes, the manufacture of alcohol from the cellulose of wood was recommended. The attempts of the Forest Products Laboratory of Madison, Wis., were mentioned. The Prodor process was described in detail. In this process the cellulose is treated with hydrochloric acid concentrated in the cold; thus, there is no destruction of glucose during the operation, as when hot acid is used. The efficiency obtained is about 250 liters of 100 per cent alcohol per ton of dry sawdust. There is in addition a residue consisting of pentoses, the dry distillation of which gives methanol. The equipment for this manufacture should be especially studied, and a new concrete that is not attacked by hydrochloric acid must be found out of which to make this equipment.

As the results of the Concours du Carburant National have shown, there is considerable interest in obtaining an absolute alcohol. Two solutions of this problem have been recommended: One consists in passing alcohol vapors into the rectifier over a column filled with lime; the consumption per hectoliter of alcohol is from 30 to 35 kg. of lime; this industry should have a place in factories where sugar is made and where lime is employed. Another process of dehydration consists in passing alcohol vapors over glycerol, either pure or added to potassium carbonate, calcium chloride, or potassium acetate. Under these conditions the dehydration is complete and gives a 100 per cent alcohol which can be used in a mixture with oil in proportion up to one-tenth. The Parisian busses now consume 20,000 hectoliters per month of the alcohol-benzene mixture.

One of the most curious communications made in this Section was that of Mr. Damiens and Mr. Loisy, who have been studying the gases from coke furnaces; these gases contain ethylene. They have taken the old reaction of Berthelot and tried to transform this ethylene into alcohol, accomplishing this by the use of catalysts. The one which gives the best efficiency is the oxide of copper which in the presence of sulfuric acid gives the subsulfate.

They have studied the factor of concentration of sulfuric acid and shown that a water content of 2 per cent decreases most the absorption speed of ethylene by the sulfuric acid. They have also shown that the optimum temperature for this absorption is 60° C. But the most interesting thing about this absorption mechanism is that when working in the cold, they obtain an ethyl sulfuric acid, which on hydrolysis gives alcohol. On the other hand, with high temperature, they obtain no longer an oxygenated product, but a polymerization of the ethylene, and the final product obtained consists of an oil of a density of 0.77 and a boiling point of 110° C.

This process, which permits obtaining either alcohol or oil, is not only a laboratory process. It has been the object of industrial attempts on a large scale, which have shown good operation.

SECTION OF VEGETABLE OILS—Mr. Maihle developed his method of hydrogenation of vegetable and animal oils, which makes possible the transformation of these oils in petroleum.

This very interesting Congress was completed by the Exposition where all the engines using combustible liquids were shown in operation, and especially the engines of the Powders Service, using all the recommended mixtures successively, as well as the motors of mazout of the Inventions Service, where the mazout is first distilled and the gases of distillation are burned. We were able to compare this process with that using the pulverization of mazout and its entrainment through a current of air.

The visits to the factories in the vicinity of Paris, in Alsace-Lorraine, and in the Sarre region, ended the meeting of the Congress.

October 31, 1922

LONDON LETTER

By HUGH GRIFFITHS, 15 New Bridge St., London, E. C. 4, England

LOW TEMPERATURE RESEARCH

An encouraging new feature in meetings of scientific societies is the joint discussion held by several societies. It is realized that this kind of coöperation covers overlapping fringes of activity, and new points of view are presented which are stimulating to the specialist members who are liable to get narrow views.

An interesting joint meeting of the Faraday Society and the British Cold Storage and Ice Association has just been held. The physical papers included contributions from Dr. Onnes of Leyden, who has succeeded in reaching within less than one degree of absolute zero. Dr. Crommelin gave a detailed description of the apparatus employed for research work at Leyden, which is well worth the attention of all makers in research on liquefied gases and gases at low temperatures.

The technical papers included a full discussion of modern methods of manufacturing oxygen by K. S. Murray of the British Oxygen Co. Ltd., a paper on hydrogen manufacture by G. Claude,¹ and a paper on heat insulation materials by Dr. Ezer Griffiths.

The information given by Mr. Murray was largely new and very complete, and the somewhat surprising information was given, that actual experience with various systems had shown that the product of 1000 cu. ft. of oxygen of 98.5 per cent purity required not less than 30 to 33 b. h. p. hours. It was also mentioned that while oxygen had been employed in the chemical industry in Germany in the production of nitric and acetic acids, the use of oxygen for chemical purposes was really in its infancy, and the opinion was expressed that future development of oxygen as a raw material for chemical manufacturers was certain.

Dr. Claude's paper, as would be expected, had special reference to synthetic ammonia, and the system of hydrogen production discussed is that at present used at Grande Paroisse. The process consists of liquefying the carbon monoxide from water gas, etc., under a pressure of 200 to 450 lbs. per sq. in.

It was rather disappointing to find that the purely chemical applications of refrigeration were not discussed, particularly as in England many processes involving the use of refrigeration have recently been devised. The problem of "niter cake" is always with us, and there are some who believe that the only solution will be found in freezing out Glauber's salt from a solution of this product. The application of refrigeration in the manufacture of perfume ingredients from essential oils is fairly extensive, but the methods usually employed are primitive, and the plants somewhat crude.

HYDRONAPHTHALENES

Since the war, attention has been directed toward Rodleben, where there is a plant capable of producing about 100 tons per day of hydrogenated naphthalenes. During the war this installation produced a substitute for turpentine, and the naphthalene derivatives were employed as solvents for synthetic resins of the bakelite type.

The tetrahydro- and decahydronaphthalenes are not difficult to manufacture, and they have been proposed as substitutes for turpentine. A recent investigation carried out by Coleman and Bilham for the Department of Scientific and Industrial Research gives some definite information regarding these products. The report of these investigations deals chiefly with "Dekalin," which is a mixture containing about 80 per cent decahydronaphthalene and 20 per cent tetrahydronaphthalene. In physical properties this mixture is similar to turpentine, but is less volatile and less viscous, and has a somewhat higher flash point. Dekalin and various similar materials have come into use in Germany in the paint and varnish industry, and it appears from the report of Coleman and Bilham that the new materials are actually better than turpentine. They possess in common with turpentine the property of acting as oxygen carriers, therefore inducing autoxidation of the drying constituents of a paint or varnish.

COLLOID CHEMISTRY

The study of technical problems by the methods of colloid chemistry is becoming very fashionable, and this method has recently been sanctioned in England by government support.

Volumes dealing with the application of colloid chemistry to industrial matters are now issued yearly through H. M. Stationery Office by the Department of Scientific and Industrial Research.

This year the fourth report has appeared, and is much more comprehensive and bulky than the previous issues. An extra volume has also been published from the same source, containing a record of the discussion held jointly by the Faraday Society and the Physical Society. These volumes contain some excellent information on the application of colloid theories to a long range of industrial problems.

The flotation process comes in for very full treatment, and soap boiling, steel, rubber, glass, lubricants, and colloid fuels are all considered. The papers on the theory of the flotation process by Edwin Edser are of exceptional merit. There is also included in the first report a paper on catalytic hydrogenation by E. F. Armstrong and T. P. Hilditch.

One usually feels in reading the literature of colloid chemistry that the explanations frequently given are merely translations of ideas into words, and that the state of knowledge is very indefinite. The volumes mentioned are singularly free from this defect, and most of the papers show serious endeavor to treat colloidal problems in a strictly physical and scientific manner.

October 23, 1922

Canadian Chemical Production Well Maintained

The gross value of chemicals and allied products manufactured in Canada in 1920 was approximately \$122,000,000, according to a report published from the Dominion Bureau of Statistics at Ottawa.

The report states that the actual capital invested in the 456 plants operating in this group of industries in 1920 was \$120,000,000. Pigments, paints, and varnishes made in 48 plants were valued at \$27,000,000. The report covers ten principal industries producing, respectively, coal tar and its products; acids, alkalis, salts, and compressed gases; explosives, ammunition, fireworks, and matches; fertilizers; medicinal and pharmaceutical preparations; paints, pigments, and varnishes; soap, perfumery, cosmetics, and toilet preparations; inks, dyes, and colors; wood distillates and extracts; miscellaneous chemicals.

The imports of chemicals and allied products into Canada have gradually increased from \$3,469,000 in 1895 to \$24,000,000 in the twelve months ending March 1922. The exports of Canadian products of the same class have risen from \$760,000 in 1892 to \$9,000,000 in the twelve months ending March of the present year. During the war the great production of explosives in Canada and the shipment of this commodity to the war zone raised the Canadian exports of chemical products to a grand total of \$57,000,000 in the twelve months ending March 1919. The present export figures show that much of the advantage gained in the war-time development has been retained, and the fact that the summary statistics for the calendar year 1921 showed that 444 plants were in operation as compared with 456 in the preceding year is further evidence that the chemical industries of Canada are more than holding their own.

Interesting data on the comparative values and compositions of beet and cane molasses have been reported in the *Journal of the Society of Chemical Industry*. The following table shows the results:

	Water	Ash	Albumi- noids	Carbo- hydrates
Cuban cane	21.12	6.65	4.68	67.55
English refinery cane	24.20	6.07	1.50	68.23
German beet	23.84	9.60	9.57	56.99
American beet	21.00	12.17	...	66.83
English refinery beet	20.00	10.00	...	70.00

Beet had a high ash and nitrogen content and nearly half of its sugar was invert. Cane molasses was found preferable for feeding purposes.

¹ See page 1118 of this issue

JAPAN LETTER

By K. KASHIMA, 1125 Ikebukuro, near Tokyo, Japan

NEW PATENT LAWS

The Patent Bureau has recently been enlarged and the patent laws have been revised. The following important improvements were made:

1—A patent should be granted to its inventor, but the true inventor is often difficult to find. A patent is granted to the first applicant, and therefore when an invention is complete patent application should be made promptly. (Art. 8)

2—An application shall be made public before the patent is granted, to give opportunity for objections or protests. (Art. 73 and 74)

3—In order to avoid misunderstanding between examiner and applicant, reasons for rejections of applications shall be shown to the applicant so that he may have opportunity to answer the objections.

4—Formerly the final decision was made by the Patent Bureau, but by the new law the applicant can ask for a second judgment and can also appeal to the Supreme Court for a final decision. (Art. 115)

5—Inventions promote the welfare of the public, and the rights should be given the inventor, even though the invention is made while he is in the service of an employer. If the employer wishes patent rights on the invention, he must pay the inventor.

6—Under the old law an examination for validity of a patent could be requested at any time during the continuation of the right. Now, validity cannot be questioned after five years from the date of the grant. (Art. 85)

7—In order to protect industry, a working clause has been inserted in the patent law. (Art. 41)

PULP INDUSTRY

The pulp industry in this country made rapid progress during the war, but in 1921 there was a decrease in the number of factories and companies, owing to bad economic conditions. The production of pulp in this year, however, was 250,027 tons, compared with that of previous years, which was as follows:

Year	Tons
1917	169,039
1918	198,596
1919	235,227
1920	268,261

It is expected that the production in this year will show an increase of about 30 per cent, or a total of about 326,285 tons. After 1923 probably one-half of the total wood for pulp will be obtained from Kabafuto.

The imports and exports of pulp and the total amount produced during the past few years are as follows:

YEAR	IMPORTS Tons	EXPORTS Tons	Total Amount Produced
1917	14,334	3,722	
1918	28,769	3,908	223,457
1919	40,581	1,106	274,702
1920	46,808	8,180	306,889
1921	38,765	1,133	287,659

Imports of pulp are mainly from Canada and Sweden, the former aiming to sell in the Orient only. Owing to the high price of woods and wages, the cost of the domestic product is slightly higher than that of the Canadian product. A new company with a capital of 3,000,000 yen has recently been established with a view to shutting out the imported product.

The import tax of pulp in this country is now 0.2 sen per pound. As the pulp industry has developed, the Treasury Department is trying to exclude the import tax, but the directors of the paper companies are now opposing it.

September 12, 1922

VITAMIN A

At the September regular meeting of the Chemical Society of Japan, Dr. K. Takahashi, of the Agricultural Department of the Tokyo Imperial University, presented an interesting report on the nature of vitamin A. About ten years ago, Dr. M. Suzuki, of the same department, reported oryzanine as vitamin B, and since that time researches on the nature of the other three vitamins have been conducted. Dr. Takahashi has succeeded in determining the nature of vitamin A.

Rats and pigeons were bred with meals prepared from 75 per cent protein, 25 per cent butter, and a small quantity of purified oryzanine, and from 75 per cent butter, 25 per cent protein, and a small quantity of the same vitamin. They grew rapidly and were well nourished. From these results it is evident that animals can grow without carbohydrates. They were then fed with meals that contained no fat but contained vitamin A, and they all showed normal growth. It must, therefore, be concluded that carbohydrates and fats in animals' meals can be replaced to some extent by proteins.

Cod-liver oil has been shown to be rich in nutritive value, which is mainly due to the presence of vitamins. Dr. Suzuki claims that he has succeeded in isolating 1 g. of almost pure vitamin A from 1000 g. of cod-liver oil, 0.0001 g. of which has proved to be effective for recovering the health of an animal dying from insufficient nutrition.

Vitamin A, isolated by Dr. Suzuki, is a light brown liquid and soluble in almost all organic solvents, giving a yellow to yellowish red solution. By adding concentrated sulfuric acid to its chloroform solution, a deep green color develops, a reaction occurring in tests for cod-liver oil. The same solution gives a green color with Japanese acid clay. It has a reducing action, reducing silver nitrate. Vitamin A is very easily destroyed by air and light, its oxidized product having a peculiar odor. It is, however, stable in alcohol, ether, and fatty acids. It is a substance like cholesterol, probably an aldehydic compound since it contains no nitrogen. It may be practically used in olive oil solution, which will have more than a hundred times the nutritive value of butter. The detailed report will appear in the *Journal of the Chemical Society of Japan*.

THE METRIC SYSTEM

Japan has always had a measuring system of her own. It was, however, systematically revised in the early part of the Meiji Era, so that it resembled the metric system, as the old system was very irregular. Now, however, the metric system is generally adopted in the scientific world, and the English system in industrial circles. The adoption of the metric system has at last been approved by the 44th Diet, and the Agricultural and Commercial Departments are now awaiting the enactment of the Imperial Ordinance for its adoption. It will probably be in force from January or April 1923. It is expected that the system will be described in the textbooks of schools after three years; government offices and large companies ought to adopt the system after five years, and complete adoption in general daily life should occur after twenty years.

October 11, 1922

Chandler Foundation Lecturer

Friends of Professor Chandler presented in 1910 to the trustees of Columbia University a sum of money which constitutes the Charles Frederick Chandler Foundation. The income from this fund is used to provide a lecture by an eminent chemist and to provide a medal to be presented to the lecturer in further recognition of his achievements in science. Previous lecturers on this foundation were L. H. Baekeland, Sc.D., W. F. Hillebrand, Ph.D., W. R. Whitney, Ph.D., F. Gowland Hopkins, Ph.D., and Edgar F. Smith, Ph.D.

The lecturer this winter will be Robert E. Swain, professor and head of the Department of Chemistry, Stanford University, Stanford, Calif.

Dr. Swain's subject will be "Atmospheric Pollution by Industrial Wastes." The lecture will be in Havemeyer Hall, Columbia University, on January 9, 1923, at 8:15 P.M.

List of Periodicals

A revised list of the periodicals abstracted by *Chemical Abstracts* was printed in the October 20 number of that journal. Reprints of this list may be obtained from the editor, E. J. Crane, Ohio State University, Columbus, Ohio, at 25 cents per copy.

Personals

The committee in charge of the annual award of the Perkin Medal has selected Dr. M. C. Whitaker as the recipient for 1923. The presentation will be made January 12, 1923, at a meeting of the American Section of the Society of Chemical Industry.

Mr. Lloyd A. Hall, formerly chief chemist of John Morrell & Co., Ottumwa, Ia., has for the past year been general manager of The Chicago Chemical Products Co., manufacturers of coal-tar dips and disinfectants.

Dr. Richard C. Lord, at one time instructor at Washington and Lee University and later engaged in industrial chemistry, has been elected assistant professor of chemistry and physics at Kenyon College, Gambier, Ohio.

Dr. James C. Andrews has severed his connection with E. I. du Pont de Nemours & Co., and is teaching physiological chemistry in the Medical School of the University of Pennsylvania.

Dr. George Barsky, formerly a research assistant of Prof. R. H. McKee, Department of Chemical Engineering, Columbia University, has been appointed to a position in the research department of the Abitibi Paper Co., Abitibi, Ont.

Mr. Leonidas R. Littleton has resigned his position as chemist with the National Aniline & Chemical Company and has accepted the professorship of chemistry at Emory and Henry College, Emory, Va.

Dr. Simon Klosky has accepted appointment as instructor at the Martin Maloney Chemical Laboratory of the Catholic University of America, Washington, D. C. Dr. Klosky was formerly with the Chemical Warfare Service at Edgewood Arsenal.

Dr. G. Davis Buchner, research chemist at the Agricultural Experiment Station of the University of Kentucky, has secured a year's leave of absence, which he will spend in Europe visiting the more important educational and scientific centers of Italy, Germany, Switzerland, France, and England.

Mr. Thomas H. Wickenden and Mr. Charles McKnight, Jr., have recently joined the development and research department of the International Nickel Co., New York, N. Y., to undertake work in connection with alloy steels.

Mr. J. B. Foote, president and treasurer of Foote Bros. Gear & Machine Company of Chicago, died on October 12, 1922. Mr. Foote was widely known for his skill as a gear maker and inventor for transmission and other machinery. He was the pioneer in making cut steel, case-hardened, tough-cored gears for heavy duty work. He was one of the first to invent and build enclosed types of transmission for reducing electric motor speeds. He shared with Henry Ford the honors of pioneering the present light weight type of farm tractor, and in this connection he was the inventor of the enclosed transmission and live axle drive. He was also the inventor of numerous automatic machines for making cans and was regarded as a foremost authority on special machinery. He is survived by his widow, and his brother, Bradford Foote, who will continue the business of Foote Brothers Gear & Machine Co., 213 N. Curtis St., Chicago, Ill.

Mr. Charles T. Bragg, formerly with the Michigan Smelting and Refining Company, is now president and general manager of the Michigan Valve & Foundry Company.

Dr. Thomas R. Duggan, of the Permutit Co., New York, for many years trustee and chairman of the House Committee of the Chemists' Club, New York, was tendered a dinner on November 3 by about seventy-five members of the Club. The occasion was the departure of Dr. Duggan for an extended visit to England. He sailed November 4 on the Aquitania.

The following instructors and assistant instructors have been added to the chemistry faculty of the University of Kansas: Robert Taft, formerly professor of chemistry, Ottawa University; E. L. Joss, formerly a member of the faculty of Oklahoma State University; F. G. Moore, formerly of Texas Agricultural College; J. M. Wainscott of Southwestern University, Kansas; William Seaman, of Brown University; Miss Helene Thomas, Miss Selma Gattlieb, W. McPherson, A. J. Miller, and M. L. Ross.

Mr. Curtis C. Meigs, formerly president of the consulting chemical engineering firm of Meigs, Bassett, & Slaughter, Inc., with offices at 1304 Finance Building, Philadelphia, Pa., has sold his interest to Bassett & Slaughter, who will conduct the business under the name of Bassett & Slaughter, Inc. Mr. Meigs has taken offices at 709-710, Stephen Girard Building and is associated with Mr. Hugo Schlatter, formerly with the Hercules Powder Co., and Mr. W. B. Goentnerand, who was assistant chief mechanical engineer for the old firm. These men will do consulting work of a chemical engineering nature.

Industrials

The import prohibition on coal-tar products into Italy has been removed; fuel oil has been made duty-free; and important changes are effected in the import duties on coal-tar dyes and intermediates, according to the commercial attaché at Rome. The changes went into effect on October 29. The prohibition on the importation of synthetic dyes and other coal-tar derivatives into Italy went into effect June 3, 1921. Under the present regulations these products may be imported, but at the increased duty of 300 gold lire per 100 kilos instead of the former duty of 120 lire. By the same decree the import duties on nitrobenzol and aniline salts have been raised one-third.

During October 1922 twenty-three companies were formed to engage in the manufacture and distribution of chemicals, drugs, and dyes, with a total indicated investment of \$5,950,000, as compared with \$5,300,000 in September and \$5,850,000 in August. This is slightly below the total capitalization in October 1921, which amounted to \$6,675,000.

A joint committee representing the National Association of Wool Manufacturers, the American Association of Worsted and Woolen Manufacturers, and the National Association of Woolen and Worsted Spinners has been named to aid the Bureau of Standards in scientific research work affecting the woolen industry. The committee will meet in Washington in the near future for the purpose of aiding in the drawing up of a program which will more fully utilize the facilities of the bureau in considering general and specific problems of research and standardization in the textile trades.

The Bureau of Labor Statistics has reported a rise of two points in September in the government index number of wholesale prices in chemicals and drugs. The September number is 124, as compared with 122 in August. The chemicals and drugs number is 4.7 per cent below that for September 1921, while the number for all commodities is 8.5 per cent higher.

American industry is spending about \$70,000,000 annually on scientific research, according to the Fabricated Production Department of the Chamber of Commerce of the United States. About one-half of this sum is spent by American manufacturers in the conduct of laboratory research, while the remainder is expended in experimental and development work in plants. As a result of scientific research work, approximately \$500,000,000 are being saved annually by industry in this country.

As an incentive to members and students of the Canadian Institute of Chemistry resident in Canada, prizes amounting to \$75 have been created by three Institute members for the best two articles accepted for publication by any Canadian magazine, which are national in scope and of a business or literary nature. The competition will close May 1, 1923. Prize winners will be chosen by a committee appointed by the council of the Institute.

After extensive investigations of new laboratories now being erected, Dr. Charles E. Coates has submitted to the building committee a plan for the new chemical laboratory to be built at the Louisiana Agricultural College. Approximately \$450,000 are available for the erection of this laboratory, and the buildings are to be planned to permit additions when necessary.

At a recent meeting of the directors of E. I. du Pont de Nemours & Co., Inc., it was voted to increase the authorized capital stock from \$80,000,000 to \$100,000,000, by adding 200,000 shares of \$100 par value. The present outstanding capital is \$63,378,300, and the directors will declare a 50 per cent stock dividend, with the approval of the stockholders who have been called to meet on December 4 in Wilmington.

The Sales Promotion Section of the Office of Director of Sales, War Department, Washington, D. C., has recently issued a booklet, "War Surplus," which describes the methods resorted to by the War Department in the disposal of its stocks of surplus property, and tells what these stocks contain, where the property is located, and how to buy it. Quartermasters' supplies form the major part of the remaining surplus to be sold, but the Ordnance Department, Air Service, Signal Corps, Medical Department, Chemical Warfare Service, and Corps of Engineers have considerable stocks to be disposed of.

The Chemical Equipment Company is opening a new office at 109 Broad St., New York City, with Mr. G. M. Hickey, formerly of the Celite Products Co., in charge.

It has been announced that the Stauffer Chemical Company is to move its plant from San Francisco to Chester, Pa. Ten acres of land adjacent to the Sinclair Oil Company development have been acquired and several million dollars are to be expended. The buildings alone will cost \$500,000.

BOOK REVIEWS

Chemical Technology and Analysis of Oils, Fats, and Waxes.

By J. LEWKOWITZSCH, M.A., F.I.C. Edited by GEORGE H. WARBURTON. 6th edition. Vol. I, 1921, 682 pp.; Vol. II, 1922, 954 pp. Macmillan & Co., London.

The 5th edition of this work was published in 1913. A great many interesting developments have taken place in the fat and oil industry since that time, which the new edition seems to have covered in a very effective manner. The author very pertinently states in his preface that the greatest progress has been along the lines of the technological side in the development and investigation of new sources of oils and fats, with the hope of furnishing new supplies of food oils. The editor has been able to introduce most of the new material without materially increasing the size of either of the two volumes, and one cannot go through them without realizing that it is a very remarkable piece of work and is undoubtedly the standard book on the subject in the English language.

The first volume covers quite completely the classification of oils and fats, and their methods of analysis and study. The methods of analysis are distinctly English or European methods. The author has largely overlooked the methods of analysis used in this country which have been developed by the Fat and Oil Committees of the American Chemical Society and the American Oil Chemists' Society. In fact, it is the distinct weakness in this book from the standpoint of the American student.

In Chapter 1 the influence of light, moisture, and other materials on the keeping qualities of fat is very important and most complete, and contains the more recent developments on this subject, making it an extremely valuable compilation.

On page 299 there is a statement that the unsaponifiable matters of cottonseed oil contain considerable amounts of sulfur. This statement, from the experience of analysis in this country handling American oils, is certainly incorrect, since a great many tests made on cottonseed oils in this country have shown that they are free from sulfur.

Another point where there seems to be a certain amount of confusion is with regard to the titer test as used in the United States. The author seems to think that the Dalican method is accepted in the United States. This, as a matter of fact, is not correct. The method for titer determination is that adopted by the American Association of Official Agricultural Chemists and the Fat and Oil Committee of the American Chemical Society.

The second volume contains only two chapters—one on the commercial preparation of the raw materials used in the fat and oil industries, and the second chapter on the technology of natural oils, fats, and waxes, with methods of preparing, refining, and detecting adulterations. This discussion of the commercial preparation of oils and fats is the weakest part of the book. In fact, only 39 pages are devoted to this subject and almost none of it has any bearing upon modern American practice. The second chapter, however, is practically an encyclopedia of our present knowledge of the composition and adulteration of fats and oils. Practically every known fat and oil are recorded, with information as to its composition, source, and method of preparation, and the present edition shows that there has been a great deal of new material along these lines developed since the previous edition. On page 51 there seems to be a serious error in the tabulation of the American linseed crop for 1915–16–17. Just what these figures should be, it is hard to say.

The only criticism that might be made of the technological side of this book is that the author is evidently not familiar with

the cottonseed oil industry or the manufacture of lard in the United States, and has not kept up with the changes in rules that have been made in these industries within the last few years in this country. It seems to me that it would certainly be very desirable for the editor, in future revisions, to get the cooperation of American authorities on these two great oil and fat industries, which are so largely American industries.

L. M. TOLMAN

Handbook of the Petroleum Industry. Vols. I and II. DAVID T. DAY, Editor-in-Chief. 2070 pp. John Wiley & Sons, Inc., New York, 1922. Price, \$15.00.

This book has served a valuable purpose in bringing together in two volumes a vast amount of scattered material which in the past has been largely inaccessible to the average oil man. It would have been difficult to pick an editor better qualified for such a task than Dr. Day.

The authors of the various chapters are generally well known in the industry, and speak with authority. This method of compiling is both the strength and weakness of the work. While one author has treated his subject in textbook form, another has followed that of a popular treatise, while still another has followed the real handbook idea in giving formulas, costs, tables, thus furnishing the tools used by the specialist. This lack of balance was doubtless inevitable.

In the preface the editor speaks of our dwindling oil reserve as from five to seven billion barrels. It is not clear why he ignores the exhaustive estimate of nine billions made last year by a representative national committee, nor why it should not have been explained that with rising prices for crude more efficient methods will undoubtedly greatly increase this reserve.

In an otherwise clearly written chapter on the occurrence of oil, in which is included geology, there is a sacrifice of perspective for the sake of tabulation. The author disregards the fine pioneer work of Washburne, McCoy, Roswell Johnson, J. O. Lewis, and others, in their study of the effect of the laws of physical chemistry on problems of migration and accumulation, and merely gives a somewhat elementary synopsis of the anticlinal theory and gravitational separation. The list of occurrences in foreign fields does not reflect the present state of knowledge of those regions.

The chapter on development and production is a remarkably complete description of the tools and material used, and includes many fine illustrations. That phase of the subject dealing with the production of oil from a lease is less good. There is very little of value upon the care of wells, cleaning-out, shooting, and water problems, while a good deal of space is devoted to a popular description of spectacular conditions in the Mexican fields. Operating costs and depletion of a property are not touched upon, nor any mention of acreage yields in various sands and localities. The Smith-Dunn process is unfortunately described as an adaptation of the air-lift system.

One of the best chapters in the book is that upon field geological methods, especially upon the barometric method. It can well be used as a text, and to the geologist is worth the price of the whole book.

The chapter on statistics gives much valuable material. The graphs used are somewhat elementary, and would have been improved by the use of some of the analytical methods, as in Pogue's excellent work, to show relations between consumption and production and prices.

The chapters on transportation, refining, and testing indicate that greater progress has been made in the manufacturing branches of the oil industry than in the art of production. A discussion of costs would have been of value in the chapter on transportation, as is given in that on refining and also in the exceedingly interesting chapter on oil shales. This latter includes a good discussion of market conditions, costs of mining and transportation, character of the oil, by-products and their markets, with a valuable list of occurrences—all of which is very timely.

The chapters on fuel oil, the internal combustion engine, and lubrication leave little to be desired in each field, with their discussions, formulas, and tabulated material. That on pipe is almost entirely from a manufacturer's standpoint. It would be more valuable to the industry if there were some discussion of the use of the various types of pipe and casing in the field. Why is one weight and size used in California and another in Louisiana, and still another in Oklahoma?

The engineer and the chemist must still have several books dealing with different phases of the oil problem on their desks, but among them that by Dr. Day will find a prominent place.

L. G. HUNTLEY

The Origin of Spectra. By PAUL D. FOOTE AND F. L. MOHLER. A. C. S. Monograph No. 8. 250 pp. Chemical Catalog Co., Inc., New York, 1922. Price, \$4.50.

The year 1922 has placed in the hands of spectroscopists several noteworthy books, of which the one under review is important. Foote and Mohler have undertaken, with remarkable success, to correlate the experimental facts of spectroscopy with the general theory of atomic structure which we owe mainly to Planck, Bohr, and Sommerfeld.

How very far away we are from the days of Bunsen, when nearly every new chemical element was being discovered by "spectrum analysis" and when Huggins was learning the composition of the stars; and how far we are also from the days when Kayser, Runge, and Rydberg were first pointing out the orderly series which exists in the chaos of wave lengths, may be realized by considering the remark on page 109, that spectroscopy is the science which is mainly concerned with the interorbital transition of a valence electron which has previously been ejected to an outer orbit.

The Bohr-Sommerfeld atom is accepted frankly and fully. The authors have no hesitation. They possess the courage of their convictions. In many places they point out the need of more information and the difficulty of certain experimental determinations, but never a doubt is entertained concerning the theory.

The first chapter, occupying nearly a quarter of the entire volume, contains a clear exposition of the quantum theory as applied to spectra. The consequences and predictions of the theory are set forth in a manner which is at once striking, unifying, and helpful. The authors never for a moment allow Mendelejeff's table to drop out of their consciousness.

The second chapter dealing with energy diagrams, energy levels, etc., might well have included a little more detail—a little more "connective tissue." A discussion of ionization and resonance potentials follows in Chapter 3; then a fourth chapter concerning line absorption spectra of atoms, full of interest from start to finish. In the fifth chapter is reached the heart of the matter, the emission of line spectra. This is the immediate problem suggested by the well-chosen title of the volume. Here the authors are particularly in the field of their own valuable contributions to knowledge; the discussion is consecutive and exceedingly clear. Later chapters deal with the mooted question of thermal excitation of spectra, with the difficult problem of flame spectra, with thermo-chemical relations, and briefly with X-ray spectra.

Concerning the volume as a whole, it is certain to make considerable demands upon the attention of the reader who desires to distinguish carefully between fact and theory. The authors do not always talk in terms of the laboratory. Ionization and resonance potentials, for example, are defined, not in terms of experiment, but in terms of the dominating model.

The value of the book for reference to recent literature is indicated by the fact that the index of names of authors includes no less than one hundred and seventy-five entries.

The authors have certainly earned the thanks and congratulations of all English-speaking students of spectroscopy; for not only is this volume indispensable to physicists and astrophysicists, but, since the spectrum of an atom is the most characteristic thing about it—not excepting even its atomic weight—the book will prove equally necessary to chemists.

HENRY CREW

Clay Products Cyclopedia. Industrial Publications, Inc., Chicago, 1922. 200 pp. Price, \$3.00.

This book represents a praiseworthy effort to give to the clay industry information on a large variety of subjects pertaining to ceramics. The nature of the alphabetical and departmental arrangement precludes, of course, the treatment of the many topics in their natural order. The question arises whether it would not be better in future editions to adopt the topical and connected arrangement by chapters as is done in the standard handbooks. The information has been collected from many sources, most of which have been acknowledged, but in several cases this has been overlooked. Such clay-testing methods as are given on pages 142 to 147 might have been eliminated with profit. Misprints, which are difficult to avoid in a work of this kind containing so much tabulated information, are much less numerous than might be expected. The work of compilation has been well done and the book is of real service to the plant executives and operators for whom it is intended.

A. V. BLEININGER

Food Products from Afar. By E. H. S. BAILEY, PH.D., AND H. S. BAILEY, A.B., B.S. 287 pp. The Century Co., New York, 1922. Price, \$3.00.

The book is delightfully written and the typographical work, including the reproduction of numerous photographs, is a credit to the printer's craft. Details of the nature and the production or manufacture of foods exotic to the United States are vividly brought to the attention of the reader, be he epicure, nutritionist, or technical chemist. The two former classes may read without danger of being swamped in chemical terms, while the food chemist will find information to aid him in his work for which he would have to search long elsewhere.

After a preliminary chapter on the sociology of foods, are chapters under appropriate captions dealing with Italian pastes, nuts, edible oils, cheese, Arabian and Mediterranean products, rice and spice, foods of the Far East, tropical foods, coffee, Latin-American foods, stimulants and sedatives, bananas, and fish foods, most of which in these days are imported into the United States, and in addition certain unique foods to which the American palate is not as yet trained.

The reviewer feels that the authors, both of whom stand in the front ranks of food chemists, have conferred a greater favor on men of their own calling by writing a book of this character than if they had treated the subject, at this time, from the standpoint of nutritive value or vitamin content.

A. L. WINTON

COMMERCE REPORTS

Notice—Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is \$3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.

October

The new Junquera process for extracting nitrate of soda is described. Official tests of the process were witnessed by many men prominent in the nitrate industry, and the impression seems to be general that the inventor has in large part made good his claims. There is a disposition to recognize that a new invention has been made which, when improved, may revolutionize the industry. (P. 23)

Extensive development of steam electric power by utilization of the lignite deposits of Italy is being considered under the government subsidy plan for making use of the national fuel resources. (Pp. 26-7)

A recent French decree prohibits the exportation of uranium ores from the French colonies and protectorates, except Morocco and Tunis, to countries other than France and its possessions and protectorates. The declared purpose of this decree is to give French chemical manufacturers preferred access to the radium-bearing minerals of Madagascar. (P. 54)

A French decree of September 4, 1922, suspends the maximum duty of 8 francs per 100 kilos hitherto levied on crude ammonium sulfate imported into that country. (P. 55)

The Venezuelan government has placed potassium carbonate, sodium carbonate and powdered white marble on the free list and a duty upon potassium hydrate and sodium hydrate. (P. 56)

A pronounced shortage of zinc exists in Germany at present. Visible stocks are estimated at 8000 metric tons, as compared with 14,000 metric tons a year ago. One of the most important factors said to be responsible for this shortage was the loss of 80 per cent of the former Silesian zinc production to Poland. (P. 73)

Reports from Fitzgerald, Alberta, indicate that silver deposits which will equal the silver mines of northern Ontario, have been discovered northeast of that town. It is said to be a high-grade, free-milling ore. (P. 76)

Trial borings for oil in northern Kerafuto clearly reveal that the prospects for the production of oil in that region are very good. (P. 95)

The output of potash in France during the second quarter of 1922 showed an improvement over that of the preceding quarter, being, respectively, 46,282 and 38,733 tons of pure potash. (P. 98)

The American Embassy at Paris has been informed by the Alsatian Potash Commercial Company that while general conversations are being held relative to a potash agreement, no decisions have been reached. (P. 98)

A bill has been introduced in the lower house of the Brazilian Congress which provides for an increase in import duty on bleaching powder and on caustic soda. (P. 119)

Substances imported into Salvador for the purification of water not specified in the customs tariff are to be classed under "Chemical products and industrial preparations," and are subject to duty. (P. 120)

The total production of petroleum in the Dutch East Indies during the calendar year 1921 amounted to 2,361,509 metric tons as compared with 2,365,320 tons in 1920 and 2,159,862 tons in 1919. (P. 153)

Increasing interest is being evidenced in the production of oil from bituminous schists in Italy, production amounting to 16,325 tons in 1920 and 3150 tons in 1921. (P. 153)

The export trade of the United States in chemicals and allied products is increasing so rapidly that it is not unlikely the total value for the year will exceed that for 1921. (Pp. 161-2)

A survey of the French manufacture of coloring matters is most discouraging. This same depression appears to be symptomatic of industrial chemicals in general in France. (P. 162)

The new schedule of German potash prices is given. (P. 162)

The duty on copra exported from New Guinea has been reduced for a period of one year, beginning June 1, 1922. (P. 178)

Beginning with September 1922, statistics showing exports from the United States, by countries of destination, of certain specified chemicals will be issued in mimeographed form by the Bureau of Foreign and Domestic Commerce. (P. 211)

Deposits of kieselguhr have recently been discovered near Cheribon, Java, and experiments are being made at several sugar mills to determine whether it can be satisfactorily used in place of the imported product. (P. 211)

Extension of the French artificial-silk industry has not kept pace with the increasing French popularity of artificial-silk goods, and the nine mills engaged solely in the manufacture of this material are all booked up for months ahead. (P. 219)

German deliveries of dyestuffs to the allied powers are described. An interesting fact is that the largest amounts have been sent to Italy, rather than to France and Belgium as popularly believed. (Pp. 246-7)

The Governor General of the Union of South Africa has proclaimed a rebate of the whole or part of the import duty on the following articles, when imported in accordance with certain prescribed regulations and used for certain designated manufacturing purposes: oils, used in the lubricating of yarn in the process of weaving, rebate 17 per cent of the duty; gums and turpentine used in the manufacture of paints, rebate the whole duty on gums and 17 per cent on turpentine; solvent naphtha, sealite, and similar fluxes, used in the sealing of containers of commodities, rebate the whole duty. (P. 254)

Chlorate of soda and perchlorate of ammonia are offered to American buyers by a firm in Turin, Italy. Further particulars may be obtained from the Chemical Division of the Bureau of Foreign and Domestic Commerce. (P. 272)

A market for American fertilizers is said to exist in the Isle of Pines, and for ammonium sulfate at Dunkirk. (P. 272)

"Springbok" motor spirit is the name of a new gasoline substitute which has been invented by an attorney of So. Africa. This product is made from the juice of the prickly pear mixed with chemicals. It has been severely tested on various makes of cars and is highly recommended, being noncorrosive, odorless, and equal to or better than gasoline in power and flexibility, a mileage of 22.4 being obtained in a six-cylinder car. (P. 277)

Dr. Edwin Bluemner of Berlin claims to have invented a process for the production of synthetic benzene. (P. 278)

It is reported that a professor in one of the German technical schools has been engaged for the last three years in the development of a new process for obtaining gasoline from crude oil. The inventor believes that his invention makes possible a production of from 30 to 80 per cent of gasoline from coal tar and bituminous coal, as well as from the hitherto waste crude from which the maximum amount had been obtained under the old systems. (P. 278)

Gonakie, the pods of which produce a tanning material of considerable value, is suggested as a possible substitute for sumac. (Pp. 291-2)

The German prices on unbleached sulfites have been revised—for the most part downward. (P. 295)

Raw lime and limestone may be exported from Czechoslovakia without paying a manipulation fee and without obtaining an export license. (P. 307)

The British Board of Trade has removed the restriction on the exportation of all kinds of fertilizers and reimposed the restriction on the exportation of the following explosives: Dynobel, Samsonite, and Thames powder. (P. 308)

Special Supplements Issued: Algeria, Haiti, and Venezuela.

CURRENT PUBLICATIONS

NEW BOOKS

- Analysis: A Method for the Identification of Pure Organic Compounds.** Vol. IV. SAMUEL P. MULLIKEN. 238 pp. Price, \$5.00. John Wiley & Sons, Inc., New York.
- Artificial Rubber: Künstlicher Kautschuk für Elektrische Isolierzwecke.** KURT GEISLER. 89 pp. Price, \$1.00. Verein Deutscher Ingenieure, Berlin.
- Atomic Form with Special Reference to the Carbon Atom.** E. E. PRICE. 148 pp. Price, 5s. Longmans, Green & Co., London.
- Belt Conveyors and Belt Elevators.** FREDERICK V. HETZEL. 333 pp. Price, \$5.00. John Wiley & Sons, Inc., New York.
- Camphor: Le Camphre et sa Synthèse.** A. DUBOSC. La Culture Industrielle du Camphrier. L. TRABUT. 64 pp. Price, 6 fr. Dunod, Paris.
- Carotinoids and Related Pigments: The Chromolipoids.** LEROY S. PALMER. American Chemical Society Monograph Series. 300 pp. Price, \$4.50. Chemical Catalog Co., Inc., New York.
- Cellulose: Researches on Cellulose.** CHARLES F. CROSS AND CHARLES DORÉ. 253 pp. Price, \$5.00. Longmans, Green & Co., New York.
- Chemistry of To-day.** P. G. BULL. 311 pp. Price, 8s. 6d. Seeley Service & Co., Ltd., London.
- Colour Index. Part I.** F. M. ROWE, EDITOR. 24 pp. Subscription price for the whole work, 84s. Society of Dyers and Colourists, Bradford, England.
- Concrete: A Manual of Reinforced Concrete.** CHARLES F. MARSH. 4th edition. 504 pp. Illustrated. Price, 21s. net. Constable & Co., Inc., London.
- Coal, Coke, and By-Products. 1913-1919. Part III.** IMPERIAL MINERAL RESOURCES BUREAU. 173 pp. Price, 7s. H. M. Stationery Office, London.
- Dyes: Traité des Matières Colorantes Organiques et de leurs Diverses Applications.** EDOUARD EHREMAN. 615 pp. Price, 58 fr. Dunod, Paris.
- Foundry Practice: A Comparison of British and American Foundry Practice with Special Reference to the Use of Refractory Sands.** P. G. H. BOSWILL. 106 pp. Price 4s. 6d. The University Press of Liverpool, Liverpool.
- Handbook of Chemical Engineering.** DONALD M. LIDDELL. 2 vols. 517 pp. Price, \$8.00. McGraw-Hill Book Co., Inc., New York.
- Heat: Notes and Examples on the Theory of Heat and Heat Engines.** JOHN CASE. 136 pp. Price, \$2.50. D. Van Nostrand Co., New York.
- Heat Transmission: Technical Records of Explosives Supply 1915-18. No. 9.** MINISTRY OF MUNITIONS AND DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. 48 pp. Price, 5s. 3¹/₂d. H. M. Stationery Office, London.
- Inorganic Chemistry: La Chimie des Complexes Inorganiques.** ROBERT SCHWARZ. Translated by ANDRÉ JULIARD. 72 pp. Illustrated. Price, 8 fr. Dunod, Paris.
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- Organic Chemistry: Cours de Chimie Organique.** F. SWARTS. 3rd edition, revised and enlarged. 674 pp. Price, 45 fr. M. Lamertin, Brussels.
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- Practical Refrigeration for Marine Engineers.** H. E. ROBERTS. 87 pp. Price, \$1.75. D. Van Nostrand Co., New York.
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- Rubber: The Analysis of Rubber.** JOHN B. TUTTLE. American Chemical Society Monograph Series. 160 pp. Price, \$2.50. Chemical Catalog Co., Inc., New York.
- Standard Specifications for Laboratory Apparatus.** MANUFACTURING CHEMISTS' ASSOCIATION OF THE UNITED STATES. Part I. Graduates and Thermometers. 49 pp. Manufacturing Chemists' Association of the United States, Washington, D. C.

- Steel: The Determination of Sulfur in Iron and Steel.** H. B. PULSIFER. 160 pp. Illustrated. Price, \$2.50. Chemical Publishing Co., Easton, Pa.
- Textiles.** A. F. BARKER, W. M. GARNER, R. SNOW, W. H. COOK, AND F. BRADBURY. Revised edition. 396 pp. Price, \$4.50. D. Van Nostrand Co., New York.
- Vanadium, 1913-1919. The Mineral Industry of the British Empire and Foreign Countries. War Period.** IMPERIAL MINERAL RESOURCES BUREAU. 19 pp. Price, 6d. H. M. Stationery Office, London.

RECENT JOURNAL ARTICLES

- Acid-Resisting Metals and Alloys.** GEORGE A. DRYSDALE. *The Coal Industry*, Vol. 5 (1922), No. 10, pp. 452-54.
- Adhesive: Sodium Silicate as an Adhesive.** REX FURNESS. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 18, pp. 381-84r.
- Application of Artificial Daylight to Laboratory Purposes (Sheringham System).** S. H. GROOM. *The Analyst*, Vol. 47 (1922), No. 559, pp. 419-23.
- Artificial Silk and Its Applications in the Textile Industry.** P. E. KING. *American Dyestuff Reporter*, Vol. 11 (1922), No. 9, pp. 317-18, 329-32.
- Artificial Silk: The Manufacture of Artificial Silk.** REX FURNESS. *The Chemical Age (London)*, Vol. 7 (1922), No. 174, pp. 522-24.
- Bingham Viscometer: The Drainage Error in the Bingham Viscometer.** WINSLOW H. HERSHEL. *Journal of the Optical Society of America and Review of Scientific Instruments*, Vol. 6 (1922), No. 8, pp. 875-98.
- Blast Furnace: Bases of Modern Blast Furnace Practice.** A. K. REESE. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 10, pp. 495-99.
- Boiler Tube Slag: How to Combat Formation of Slag on Boiler Tubes.** HARRY H. BATES. *American Gas Journal*, Vol. 117 (1922), No. 17 (Whole No. 3372), pp. 370-75.
- Ceramic Research: The Organization of a Decorative Ceramic Research Department.** FREDERICK H. RHEAD. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 11, pp. 758-87.
- Chrome Tanning. XI. Some Observations on the Properties of the Common Chrome Liquors.** D. BURTON, R. P. WOOD, AND A. GLOVER. *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 9, pp. 281-87.
- Chrome Tanning: Sur le Tannage au Chrome à un Bain à Partir de l'Alun de Chrome.** P. CHAMBARD AND L. MEUNIER. *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 9, pp. 288-96.
- Coal Gas: Scrubbing and Condensing Coal Gas.** J. R. WOHRLEY. *Gas Age-Record*, Vol. 50 (1922), No. 17, pp. 521-26, 530.
- Combustion: Judging the Combustion of Gaseous Fuels from Gas Analyses.** A. G. WITTING. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 10, pp. 522-28.
- Corrosion Control by Deactivation of Water.** FRANK N. SPELLER. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 10, pp. 500-4.
- Corrosion of Cast Iron and Lead Pipes in Alkaline Soils.** J. W. SHIPLEY. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 18, pp. 311-16t.
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- Rubber: The Constitution of Rubber. MAITLAND C. BOSWELL. *Canadian Chemistry and Metallurgy*, Vol. 6 (1922), No. 11, pp. 237-43.
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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.

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- Fatalities at Coal Mines in August 1922. W. W. ADAMS. *Reports of Investigations* 2399. 3 pp. Issued September 1922.
- Fire and Explosion Hazards of Petroleum and Petroleum Products. S. H. KATZ AND N. A. C. SMITH. *Reports of Investigations* 2400. 11 pp. Issued September 1922.
- Gunite in Metal Mines (with Tables of Costs and a Bibliography). B. O. PICKARD. *Reports of Investigations* 2397. 30 pp. Issued September 1922.
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- Extension of the Dye and Chemical Control Act, 1921. H. R. 1247. Submitted by MR. TILSON; committed to the Committee of the Whole House, and ordered to be printed. 2 pp. 1922.
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- Cobalt, Molybdenum, Nickel, Tantalum, Titanium, Tungsten, Radium, Uranium, and Vanadium in 1921. F. L. HESS. Separate from Mineral Resources of the United States, 1921, Part I. 27 pp. Published October 23, 1922.
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- Sulfarsphenamine. Its Manufacture and Its Chemical and Chemotherapeutic Properties. CARL VOEGTLIN, J. M. JOHNSON AND HELEN DYER. *Public Health Reports*, 37 (November 10, 1922), 2783-98.
- The Tannic Acid Method for Quantitative Determination of Carbon Monoxide in the Blood. R. R. SAYERS AND W. P. YANT. *Public Health Reports*, 37 (October 6, 1922), 2433-9.

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- Industrial Ovens. A booklet of 12 pages describing the sectional type of industrial oven. THE OVEN EQUIPMENT AND MFG. CO., New Haven, Conn.

MARKET REPORT—NOVEMBER, 1922

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

Movement of chemical products from producing to consuming channels during November slowed down considerably. Although prices which worked their way to higher levels during September and October might have reacted on a reduction in demand throughout the past month, the generally small stocks of all industrial chemicals and the difficulty in getting shipments through from plants have been sufficient support to prevent any sagging in values. In fact, most sellers have been very bullish and have stiffly maintained prices. Goods available for immediate shipment from distribution points away from manufacturing centers are being held at premiums in some instances, as the railroad car shortage and slow movement of all freight has permitted such stocks to become quite low.

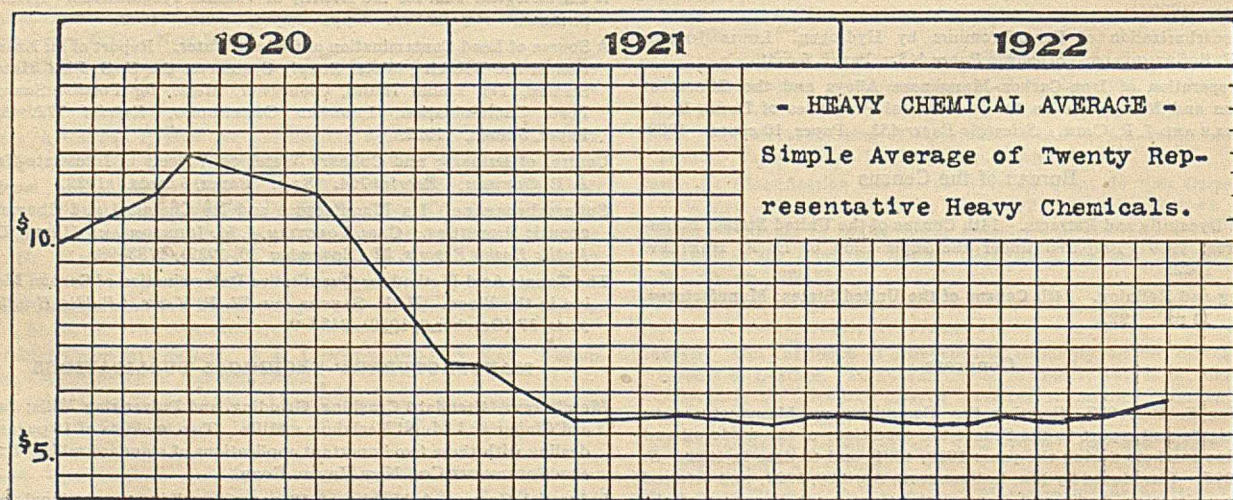
According to reports, the railroads of the country are short about 150,000 freight cars as a result of the recent strike of repairmen, this number of cars being out of commission for want of repairs. The freight embargo, or, as it might better be called, the priority order for food and coal, has caused much difficulty in shipping goods, more particularly in the West and Middle West. The only way to get goods through, according to some reports, is to send a man along with each car to insure its being kept on the move, and not side-tracked and forgotten. Indications point to the fact that thousands of chemical shipments rolling in various parts of the country are virtually lost, consignees being unable to find any trace of goods weeks and months overdue. In the case of a few medicinal products, the situation threatens to become serious.

The advance in price of acetate of lime to 3c per lb. was followed by advances in acetic acid, methanol, formaldehyde, and acetone. Higher cost of production is the main reason for the advance. Mineral acids have been in better demand. Ammonia alums and aluminium sulfate have been very scarce, due to the delayed shipments of bauxite from the South and West. Arsenic is very scarce and prices have advanced. Both foreign and domestic production have been sold and many consumers are still uncovered for the coming season. Copperas has been scarce. Yellow prussiate of soda has declined. Potassium prussiate is strong on scarcity and good demand. Makers are taking on contracts for next year for soda ash, caustic soda, and bichromates at unchanged prices. Caustic and ash are in good demand. The steady advances in the prices of tin, lead, and zinc have resulted in advances in tin crystals, all lead products, and zinc oxide. Higher potash prices have been made by the German Kali Syndicate.

Demand for animal and fish oils has been increasing and stocks are low. Lard oils, tallow, stearic, and oleic acids have advanced in price. Supplies of fish oils were well bought up by soap-makers at the close of the fishing season. Menhaden and cod oil are higher. Cottonseed oil has been very active due to scarcity of crude oil and high price of cotton. Linseed oil dropped slightly on reports of a record crop of flaxseed in Argentina. Denatured olive oil is higher. Palm and coconut oils are in good demand. Turpentine advanced to the highest mark in two years at \$1.68 per gal., the rise being due to shortage in primary markets.

Coal-tar products as a whole have been very scarce. Since the settlement of the coal strike production has been gaining slowly, but the demand is still much greater than the supply. There has been an increasing demand for 90 per cent benzene for motor fuel, which has cut into the toluene production. Supplies of cresylic acid and phenol are very low and the production of the only large maker is sold far in advance. A few odd lots are found here and there in the open market and the price asked is the highest since 1918. Some imported phenol is now offered at 35c per lb. Rumors are heard to the effect that synthetic phenol plants will soon be in operation as the price of phenol is now high enough to warrant its manufacture at a profit in competition with imported material. The demand for intermediates has been increasing, with greatest interest being shown in H-acid, gamma acid, benzidine, paranitraniline, beta-naphthol and dimethylaniline. Aniline oil is scarce on spot and prices firm. Dimethylaniline is higher on increased cost of raw materials.

In the field of medicinal chemicals less activity has been noted since the first of November. As a contrast to the broad, sharp advances of October, the past month has seen little or nothing happen except in the matter of derivatives of wood alcohol and phenol, which have both continued to skyrocket. Salicylates, strangely, have not moved upward although phenol prices are up close to 50 per cent above their November first level. American refiners have advanced camphor prices. A spot shortage of menthol finds prices on the rise. After the sharp rises in bismuth and mercury preparations in October, the past month has seen a steady demand at unchanged quotations. A number of fine chemicals are being imported from abroad in spite of the higher tariff rates. This is particularly true in rare alkaloids, and in a number of the less common medicinal products.



FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

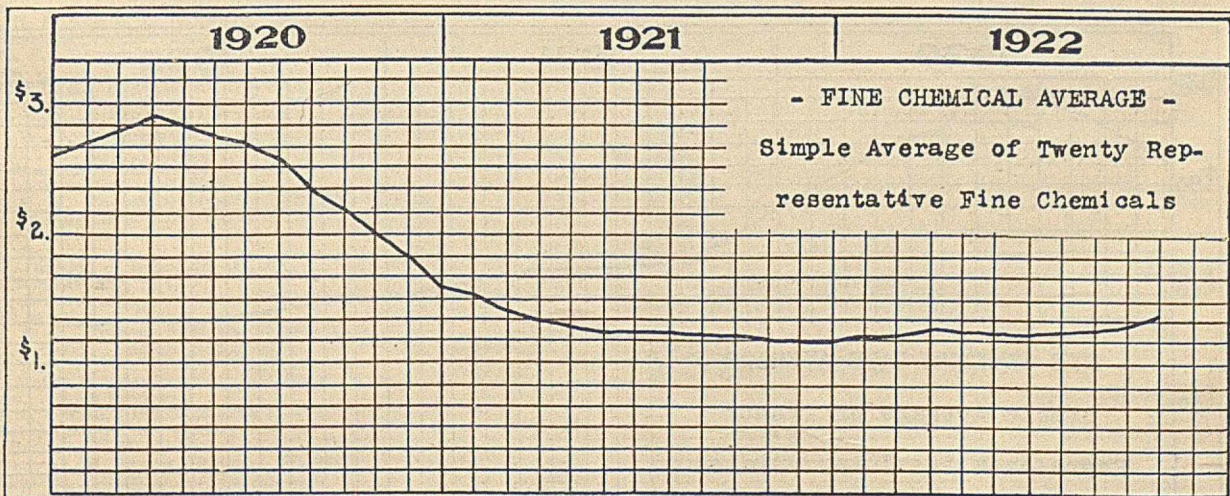
	Nov. 1	Nov. 15	Jan. 1922
Acid, Boric, cryst. bbls. lb.	.11½	.11½	.12½
Hydrochloric, comm'l. 20° lb.	.01½	.01½	.01½
Hydrofluoric, 30% bbls. lb.	.07	.07	.07
Hydroiodic, sp. gr. 1.150... lb.	2.25	2.25	2.00
Nitric, 42°, chys. c/l wks. lb.	.06½	.06½	.06
Phosphoric, 50% tech.... lb.	.08	.08	.10
Sulfuric, C. P. lb.	.08	.07	.07
66° tks. wks. ton	15.00	15.00	16.00
Oleum 20% ton	18.00	18.00	19.00
Alum, Ammonia, lump. lb.	.03½	.03½	.03½
Potash, lump. lb.	*.03	*.03½	*.03½
Chrome. lb.	.06	.06	.07
Soda, ground. lb.	.03½	.04	.03½
Aluminium Sulfate (iron-free) lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd. lb.	1.0½	1.0½	.08
Chloride, white gran. lb.	.07½	.07½	.07½
Ammonia, anhydrous. lb.	.30	.30	.30
Ammonia Water, drums, 26°... lb.	.07½	.07½	.07½
Arsenic, white. lb.	.11	.11	.06½
Barium Chloride. ton	*100.00	*100.00	*53.00
Nitrate. lb.	*.08	*.08	*.07
Barytes, white. ton	33.50	33.50	28.00
Bleaching Powd., 35%, works 100 lbs.	2.00	2.00	2.25
Borax, cryst., bbls. lb.	.05½	.05½	.05½
Bromine, pure, wks. lb.	.29	.29	.23
Calcium Chloride, fused, f.o.b. N. Y. ton	24.50	24.50	28.75
Chlorine, liquid. lb.	.06	.06	.06
Copper Sulfate. 100 lbs.	6.00	6.00	5.55
Iodine, resublimed. lb.	4.40	4.40	3.80
Lead Acetate, white crystals. lb.	.12	.12	.11
Nitrate. lb.	.22	.22	.15
Red. lb.	.08	.09	.08
White (Carb.) lb.	.08½	.08½	.07½
Lime Acetate. 100 lbs.	3.00	3.00	1.75
Magnesium Carbonate, tech. lb.	.07½	.07½	.08
Magnesite, calcined. ton	55.00	55.00	55.00
Phosphorus, yellow. lb.	*.25	*.25	*.27
Red. lb.	*.26	*.26	*.30
Plaster of Paris. bbl.	4.25	4.25	4.25
Potassium Bichromate. lb.	.10	.10	.10½
Bromide, imported. lb.	*.19	*.19	*.13
Carbonate, calc., 80-85% lb.	*.05½	*.05½	*.04½
Chlorate, cryst. lb.	*.07½	*.08½	*.05½
Hydroxide, 88-92% lb.	*.06½	*.06½	*.06
Iodide, bulk. lb.	3.50	3.50	2.90
Nitrate. lb.	.08	.08	.08
Permanganate, U. S. P. lb.	*.17	*.17	*.15
Prussiate, red. lb.	*.90	*.90	*.29
Yellow. lb.	*.38	*.39	*.24½
Salt Cake, bulk. ton	25.00	25.00	17.00
Silver Nitrate. oz.	.46	.45½	.44½
Soda Ash, 58%, bags. 100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y. 100 lbs.	3.75	3.75	3.80

*Resale or Imported (not an American makers' price).

	Nov. 1	Nov. 15	Jan. 1922
Sodium Acetate. lb.	.07½	.07½	.04
Bicarbonate. 100 lbs.	2.00	2.00	2.00
Bichromate. lb.	.07½	.07½	.07½
Bisulfite, powd. lb.	.04½	.04½	.04½
Chlorate. lb.	.06½	.06½	.07½
Cyanide, 96-98% lb.	.23	.23	.28
Fluoride, tech. lb.	.09½	.09½	.09½
Hyposulfite, bbls. 100 lbs.	3.20	3.20	3.60
Nitrate, 95% 100 lbs.	2.40	2.40	2.32½
Nitrite. lb.	.09	.09	.06½
Prussiate, yellow. lb.	.23	.22	.16½
Phosphate (di-sod.) tech. lb.	.04½	.04½	.04½
Silicate, 40° lb.	.01½	.01½	.01½
Sulfide, 60%, fused. lb.	.04	.04	.05
Strontium Nitrate. lb.	*.10	*.10	*.10
Sulfur, flowers. 100 lbs.	3.00	3.00	2.75
Crude, mines. long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n. lb.	.10½	.10½	.09½
Oxide. lb.	.38	.38	.37
Zinc Chloride, U. S. P. lb.	.20	.20	.35
Oxide, bbls. lb.	.07	.07	.08

ORGANIC CHEMICALS

	Nov. 1	Nov. 15	Jan. 1922
Acetanilide, U. S. P. bbls. lb.	*.30	*.38	*.29
Acid, Acetic, 28 p. c. 100 lbs.	2.92½	2.92½	2.87½
Glacial. lb.	.11½	.11½	.10
Benzoic, U. S. P. lb.	.60	.60	.60
Carbolic, cryst., U. S. P., drs. lb.	.30	.35	.12
50- to 110-lb. tins. lb.	.37	.44	.18
Citric, crystals, kegs. lb.	*.50	*.50	*.43
Oxalic, cryst., bbls., wks. lb.	.15	.15	.14
Pyrogallic, resublimed. lb.	1.60	1.60	1.75
Salicylic, U. S. P. lb.	.35	.35	.24
Tannic, U. S. P., bbls. lb.	.70	.70	.75
Tartaric, cryst., U. S. P. lb.	*.30	*.30	*.25
Acetone, drums. lb.	.19	.18½	.12
Alcohol, denatured, complete. gal.	.38	.38	.45
Ethyl, 190 proof, bbls. gal.	4.65	4.65	4.75
Amyl Acetate. gal.	2.00	2.00	2.00
Camphor, Jap, refined, cases. lb.	.87	.85	.90
Carbon Bisulfide, c/l. lb.	.06	.06	.06½
Tetrachloride. lb.	.10	.10	.10½
Chloroform, U. S. P., drums. lb.	.25	.25	.43
Creosote, U. S. P. lb.	.40	.40	.40
Cresol, U. S. P. lb.	.18	.18	.14
Dextrin, corn. 100 lbs.	3.09	3.09	2.70
Imported Potato. lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs. lb.	.14	.14	.14
Formaldehyde, bbls. lb.	.13½	.13½	.10½
Glycerol, dynamite, drums. lb.	.17½	.17½	.14½
Methanol, pure, bbls. gal.	.90	1.02	.75
Methylene Blue, med. lb.	3.00	3.00	4.00
Petrolatum, light amber. lb.	.04½	.04½	.05½
Pyridine. gal.	1.75	1.75	1.75
Starch, corn, pow'd. 100 lbs.	2.47	2.47	2.13
Potato, Jap. lb.	.07	.07	.06½
Sago. lb.	.03½	.03½	.04



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Nov. 1	Nov. 15	Jan. 1922
Beeswax, pure, white.....lb.	.32	.32	.33
Castor Oil, No. 3.....lb.	.12	.12	.10½
Ceresin, yellow.....lb.	.08	.08	.07½
Corn Oil, crude, tanks, mills...lb.	.07¼	.07¼	.06¾
Cottonseed Oil, crude, f. o. b. mill.....lb.	.08	.08¼	.07
Linseed Oil, raw, c/l.....gal.	.89	.88	.69
Menhaden Oil, crude, mills...gal.	.43	.48	.35
Neat's-foot Oil, 20°.....lb.	.18	.18	.16¾
Paraffin, 128-130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs....bbl.	6.95	6.70	5.30
Rosin Oil, first run.....gal.	.43	.43	.36
Shellac, T. N.....lb.	.65	.72	.66
Sperm Oil, bleached winter, 38°.....gal.	1.05	1.05	1.70
Stearic Acid, double pressed..lb.	.10	.10	.09¾
Tallow Oil, acidless.....lb.	.10¾	.11¾	.10
Turpentine, spirits of.....gal.	1.62	1.57	.82½

METALS

	Nov. 1	Nov. 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.20	.22	.17
Antimony, ordinary.....100 lbs.	7.00	6.65	4.55
Bismuth.....lb.	2.60	2.60	1.80
Copper, electrolytic.....lb.	.13⅞	.13⅞	.13¼
Lake.....lb.	.14	.14	.13¼
Lead, N. Y.....100 lbs.	6.50	7.25	4.70
Nickel, electrolytic.....lb.	.36	.36	.45
Platinum, refined, soft.....oz.	108.00	108.00	78.00
Quicksilver, flask......75 lbs. ca.	71.00	71.00	52.00
Silver, foreign.....oz.	.69¼	.66½	.65¼
Tin.....lb.	.35¼	.37½	.32¾
Tungsten Wolframite....per unit	3.25	3.60	2.00
Zinc, N. Y.....100 lbs.	8.00	8.25	5.20

FERTILIZER MATERIALS

	Nov. 1	Nov. 15	Jan. 1922
Ammonium Sulfate, expt., 100 lbs.	3.55	3.55	2.60
Blood, dried, f. o. b. N. Y....unit	4.25	4.35	3.50
Bone, 3 and 50, ground, raw...ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia.....	2.25	2.25	2.25
Fish Scrap, dried, wks.....unit	4.25	4.00	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78-80%.....ton	4.00	4.00	8.00
Potassium Muriate, 80%.....unit	.70	.70	*.75
Tankage, high-grade, f. o. b. Chicago.....unit	4.50 & .10	4.35 & .10	3.00 & .10

COAL-TAR CHEMICALS

Crudes			
	Nov. 1	Nov. 15	Jan. 1922
Anthracene, 80-85%.....lb.	.75	.75	.75
Benzene, pure, tanks.....gal.	.30	.30	.29
Naphthalene, flake.....lb.	.06¼	.06¼	.07¼
Phenol, drums.....lb.	.30	.33	.11

Crudes (concluded)

	Nov. 1	Nov. 15	Jan. 1922
Toluene, pure, tanks.....gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks.....gal.	.45	.45	.45

Intermediates

Acids:

	Nov. 1	Nov. 15	Jan. 1922
Anthranilic.....lb.	1.10	1.10	1.10
Benzoic, tech.....lb.	.50	.50	.50
Cleve's.....lb.	1.50	1.50	1.50
Gamma.....lb.	1.80	1.80	2.25
H.....lb.	.75	.75	1.00
Metanilic.....lb.	1.00	1.00	1.60
Monosulfonic F.....lb.	2.30	2.30	2.30
Naphthionic, crude.....lb.	.60	.60	.65
Nevile & Winther's.....lb.	1.20	1.15	1.30
Picric.....lb.	.20	.20	.25
Sulfanilic.....lb.	.17	.17	.26
Tobias'.....lb.	1.50	1.50	2.00
Aminoazobenzene.....lb.	1.15	1.15	1.15
Aniline Oil.....lb.	.16	.16	.17
Aniline Salt.....lb.	.24	.24	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech.....lb.	.65	.55	.45
U. S. P.....lb.	1.40	1.40	1.25
Benzidine Base.....lb.	.85	.85	.90
Benzidine Sulfate.....lb.	.70	.70	.70
Diaminophenol.....lb.	3.75	3.75	5.50
Dianisidine.....lb.	4.50	4.50	4.75
p-Dichlorobenzene.....lb.	.06	.06	.15
Diethylaniline.....lb.	.60	.60	.90
Dimethylaniline.....lb.	.38	.41	.40
Dinitrobenzene.....lb.	.20	.20	.21
Dinitrotoluene.....lb.	.20	.20	.25
Diphenylamine.....lb.	.52	.52	.58
G Salt.....lb.	.65	.65	.70
Hydroquinol.....lb.	1.15	1.15	1.35
Monochlorobenzene.....lb.	.08	.08	.10
Monochloroaniline.....lb.	1.00	1.00	1.00
b-Naphthol, dist.....lb.	.24	.24	.30
a-Naphthylamine.....lb.	.30	.30	.30
b-Naphthylamine.....lb.	.95	.95	1.05
m-Nitroaniline.....lb.	.62	.62	.85
p-Nitroaniline.....lb.	.73	.73	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol.....lb.	.72	.72	.75
o-Nitrotoluene.....lb.	.09	.09	.15
p-Nitrotoluene.....lb.	.60	.60	.70
m-Phenylenediamine.....lb.	.90	.90	1.10
p-Phenylenediamine.....lb.	1.50	1.50	1.60
Phthalic Anhydride.....lb.	.35	.35	.38
R Salt.....lb.	.55	.55	.60
Resorcinol, tech.....lb.	1.30	1.30	1.50
U. S. P.....lb.	2.00	2.00	2.00
Schaeffer's Salt.....lb.	.60	.60	.70
Sodium Naphthionate.....lb.	.60	.60	.70
Thiocarbamide.....lb.	.35	.35	.40
Tolidine (base).....lb.	1.15	1.15	1.20
Toluidine, mixed.....lb.	.30	.30	.30
o-Toluidine.....lb.	.14	.14	.20
p-Toluidine.....lb.	.95	.95	1.10
m-Toluylenediamine.....lb.	.95	.95	1.10
Xylidine.....lb.	.42	.42	.40

