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EDITORIALS

Our Unemployment Problem

No profession or class is free from the ill effects of such extensive unemployment as has occurred in the last year, but fate seems to have dealt in a particularly unkind fashion with the chemist. It has been something of a shock, after all of our efforts to have industry understand and appreciate what the chemist has done, to find him given so little consideration and in many cases among the very first to be dismissed with the approach of business curtailment.

The situation presents one of our principal tasks for the future. We cannot create new places for our unemployed chemists directly by such plans as have been proposed for the reduction of unemployment. The business before us is to convince the average business man that he can far better afford to dispense with nearly any other department than to close his research and control laboratories.

It is obvious that the chemists themselves must aid in such a campaign. Indeed, they must do the work. *THIS JOURNAL* will endeavor to assist them in every possible way. We shall henceforth devote space each month, under the heading "The Earning Power of Research," to the recital of instances where genuine scientific research conducted in educational institution or plant has proved of real commercial value, and more than justified the expense involved. We realize that much that will be offered will contain nothing new for many of our readers. We know, however, that a specialist in one field frequently knows little of what his neighbor is doing; so we urge readers to send us in detail examples from their own experience and reading which will enable our fellow chemists to recommend scientific research and laboratory control to their executives, on the basis of past performance and future promise. *THIS JOURNAL*, on its part, will endeavor to supply information on topics of current chemical interest, for the same purpose.

We chemists need someone to pray for us as did a pastor for a revivalist. He said, "Brother Jones, before you begins this discourse, there are some powerful bad negroes in this here congregation, and I want to pray for you," which he did in this fashion: "O Lord, give Brother Jones the eye of the eagle, that he may see sin from afar. Glue his ear to the gospel telephone, and connect him with the central skies. Illuminate his brow with a brightness that will make the fires of hell look like a tallow candle. Nail his hands to the gospel plough, and bow his head in some lonesome valley where prayer is much wanted to be said, and anoint him all over with the kerosene oil of Thy salvation and set him afire."

The War on Chemical Warfare

Neither the chemist nor the chemical manufacturer introduced chemical warfare to our Government. Our country called upon the scientists to provide new means of defense and adequate means of offense to cope with the enemy. The chemists one and all responded. The result is a matter of history. Notwithstanding the facts presented and supported by ample data to prove the humaneness, efficiency, and comparatively low cost of being prepared to defend ourselves by chemical methods approved and adopted by other nations, a popular sentimental feeling against chemical warfare has been aroused in our country by factors which we do not yet fully understand. The carefully considered recommendations of the committee of experts, of which

the President of our Society was chairman, were disregarded. Submarines and aircraft were treated gently as compared with chemical warfare, it being admitted that neither of these devices could be controlled at this time by agreement, and that their development is more easily followed than chemical warfare, which can be perfected without publicity.

On the 7th of January the Committee on Limitation of Armament passed the following resolutions:

The use in war of asphyxiating, poisonous or other gases and all analogous liquids, materials or devices, having been justly condemned by the general opinion of the civilized world and a prohibition of such use having been declared in treaties to which a majority of the civilized powers are parties:

Now to the end that this prohibition shall be universally accepted as a part of international law binding alike the conscience and practice of nations, the signatory powers declare their assent to such prohibition, agree to be bound thereby between themselves and invite all other civilized nations to adhere thereto.

These resolutions brought out some illuminating discussions in which Mr. Sarraut and Mr. Balfour spoke at length. While these gentlemen supported the resolutions, their remarks seemed to make it clear that they could see nothing harmful in the effort to discourage chemical warfare by agreement, but that, after all, the time has not come when research with defense as the main objective can be discontinued. The proposals made by the resolutions simply reaffirm admitted principles of international law and a mere confirmation of the law without adding any sanctions to it cannot relieve the nations from taking precautions against those who are prepared to break the law and who might easily dominate the world by their indifference to law.

Mr. Balfour pointed out the fact which has been emphasized as well by the Committee of the League of Nations at Geneva, that it is perfectly impossible to prevent a nation bent upon this method of warfare from making its preparations in time of peace, no matter what the rules of war may be. No nation, therefore, can forego the duty of examining how such attacks can be effectively met.

It seems to us that in undertaking to set a laudable example to the rest of the world in matters of so-called humane warfare, we are in no way relieved of the necessity of continuing scientific research to the end that we may at least obtain for ourselves that advanced knowledge which is undoubtedly our greatest defense. The research chemist, unlike the militarist, is not impelled by a desire to test his discoveries in the field. He has other ways of determining their efficiency, and many of them will find commercial application.

It seems unfortunate that we are to be denied the assistance of nontoxic materials such as harmless lachrymators and smokes which may save life when employed for defense. If applied literally, the resolutions may debar high explosives which give rise to large amounts of carbon monoxide. The effects of this gas may easily lead to charges of gas warfare by an enemy anxious for such an excuse for retaliation in order to employ super-gas developed in secret.

However the resolutions may be interpreted by those holding different views on chemical warfare, we urge chemists to seize every opportunity to make the general public realize the position of research in the whole problem and the necessity for its continuance upon an adequate scale.

To us, the endeavor to abolish chemical warfare throughout the world by the resolutions of the present conference reminds us of the experience of King Canute in commanding the tides not to rise.

Criticism from Germany

A review of Whitmore's monograph on "Organic Mercury Compounds" was published in No. 43, p. 443 (1921) of *Apotheker Zeitung*. At the close of the review the author, F. Dietze, says:

That American chemists should desire to create a literature of their own, independent of other countries, is easily understood. From different signs one can conclude, however, that this is to be done almost exclusively at the cost of German science and German industry. That the whole undertaking is in its foundation directed against Germany follows from the fact that the "Interallied Conference" has been godfather of the plan. The war which was ended three years ago is to be carried further in scientific and industrial lines! In view of this, one cannot welcome the publication of these monographs.

During the last half of the nineteenth century such men as J. P. Cooke, S. W. Johnson, Wolcott Gibbs, Nef, and many others still living, received their training and inspiration to research in chemistry in German laboratories. These men organized instruction and research in America after models they had seen in Germany. We owe to Germany a debt for this inspiration to research, which must never be forgotten. There is some need to recall this at a time when, because of Germany's glaring faults in other directions, some are inclined to belittle and condemn everything that Germany has done. I have no apology to make for Germany's bad faith and wrong aims in the conduct of the war, but we must be on our guard against some Americans who wish to copy her faults rather than her virtues.

American students contributed a not insignificant amount to the experimental researches which gave Germany such preëminence in chemistry at the beginning of the twentieth century. Some American chemists thought they could secure a better audience for their papers if these were published in German and this, to superficial observers, contributed still further to the apparent volume of chemical achievements in Germany. From 1880 onward, however, a steadily increasing number of American students were trained at home and the demand for chemists, both for teaching and for the industries, has been such that at the beginning of the war there were nearly half as many chemists in America as in Germany. From the statistics available, there were less than one-fifth as many in England and less than one-tenth as many in France as there were in Germany.

Under the conditions which obtained at the beginning of the twentieth century it is not surprising that some German chemists assumed the attitude that chemistry was a German science and that researches not published in German could be ignored. To Americans such an attitude is very closely related to the attempt of Germany's political leaders to impose German imperialism on other countries by force. Any similar spirit on the part of Englishmen, Frenchmen or Americans, either in the political field or in science, is just as intolerable as it was in Germans.

If the determination of Americans that we shall do our full share, in friendly coöperation with other countries, in the development of chemistry, and that we shall win recognition on the basis of the genuine value of our research work and of our publications, is considered in Germany as "a continuation of the war in the scientific domain" we must acknowledge that it is our intention to do this. But German chemists will find no chemists in the world more ready than Americans to coöperate with them in a spirit of friendly rivalry for the promotion of chemical science, provided only that they will meet us in the same spirit.

WILLIAM A. NOYES
Editor, Scientific Series,
A. C. S. Monograph

Teach Appreciation

For some time we chemists have been telling each other how little our science is appreciated and we have found it both profitable and necessary to use various means for popularizing chemistry. The A. C. S. News Service has been invaluable. Books like "Creative Chemistry" have done great service, and there have been feature stories, popular lectures, etc. The results have fully justified the efforts, but have we begun at the right place?

It seems to us that little real progress has been made in teaching chemistry to those who may never become chemists. Potential doctors, lawyers, merchants, and chiefs are given the same courses in beginning and general chemistry as are the men who have years of chemistry definitely before them. Might we not do well to begin, even in high school, by teaching chemistry as a series of practical problems, so that an interest in the application of the science might be kindled and developed before the disjointed courses in general chemistry are started? Would it not be well also to offer chemical courses in our colleges and universities designed primarily to teach appreciation for what chemistry means, what it has done, and what it may do? We cannot prepare all men to become chemists, but it is highly important that all men have a sympathetic understanding of the subject, so that the trained chemist may be received as a professional man and given a professional man's opportunity.

There is ample material to-day from which to build lecture courses popular in nature and well illustrated, which will interest any group of people in industrial chemistry and the fundamental science upon which it rests. These courses would encourage the embryonic chemist in his own work and could be made to serve to emphasize the necessity for real fundamental research. They would certainly bring to many who can devote but an hour or two a week to the subject a real appreciation of chemistry and help to acquaint those who are to become engineers, financiers, and business men with the field occupied by the chemist and the relation of his work to theirs. Then, indeed, the chemist will step into his proper place, and when soft times pass he will not be summarily dismissed along with the plumber's helper. Who will make this interesting experiment in pedagogy?

An Example

A short time ago there appeared at one of our universities a dealer in scientific apparatus who urged importation, and in stressing his capabilities as an importer claimed that he was buying for all the Jesuit colleges of the United States, importing their needs from foreign sources.

The position of *THIS JOURNAL* has frequently been stated, namely, that so long as the manufacturers of American scientific apparatus and supplies deal fairly with educational institutions, we shall vigorously support the policy of buying only American-made equipment from American firms. Consequently we wanted to know how correct the importer's statement might be, and we corresponded with one of the councilors of the Society who is in a position to determine what is taking place. As a result of his activity, questionnaires were returned to him from 41 colleges and institutions with the unanimous statement that they are committed to the exclusive purchase of American-made apparatus and supplies in so far as their needs can be met. The personal letters received with the questionnaires breathe an admirable spirit of loyalty and patriotism. It would be interesting to know to what extent the excellent example set by the Jesuit institutions is being followed at our other seats of learning.

The Earning Power of Research

There is at least one textile mill in America which has continued to run at capacity. It has experienced no season of slack orders and it has made no reduction in its scientific staff. The president of this mill—Joseph Bancroft & Sons Co.—tells us that this success has been due to the fact that his scientists by continued research have kept his mill four or five years ahead of the procession. He is producing materials that have no competition. He is offering uniquely dyed fabrics which are in a class by themselves and when there is a buyers' market, a mill in this position has an unusual advantage. The president of this mill proposes to increase research, for he knows he cannot possibly afford to curtail it.

The world's largest producer of sulfite pulp, the Brown Corporation, installed a research and control laboratory some years ago, after the chemical engineer, who now is director of research as well, had demonstrated the utility of science in the establishment. This manufacturer has been quick to realize that in research he holds two trump cards. First, he is able to produce such good pulp that in a buyers' market his product is preferred. Second, he has been able to reduce his costs so that he has an advantage in competition, and at the same time he has so increased his quality as to be granted a premium on nearly all markets. The research staff of this mill has been steadily enlarged and strengthened and year by year has been responsible for the creation of new industries based upon the utilization of by-products to an extent where they rival in commercial importance the industry which was formerly the sole activity of the establishment.

Only a few years ago the rare elements occurring in the atmosphere were merely laboratory curiosities for which no one dreamed of industrial application. One by one these elements have found their place in commerce and now after some months of intensive research neon appears as a bread winner. Ignition gages have been devised in which purified neon is used in a tube which glows when brought into contact with spark plugs and other points where current is passing. The Air Reduction Company has developed a gage in which there are no wires, while the Westinghouse Company has used neon in a Geissler-like tube for a similar purpose. Beginning with the use of this gage in detecting ignition troubles in gas engines, it now appears that the field of usefulness is much wider. The discovery of static charges around factories where inflammable vapors are present, or on fire doors, belting, and machinery which is not properly grounded suggests possible applications. The neon tube glows when applied to the outside insulation of wires carrying over 2000 volts. It will be seen that the number of applications means a large number of such gages, and there is no doubt that research in this instance will return a large percentage on the investment.

Business Men Speak

The 1420 constituent organizations of the Chamber of Commerce of the United States have just voted upon a referendum submitted by the Committee on Tariff Principles. By a vote of 1840½ to 27½ the Chamber of Commerce is committed in favor of reasonable protection for American industries subject to destructive competition from abroad and of benefit to any considerable section of the country, 1846½ to 37½ in favor of maintaining in principle the anti-dumping legislation of May 1921, and by 1868 to 26 for

tariff legislation framed and administered with a view to meeting discriminations direct or indirect by other countries against American trade. By a vote of 1793½ to 59½ the Chamber of Commerce recommends that the principle of maintenance and encouragement of our export trade should be observed in tariff legislation so far as consistent with reasonable protection for American industries of benefit to any considerable section of the country and subject to destructive competition from abroad.

In the Chamber an organization has one vote for the first 25 members, an additional vote for each 200, but no organization, however large, can have more than ten votes. It is obvious, therefore, that this vote represents the business men of the country and even Congress can hardly fail to take notice of the demand for the prompt enactment of suitable tariff legislation.

The Technical Press

It is a privilege to publish in this issue the excellent paper on "The Technical Magazine and Its New Relation to Industry," by H. C. Parmelee. We like the presentation, applaud the high standard of ethics set up for the modern technical paper, and agree with most of the conclusions reached by the author.

At the same time, we wish to make our own position clear, since we do not experience the editorial restrictions in THIS JOURNAL which the author stresses in the fourth paragraph under "The Functions of the Technical Paper." It may easily be that editors of other scientific society magazines are less fortunate than we are, but with our Committee on National Policy empowered to act for the Society, official opinions can be had whenever they are necessary. There is neither delay nor difficulty in obtaining action, and when we do speak for the Society a message goes forth with the full strength of the world's largest scientific body.

Fortunately also the interests of our individual members, our Society, and the industry which we serve are identical. Our members and readers represent the industry, and it might almost be said that they are stockholders directly concerned in the success of THIS JOURNAL and the extension of its influence.

The support of our strong Society gives us confidence and courage to undertake many a campaign and to strike out into new fields to advance science and industry. We welcome an opportunity to unite with *Chemical and Metallurgical Engineering* and with other modern technical papers in the distribution of authoritative and constructive news, in a manner satisfactory to the scientist and public alike.

Reinforcements

Burt P. Garnett has been appointed to succeed John Walker Harrington as Technical Manager of the A. C. S. News Service, Mr. Harrington having left the Service January 1 after a service which places us under many obligations. Mr. Garnett comes to us with extensive experience in newspaper work, in publicity, and other lines which well qualify him to carry on this important activity of the Society.

Wilkinson Stark has been appointed Associate Editor with offices at One Madison Avenue, New York City. He has had extensive laboratory and plant experience and will represent the JOURNAL in the field. When he calls upon you, give him your best coöperation and keep him informed as to events in the field of industrial chemistry, new processes, and research.

Dr. R. P. Fischelis, who has been a member of this staff for the past year in the capacity of special writer, will continue in the same capacity.

ORIGINAL PAPERS

Electric Heat for Thermal Processes¹By E. F. Collins²

GENERAL ELECTRIC CO., SCHENECTADY, NEW YORK

Heat energy application in this country has been largely the composite result of promotion and advertisement rather than of engineering. We have had fuel oil advocates, gas burning experts, powdered coal enthusiasts, fuel oil specialists, etc., but have, until recently, lacked the competent furnace engineer familiar with all types of furnaces, who could sit as court of appeal and give unbiased decisions regarding the true economic value of various heat sources for a specific work. To operate with gas a process that might much more advantageously be carried out with other forms of energy is not economy, yet many such cases exist to-day.

Fig. 1 shows the relative costs of four common sources of heat, *viz.*, coal, gas, fuel oil, and electricity, in terms of dollars per 100,000 B. t. u. utilized in baking ovens and fur-

trics heat is to-day recognized by competent engineers as the "last word" in carrying through many thermal processes with maximum safety, uniformity, and economy.

It is a matter of no distant time when the use of electric heat for important thermal processes will be adopted with no more hesitation than now occurs when the householder decides in favor of the electric light instead of the gas lamp for his home, even though the cost of current consumed be greater than the cost of the gas.

Fig. 1 also illustrates well a valuable characteristic of electric heat. It will be noted that the cost of burning fuels varies widely, depending upon the amount of air admitted to furnace and the resultant combustion, *e. g.*; the cost of city gas for 100,000 B. t. u. effective rises to double its value with an increase of 50 per cent in air, and such excess percentage of air is by no means rare. Fuel oil likewise increases its cost roughly four times at the same temperature (2800° F.) and the same excess of air (50 per cent). Thus it is seen to how great an extent the economic operation of the fuel furnace is in the hands of the operator. This handicap does not exist with the electric furnace, where the ratio of conversion from power to heat is 100 per cent perfect and the operator cannot affect this efficiency of conversion.

FEATURES OF ELECTRIC HEATING

Some of the more important features of electric heating which distinguish it from fuel-fired equipment are the following:

HEAT GENERATION

- 1—Released at points to give uniform or nonuniform temperature.
- 2—Heat generation balanced against heat absorption.
- 3—Heat generated at or near potential of heating chamber.
- 4—Generated in inactive or dead atmosphere—no contamination of charge. Heating chamber may be a vacuum or under heavy pressure. Artificial atmosphere possible, as hydrogen gas, nitrogen gas, and no combustion gases.

HEAT CONSERVATION RESULTING IN HIGH THERMAL EFFICIENCY

- 1—High heat lagging, no local high temperatures.
- 2—Small heating chamber and no combustion chamber.
- 3—No hot gases leaving furnace, save for ventilation (when necessary).
- 4—Automatic control of temperature so that supply balances demand.

METHOD OF ELECTRIC HEAT TRANSMISSION AND DELIVERY TO CHARGE

- 1—Convection of liquids and gases (natural).
- 2—Circulation of liquids and gases (forced).
- 3—Radiation and convection in air.
- 4—Direct radiation to work.
- 5—Direct and reflected radiation to work.
- 6—Heat generated directly in charge by current flowing through it.
- 7—Complete heat saturation of charge without surface overheating, due to perfect automatic heat control.

HEAT GENERATION

In the electric furnace, heat generation can be kept nicely balanced against heat adsorption by the charge. The importance of this fact cannot be overemphasized, since the problem of heat absorption is of first importance in all heating and, especially, combustion furnaces. It goes without saying that efficient generation or development of heat units by chemical oxidation means little, unless the B. t. u. released are in a minimum constant proportion to the B. t. u. absorbed in doing useful work. Hence the rate of heat generation and heat absorption must be skilfully controlled to

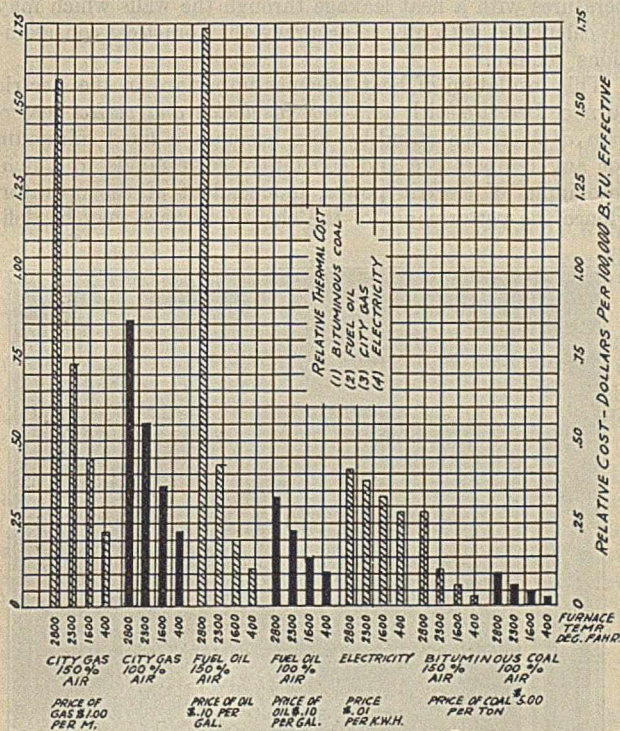


Fig. 1

naces. This chart in itself is evidence of the fact that considerations other than B. t. u. cost determine the true efficiency of thermal processes. For, were this not true, how could the electric furnace exist, and how could it show the greater over-all economy that it does in many processes to-day? Neither could the other two fuels compete with bituminous coal, did not the application of fuel oil or gas carry with it inherent advantages that completely outweighed the difference in cost of the B. t. u. supply. This is the true reason for the use of oil and gas rather than bituminous coal for many thermal processes. For the same reason elec-

¹ Presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

² Consulting Engineer in Industrial Heating, General Electric Co.

guarantee maximum over-all efficiency. To burn fuel correctly is therefore only the first step that has an immediate bearing upon practical results. This very fundamental truth should be recognized by all furnace users.

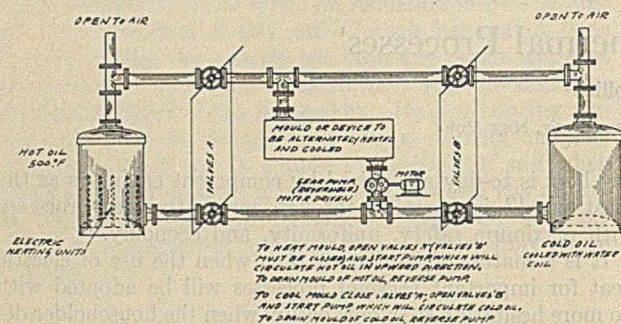


FIG. 2

HEAT TRANSMISSION TO CHARGE

Heat is transmitted by three means, *viz.*, (1) convection in liquids or gases, (2) conduction in liquids or solids, and (3) radiation through space or the ether.

When nonuniform heating occurs at different points in a fluid, uniformity of heating may or may not be established as a result of convection currents set up by difference in specific gravity resulting from the difference in temperature. Thus heat itself may establish and furnish the motive power for propelling currents of fluid, which in turn carry and distribute heat throughout the body of the fluid, or other forces may act to set the fluid in motion and thus distribute the heat. In the first case, gravity determines the direction of currents, whereas, in the second, currents may be made to travel more or less as desired. In general, uniformity of heating by convection is made more sure by the second method or by continuous agitation of the fluid, usually mechanical.

If the fluid be the product of combustion, as in a fuel fired furnace, consisting largely of carbon dioxide, water vapor, and nitrogen, currents and eddies exist in the combustion chamber owing to changes in densities depending in part on variation in temperature. These gases have a continuous flow, and practical results are obtained by removing as much heat as possible from such streams while they are passing through the furnace to the stack. Complete and properly regulated envelopment of the charge by the hot gases is necessary to a uniform and high rate of heat absorption, which is dependent upon the heat conductivity of the charge and the area of surface contact. If only parts of the body lie in the stream or if the streams vary in velocity or temperature, nonuniform heating may be expected. It should be remembered that in fuel fired furnaces, especially where forced draught is used, these currents of hot gases have a cyclonic violence and continuously shift as erratically.

CONVECTED VERSUS RADIANT HEAT—Convected heat is deposited at the surface of the body being heated. If the body is a solid, this heat must penetrate it by thermal conduction. Radiant heat, such as may be employed in the electric furnace, has a penetrating characteristic that enables it to pass directly into the charge more or less without being deposited on the surface. This results in a more rapid heating and a better or more complete penetration or distribution through the charge without excessive surface heating.

IMPORTANCE OF HEAT INSULATION

Heat must flow into or through a solid against a certain resistance which is called "the thermal resistance" of the body. As in electricity we call low resistance materials conductors and high resistance materials insulators, so in

the thermal circuit we call materials of low thermal ohms per unit length and cross section "conductors of heat," while those of high thermal ohms per unit length and cross section are known as "insulators of heat" or "thermal insulators." Some heat insulators may be injured by low temperatures; others may be subjected to high temperatures without injury, mechanical or otherwise. The latter class are usually called "heat insulating refractories." Certain refractory materials are also exceptionally good heat conductors. Many good refractories at moderate temperatures become relatively good heat conductors when heated to a considerably higher temperature. In other words, they possess a high thermal resistance when cold and a very low thermal resistance when hot. Hence the furnace designer must select proper heat insulating materials.

Knowing definitely the thermal resistance of refractories and heat insulators, we may calculate the heat which will flow into or through such material under any assumed difference in temperature or thermal potential, as follows:

$$\text{Heat quantity in B. t. u.} = \frac{\text{Thermal potential difference}}{\text{Thermal ohms}}$$

Such a method allows the selection of proper materials and the proper combination to form a simple or composite furnace wall construction suited to withstand desired temperatures with a heat leakage through the walls which may be calculated with all the accuracy that practical considerations require.

This insulation of heat becomes important in the electric furnace because with *high heat insulation and perfect conversion of heat*, the stand-by loss becomes a fixed minimum for any temperature and constantly corresponds to a definite input of electric power, independent of the operator. Hence the performance of the electric furnace may be defi-

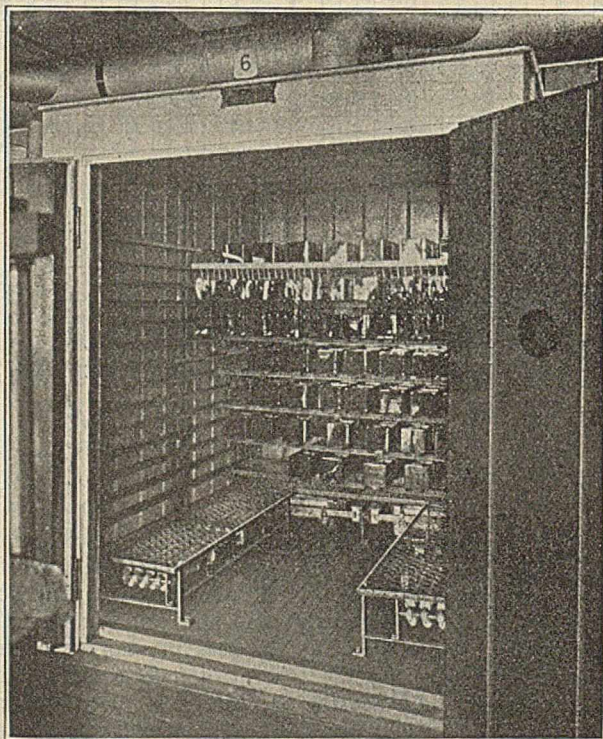


FIG. 3

nately predicted very accurately for any load. Owing to the variable combustion efficiency of the fuel fired furnace (Fig. 1), uniform performance and thermal efficiency is at the mercy of the furnace operator, the fuel, and the air supply.

APPLICATIONS OF ELECTRIC HEAT

Many successful working installations of electric heat exist to-day, and it is predicted that many more industrial processes will be improved and made more economically productive by the application of electrically generated heat. A few of the many such installations are illustrated herewith.

Fig. 2 shows a design for the application of electric heat to hot plates, hot presses, molds, vulcanizers, etc., which require alternate heating and cooling. The system is very simple and has a partial regenerative character, returning all heated oil to the tank before cooling the mold; thus it tends to require less cooling water in addition to affording a saving of heat. This arrangement has a higher inherent thermal efficiency, especially at high temperatures, than if heated and cooled alternately by steam and water.

Fig. 3 is a japan baking oven for telephone instrument parts. This oven is equipped with 18 kw. of heaters, and its dimensions are 7 ft. 10 in. high, 6 ft. wide, and 6 ft. 3 in. deep.

Fig. 4 shows one of a battery of ovens in use for making automobile engine cores. Core weights vary from 3 to 128 lbs. each. A very heavy linseed oil binder is used which makes it necessary to provide ventilation, and hence heat in excess of the requirements of the ordinary core compounds. The inside dimensions of the oven are 5 ft. wide, 10 ft. deep, and 7 ft. high. The connected load in heaters is 86 kw. Automatic temperature control is used. A baking temperature of 425° F. is used, which reduces the baking time from 1 to 3 hrs. over that required by the gas oven operating at 350°, the highest practical baking temperature with gas heating. Four of these ovens work at efficiencies varying from 10.9 to 14.6 lbs. of green cores baked per kw. hr. of power consumed. The total cores baked in four ovens for 1 wk. were 108,730 lbs., and the power consumption corresponded to 9389 kw. hrs., giving an efficiency of 11.6 lbs. of cores per kw. hr. During a year period, these ovens did not turn out a car of burned, cracked, or imperfectly baked cores.

Electric heat makes a highly efficient protective zinc coating possible by the sherardizing process. Uniformity of coating and consequent long life is secured by virtue of the close control to repeat the heat cycle again and again under the same conditions.

Fig. 5 illustrates a large japanning oven such as is used by automobile manufacturers to bake the finish on the cars. This oven has 252 kw. connected capacity, and work is carried through it continuously by conveyor. Ovens turning out a car per minute and requiring over 3000 kw. to heat have been in use for several years in one automobile shop. The electric baking of japan, paints, lacquers, varnish, etc., has come to be considered a standard process in many lines of manufacture.

Tests made on a vertical type of electrically heated glass annealing lehr show a reduction in over-all cost of product of 20 per cent over that in the gas-heated lehr. This saving was equivalent to seventy-five times the cost of the electric power for heating the lehr. This type of lehr for annealing glass presents many positive advantages for rapid, uniform, and economic annealing of most commercial glass. The box type oven or lehr, electrically heated, serves with equal advantage for other types of glass, including optical and telescopic lenses. Some of these advantages are as follows: (1) High thermal economy, (2) satisfactory heat distribution, (3) small floor space, (4) possibility of location near fabricator, receiving the ware at higher temperature, (5) reduction in labor, (6) lack of opportunity for ware to absorb products of combustion, (7) low temperature gradients, (8) automatic heat control ($\pm 2.5^\circ$ C. may be secured), (9) annealing time less than one-half of the present-day

fuel fired lehr, (10) practical elimination of rejects, distortion, and breakage due to heat treatment, (11) freedom

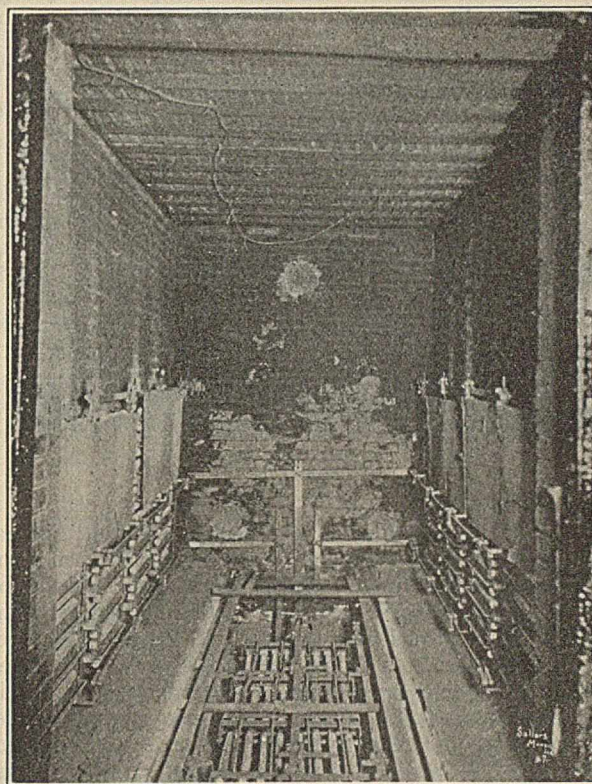


FIG. 4

from sulfuring of the ware and the production of a bright polished surface requiring no subsequent cleaning and washing, and (12) a sterile and absolutely clean product, such that prescriptions where this is important, as in medicinals, may be filled in and sealed immediately after leaving lehr.

A portable metallic resistor furnace, with a hearth dimension of 10.5 in. wide by 21 in. long, is ideally suited for annealing, hardening, and tempering or drawing files or small tools in the ordinary tool room. It is likewise suited to any heating requirements where the charges do not require more than 1800° F. Some of its advantages over fuel fired unmuffled furnaces are as follows: (1) Radiant heat, (2) satisfactory heat distribution, (3) automatic control of temperatures if desired, (4) practically nonoxidizing atmosphere if desired, (5) small amount of heat given off to the room, (6) no products of combustion or obnoxious gases given off to heating chamber or room, (7) ratio of heat generation to heat absorption by charge correctly maintained, (8) uniform and complete penetration of heat through charge without overheating of corners, fins, or surfaces, (9) ability to repeat desired heat cycle giving uniformity of product, (10) a reduction, generally, in labor, and (11) a better over-all economy and the production of higher quality product at the same or slightly higher cost or the same quality at a lesser over-all cost.

Fig. 6 is a view of the interior heating units, hearth and walls, of a furnace with a rotating hearth which is being used for heat treating parts in an automobile factory. Its resistors are metallic and its temperature limit is 180° F. It operates normally at 1550° F., 3 phase, 440 volts with 270 kw. connected capacity. The furnace has automatic temperature control and operates to heat such parts as engine, crank-shafts, etc.

Electrically heated furnaces are well adapted to baking vitreous enamels. One of the chief disadvantages of the coal, gas, or oil fired furnace is that the muffle periodically sags and breaks, with resultant loss of product and of time for

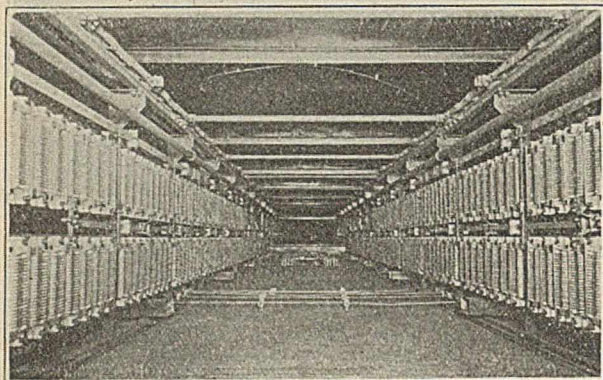


FIG. 5

repairs. This is avoided in the electric furnace. Another disadvantage which is not met in the electric furnace is the presence of sulfur fumes. Furthermore, even distribution of heat can be obtained only with electric installation. The furnace can be loaded from the rear wall almost to the door and burned down to a finish, leaving a clean white enamel.

The cost of the electric furnace is considerably higher in original investment, but the saving in space and cleanliness soon make the difference in price a matter of secondary importance. The power cost is also higher. However, with the additional output, tests show that the actual cost per pound of metal handled will compare very favorably with any other form of fuel. When the electric furnace is able to handle at least 170 heats in 10 hrs. against 130 heats by the coal furnace, with a 25 per cent greater weight of charge, and without a single reject, the comparison in cost of fuel assumes a different proposition, and a value actually in favor of electric heat. The electric furnace can be brought from cold to 1700° F. in 12 hrs. A coal furnace would require about 3 days, an oil furnace 24 hrs., and a gas furnace 16 to 20 hrs. The outstanding features of the furnace have been the extreme speed at which it can be heated up, and at which it

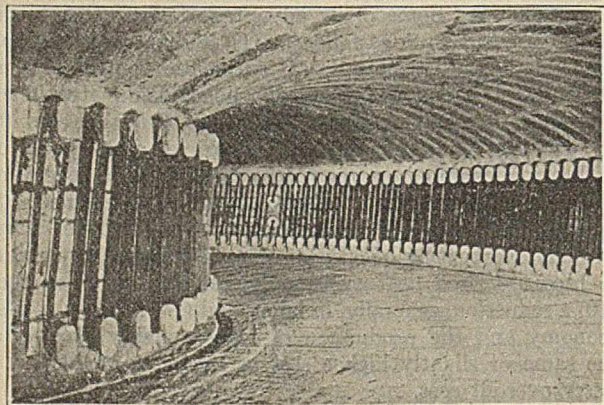


FIG. 6

can be operated. Heats have been completed in 1 min. 50 sec. that would have taken 3 min. 40 sec. in an oil furnace.

The muffled arc type of electric furnace is used as a melting furnace, both of the laboratory type and in larger units. A furnace with a hearth capacity of 2000 lbs. of brass and

with 250 kw. connected will melt yellow brass in pig or heavy scrap form at the rate of 1500 lbs. per hr., with a metal loss of less than 1.5 per cent and a power consumption not in excess of 270 kw. hrs. per ton. Copper is melted at the rate of 1300 lbs. per hr. with a power consumption of 350 kw. hrs. per ton.

This power consumption is based on melting not less than 1500-lb. charges and allowing 20 min. per heat for charging, pouring, and foundry delays. Such a furnace is normally provided with a tilting motor and three electrode motors, all of which are of AC type, so that the necessity for a DC motor generator set, usually required for furnishing direct current to the control motors, is eliminated. This type of furnace operates at a temperature up to and including that required for melting nickel and monel metal. A power factor of 95 per cent and better is realized, together with freedom from lead fluctuations.

Other applications of electric heating include cartridge unit heaters (similar in shape to the ordinary gun cartridge), which are used in shoe making machines, cigaret making machines, stills, sterilizers, paper cup machines, etc. Electrically heated compound melting pots find extensive use for glue in wood working shops, in battery works, book binding and printing houses, and piano, paper box, and automobile factories.

CONCLUSION

These few illustrations out of the many working installations in various processes have been used to indicate the applicability of electric heat to advantage throughout the whole industrial heating field. It is not to be inferred that electric heat is without a competitor in all places and under all conditions. There are, however, a very great number of applications where electric heat may be used to advantage. These applications in various processes occur with so great frequency that it behooves the user of heat processes to question his furnace engineer thoroughly concerning the possibilities of electric heating before revamping existing installations or adding new thermal process equipment.

Biscuit and Cracker Manufacturers' Association

As a next step in the development of The Technical Bureau of the Biscuit & Cracker Manufacturers' Association, the Technical Committee has been authorized to secure the services of A. V. H. Mory, well known for his success in the organization and direction of industrial laboratories. A good start has already been made in the work of the Bureau, which was launched in 1919, as another step in the direction of insuring the highest quality and uniformity for the Association's products.

Mr. Mory has had broad experience as head of the chemical department of Armour & Company's Kansas City plant, chief of the Government Food and Drug Inspection Laboratory at Kansas City, Mo., director of the Technical Laboratories of Sears, Roebuck & Co., and more recently with the Procter & Gamble Company.

The new Technical Bureau Director, who is well known for his belief in directness, simplicity, and common sense in all the relations of science to industry, will find in his new field plenty of opportunity for accomplishment.

St. Louis Meeting, American Ceramic Society

The advance announcement of the 24th Annual Meeting of the American Ceramic Society, February 27 to March 3, 1922, includes three days devoted to the presentation and discussion of papers on manufacturing problems, and two days of visiting industrial plants. Round-table discussions are planned on a large number of subjects, such as heat conductivity and insulation, abrasives, feldspar resources and deposits, raw materials for the glass industry, wet process enamels for cast iron, and glass house refractories. Forty papers are at present included on the program, and more are being added.

The Flow of Fluids through Commercial Pipe Lines^{1,2}

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The information at hand concerning the flow of fluids in pipe lines is discordant, scattered, and incomplete except in a few special fields. The great bulk of the work to date has been devoted to the flow of water, from which empirical relationships and constants have been derived, but even in this case a study of the results reveals considerable disagreement among the investigators. Another range which has been carefully studied is the flow of viscous liquids, such as heavy oils and glycerol, through comparatively small tubes. Comparatively little reliable experimental work has been published on the flow of very viscous liquids through commercial pipes, and practically none has touched on the frictional resistance of elbows in viscous flow.

Certain general principles with regard to the flow of fluids are, of course, generally recognized. Thus it is well known that there are two general types of motion for liquids—usually called viscous and turbulent flow. Viscous flow is characteristic of low velocities, small pipes, or very viscous liquids. In this form of motion, all the particles move in lines parallel to the movement of the mass as a whole, though the velocity of motion drops off rapidly from a maximum at the center to zero at the outside of the pipe. The average velocity over the entire cross-section of the pipe is one-half the maximum value at the center of the pipe.⁵ This form of motion is shown graphically in Fig. 1. It is to be noted that there are no "cross" or mixing currents. It is well established that Poiseuille's formula holds for this type of motion. Expressed in convenient engineering units, this takes the modified form:⁶

$$p = \frac{0.000668 z l v}{D^2}$$

In the case of every fluid, as the velocity is increased a point is eventually reached where a rapid transition takes place from viscous flow to an eddying, mixing type of motion known as turbulent flow, and here the net velocity distribution curve is much flatter, the average velocity being about 80 per cent of that at the center. (See Fig. 1.) The transition velocity is called the critical velocity and its magnitude depends upon the viscosity and density of the liquid and the size (and roughness) of the pipe (increasing in direct proportion to the first factor, and in inverse proportion to the other two).

The formula most frequently used for turbulent flow is that of Fanning, which in engineering units can be expressed:

$$p = \frac{0.323 f l s v^2}{D}$$

It will be noted that the principal differences between the formulas for viscous and turbulent flow are that in the latter

case the velocity occurs as the square rather than the first power, while the diameter of the pipe occurs as the first power rather than the square. Furthermore, the viscous flow formula includes the viscosity of the fluid as one factor and does not require any variable coefficient, while the turbulent flow formula apparently disregards the viscosity of the liquid, and adds a variable friction factor, f , which is a rather complicated function of velocity, pipe diameter, viscosity, density, and the condition of the pipe surface.

It is thus apparent that the above formula for turbulent flow is only a rough approximation of its true law of motion, and the results can be made accurate only by varying the values used for the friction factor f . Attempts to formulate a general equation have resulted in the use of fractional

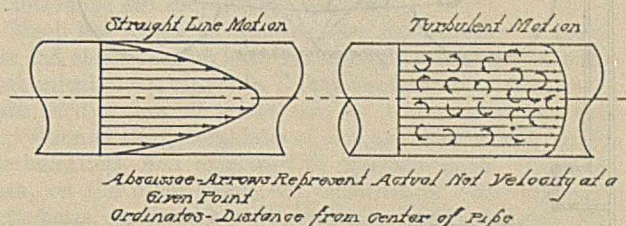


FIG. 1—COMPARISON OF VISCOUS AND TURBULENT FLOW IN PIPE LINES

exponents for v and D , but no two writers agree as to the exact magnitude of the exponents, except to place that of v generally between 1.6 and 1.9, and that of D between 1.4 and 1.1. These attempts have failed, since these exponents hold approximately constant only over a limited range of velocity and diameter. Corrections for roughness are also a disturbing factor. One or two writers suggest putting z into the numerator of Fanning's equation with a small fractional exponent in the neighborhood of 0.4. The difficulty of using such equations in practical work is obvious.

The object of the experimental work described herein was to fill in the gaps in the existing data on the flow of fluids in pipes of commercial size and roughness, especially for very viscous liquids and in the critical region between viscous and turbulent flow; and to determine with reasonable accuracy correction factors for the pressure drop around bends. By combining these data with a critical survey of existing information, it has been found possible to develop a simple but comprehensive method of treatment of the whole subject of the flow of all types of fluids through commercial pipe lines, using a single method of calculation for all types of flow.

This work was undertaken at the instigation of Dr. W. K. Lewis and has profited greatly by his suggestions and advice. Acknowledgments are also due to the National Tube Company, who supplied most of the pipe and financed the bulk of the experimental work; to the Hammel Oil Burning Equipment Company, who paid for the installation of the 4-in. pipe line and for some additional experimental work; and to the Parks-Cramer Company and The Texas Company, who supplied the oils used.

APPARATUS

The installation for the experimental work is shown diagrammatically with essential dimensions in Fig. 2, and by photographs, Figs. 3 and 4. It included a 35-h.p. motor driving a rotary gear pump connected on the suction side by 4-in. pipe to a 10-ft. by 5-ft. diameter storage tank. The discharge of the pump was connected by convenient valves

¹ Received December 10, 1921.

² Published as Contribution No. 40 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

³ Director, Research Laboratory of Applied Chemistry, M. I. T.

⁴ Assistant Professor of Chemical Engineering, M. I. T.

⁵ This may be proved mathematically, from the definition of absolute viscosity (see Lamb, "Hydromechanics of Fluids," 1916) and has been verified experimentally by Stanton and Pannell [Collected Researches, National Physical Laboratory, Teddington, England, 11 (1914)].

⁶ The following nomenclature is used throughout this paper:

f = friction factor (Fanning)	s = specific gravity of liquid
l = length of pipe (ft.)	D = inside pipe diameter (in.)
v = average linear velocity in pipe line (ft./sec.)	Q = flow (gal./min.)
z = viscosity in centipoises (= relative to water at 68° F.)	The precise definition and measurement of these quantities is discussed later.
p = pressure drop (lbs./sq. in.)	

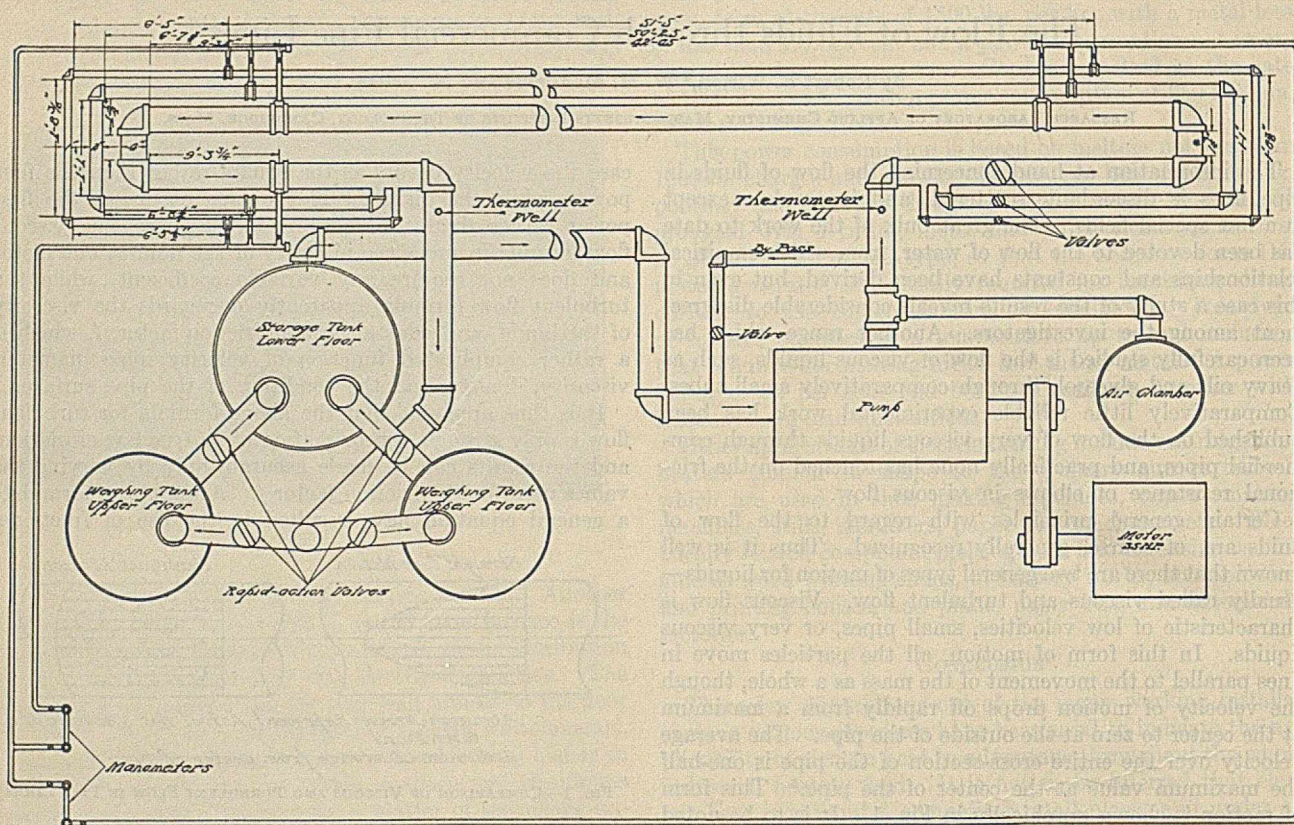


FIG. 2—DIAGRAMMATIC LAYOUT OF APPARATUS FOR PUMPING VISCOUS LIQUIDS
(Not drawn to scale)

to about 150 ft. each of 4-in., 2-in., and 1-in. "Welding Scale Free" standard steel pipe, made by the National Tube Company. The actual diameters were measured and found to correspond within the limits of error to the standard dimensions (Table II). These lines led to a common 4-in. riser equipped with quick-acting valves leading to two weighing tanks 5 ft. by 4 ft. in diameter. The weighing tanks were on the floor above storage tank, which conveniently allowed the liquid to flow back to the storage tank by gravity. The pressure drop was measured by means of a vertical glass U-tube about 10 ft. high containing water on mercury, which measured pressure differences up to 100 lbs. per sq. in. This manometer was connected by $\frac{3}{8}$ -in. pipe lines to include either 42.04 ft. of 4-in. straight pipe, 50.21 ft. of 2-in. straight pipe, or 51.42 ft. of 1-in. straight pipe by valve manipulation. The straight pipe was continued about 10 ft. on each side of manometer connections to eliminate all effect of the bends. The manometer pipe lines containing oil led to a 3-in. diameter chamber above the manometer half full of water, while the lines from this chamber to the mercury manometer were full of water. This scheme allowed instantaneous pressure readings, despite the high viscosity of the oils. The pressure drop in lbs. per sq. in. for this system can readily be shown to be $\frac{(13.6-1) \times 14.7}{13.6 \times 2.54 \times 30}$ or

0.179 times the manometer reading (R) in cm. A similar but smaller manometer measured the pressure drop around the bends, which in each case consisted of two standard 90° elbows (in the three pipe sizes listed above) connected by a close nipple, with straight pipe leading to the manometer connections which were from 6 ft. to 10 ft. on each side of the bends. The storage tank was equipped with a steam coil for heating the liquids. Mercury thermometers were provided to indicate the temperatures of the oil at entrance and exit, while a by-pass around the pump afforded adequate

control of the flow. A large air chamber beyond the pump served to damp out pressure fluctuations.

PROCEDURE

A series of runs was made at a definite oil temperature varying from low to high rates of flow and vice versa. The whole system was first brought to a condition of steady flow, and then suddenly switched into the empty weighing tank, recording the time with a stop watch. The average duration of an individual run was from 1 to 4 min., during which time the discharge was accurately weighed, the pressure drops in the straight pipe and around the bend were noted, and the entrance and exit temperatures were read. A series of seven to ten runs at different velocities was made with each oil at each temperature. The total number runs made in the course of the experiments was about 400.

As noted previously, the "pressure drop around the bend" included the drop due to two elbows and three connecting sections of straight pipe. In order to calculate the effect due to the elbows alone, a correction obviously had to be made.

The pressure drop through the straight pipe between manometer connections (excluding the two elbows) was calculated from the data secured at the same time on straight pipe alone, and this amount was subtracted from the total pressure drop around the bend as measured by the manometer. This value divided by two gave the pressure drop for one standard 90° elbow.

Four different oils were used in the course of this investigation. They may be briefly described as follows:

1—Mexican petroleum, a crude asphalt base oil, one of the most viscous oils handled commercially, was used to obtain data in the upper⁷ viscous flow region.

⁷ The words "upper" and "lower" in this paper refer to regions with comparatively high or comparatively low values of f as indicated on Fig. 12, etc.

2—For the lower⁷ part of the viscous flow region, recourse was had to Meproline, a refined paraffin base oil used in oil heating systems. This oil had a somewhat lower viscosity than

recommended may well refer at once to the later section describing only the recommended methods of calculation. However, in order to present the basis for and show the validity of these final conclusions, it is necessary to discuss in some detail the theory and existing data pertaining to the flow of fluids.

The engineer who is habitually making calculations for the flow of a given type of fluids through pipe lines is usually able to assemble from various sources some data or empirical equations applicable with fair accuracy to the particular set of conditions in which he is interested, and to develop a reasonably satisfactory procedure for making the necessary calculations. Even for the comparatively simple case of water, however, interpolations must be made from values given in tables for arbitrary friction factors, and the values given by two different references are likely to vary by as much as 30 or 40 per cent. Furthermore, no mention is made in most texts on hydraulics of the possibility of straight line flow for water, which does take place in small tubes at moderate velocities. The use of the customary formula in this range will cause enormous errors.

Much less fortunate, however, are the majority of chemists and engineers who have but infrequent occasion to make such calculations, especially if they venture out of the beaten path of the flow of water, air, or steam. Fundamental exposition of the general laws of flow are rare, usually highly mathematical, and expressed in absolute units. Practical data, on the other hand, are scattered in many different periodicals, expressed in a wide variety of units, and generally cover only a narrow range of data on a given article. In the typical reference handbooks different empirical formulas are given for the flow of air, steam, and water, but even with the aid of all the foregoing information it is impossible for one unfamiliar with the subject to calculate the rate of flow of an oil, knowing merely the Saybolt seconds, or of a gas, knowing its viscosity. As a result of this situation, the average engineer has almost completely lost sight of the fact that *all* fluids obey identically the same fundamental laws of flow.

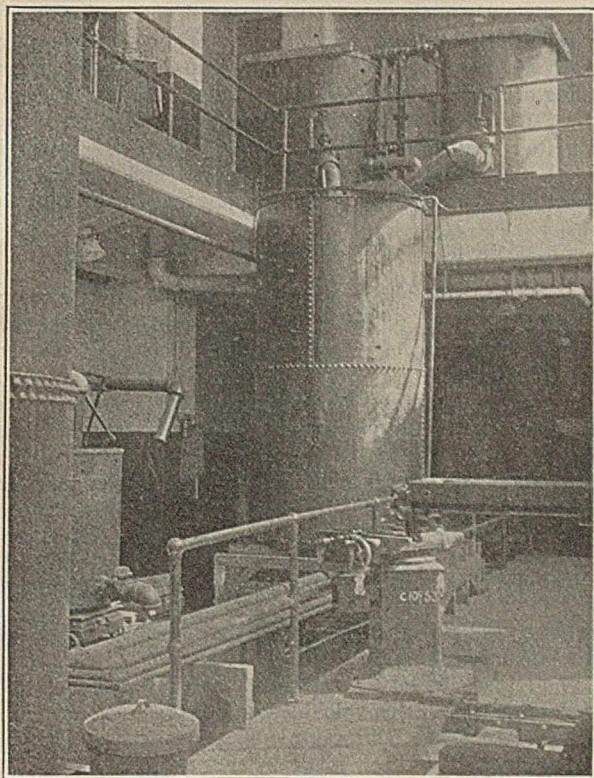


FIG. 3—SHOWING TWO WEIGHING TANKS (ABOVE), STORAGE TANK, AND ONE END OF PIPE LINES

the Mexican petroleum and could be heated much hotter without changing in composition, so it was used over a wide range of viscosities.

3—Port Arthur light crude, a rather fluid fuel oil, was used to cover the upper portion of the turbulent flow region, in which few data were available.

4—Modified Port Arthur, made by adding one barrel of Mexican petroleum to fourteen barrels of the above oil, was employed in order to get a series of points in, and on both sides of, the critical range.

Table I summarizes all essential information with regard to the four oils.

OIL	SOURCE	GRAVITY AT 70° F.						VISCOSITY	
		Sp. Gr.	° Bé.	CENTIPOISES		SAYBOLT SECONDS			
				70° F.	100° F.	70° F.	100° F.		
Mexican Petroleum	Hammel Oil Burning Equip. Co.	0.962	15.7	4370	970	20700	4700		
Meproline	Parks-Cramer Co.	0.900	25.4	3400	815	17100	4200		
Port Arthur Light Crude	The Texas Company	0.903	25.0	65.7	30.7	330	157		
Modified Port Arthur	The Texas Company	0.910	23.8	86.0	39.6	430	202		

The viscosity-temperature curves for the four oils are shown on Fig. 5.

The results obtained from the 400 runs on the four oils, together with those in the literature on the flow of water, air and steam, and a little on oil, were sufficient to cover the whole range of conditions likely to be encountered in commercial practice.

DISCUSSION OF RESULTS

METHOD OF PRESENTATION—The reader who is interested solely in the practical use of the methods of calculation herein

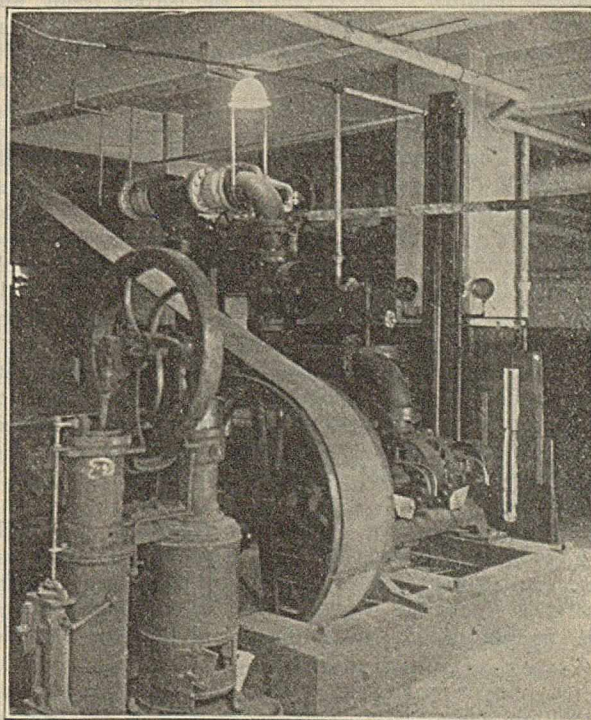
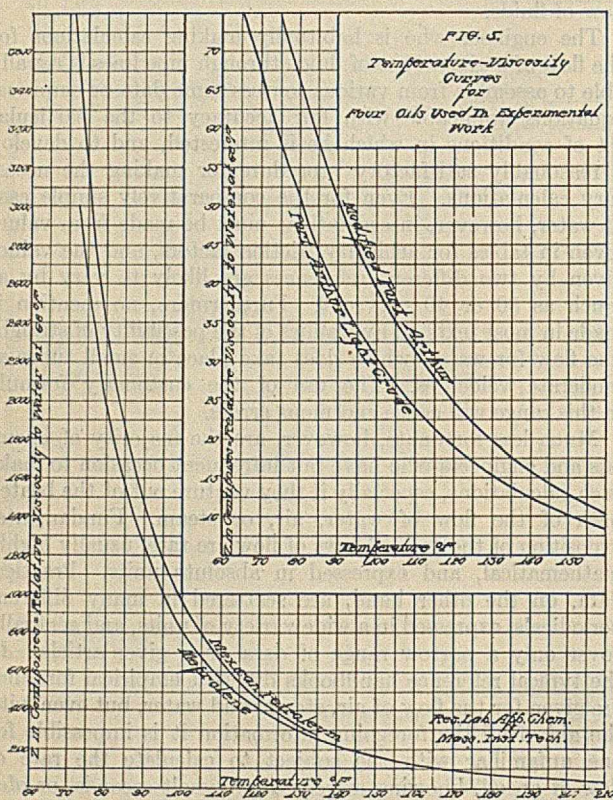


FIG. 4—SHOWING PUMP AND MANOMETERS

Most of the foregoing difficulties are due simply to the failure to treat the whole subject of the flow of fluids in a comprehensive manner and in a place readily accessible to the average individual. There are, however, two more



serious difficulties which are somewhat harder to solve satisfactorily: first, the fact that the two kinds of motion follow two different formulas, which greatly complicates the calculations required to be certain of the correct result; and second, the fact that in the formula for turbulent flow there is a variable coefficient f , which is a somewhat indefinite function of velocity, pipe diameter, viscosity, density, and condition of the pipe surface.

When dealing with water alone, where the density is substantially constant, and variations in viscosity are usually disregarded (though they should not be), it is of course possible to meet the situation fairly well by the use of tables showing the value of f for different velocities and pipe sizes. When, however, an attempt is made to extend the formula to cover other liquids and gases, thus bringing in two additional variables, viscosity and density, which affect f , the situation apparently becomes well-nigh hopeless. As a result the common practice has been to work out separate formulas or flow tables holding over certain ranges for each of the common fluids, and to leave the rest of the subject to be covered by some very rough general formulas, frequently with fractional exponents applicable only over a limited range.

Fortunately, however, it has been predicted, apparently first by Stokes⁸ in England about seventy years ago, and since then rediscovered by several others⁹ interested in the theoretical side of the flow of fluids, that although the variable friction factor f is a function of the four variables

above mentioned, it is not an independent function of these quantities, but a function only of the expression $\frac{Dv_s}{z}$.¹⁰

This obviously makes possible a great simplification in the treatment of the subject, but it has unfortunately been mentioned almost exclusively in highly mathematical papers dealing primarily with the theoretical side of the flow of fluids.

In 1912 Blasius¹¹ gave a good review of the theory, recalculated the data of Saph and Schoder¹² for water in smooth brass and galvanized iron pipes and the data of Nussett¹³ for compressed air, and showed that f was a function

of $\frac{Dv_s}{z}$, as required by the theory. This paper has apparently

been almost completely overlooked outside of Germany.

By far the most thorough existing treatment of the subject from this point of view is in connection with the recent work (during the war) of the British National Physical Laboratory,¹⁴ who used the method in the presentation of accurate data over a wide range. This work of the N. P. L., primarily on air and water, in very smooth tubes up to 3 in. in diameter, definitely substantiated for these conditions the prediction of Stokes and others that the friction factor f is, within the limits of error, a function of the simple ratio $\frac{Dv_s}{z}$ rather than an independent function of the separate

variables. These important results have received surprisingly little attention in this country.¹⁵

While the method of treatment hereinafter followed is based primarily on this valuable work of the National Physical Laboratory, the following modifications or amplifications of that work have been made in this article:

1—For the sake of convenience in practical use, all results are expressed in English engineering units, rather than absolute or metric units.

2—Less emphasis is placed on the unstable region of flow between viscous and turbulent motion.

3—Extensive data have been obtained on commercially smooth pipes with standard couplings, which are shown to give different results from the extremely smooth drawn brass tubes used by the N. P. L.

4—Data have been secured, mainly from the literature, on much larger sizes of pipe than the comparatively small tubes used by the N. P. L.

5—Many more data have been secured on the flow of highly viscous liquids through commercial pipes.

6—Complete details are given to make possible the use of a single method of calculation for all types of flow, which is highly desirable from a practical standpoint.

¹⁰ This is due to the fact that f is a factor "without dimensions," and hence can only be a function of another expression without dimensions. The only combination of the four factors D , v , s , and z which cancels out all dimensions, is the expression $\frac{Dv_s}{z}$. It is not necessarily independent of

the units used, unless consistent absolute (either English or French) units are used for all quantities, which is not the case in this article.

¹¹ Z. Ver. deut. Ing., 56 (1912), 639.

¹² Trans. Am. Soc. Civil Eng., 51 (1903), 253.

¹³ "Mitteilungen über Forschungsarbeiten," 44.

¹⁴ Collected Researches, National Physical Laboratory, Teddington, England, Stanton and Pannell, Vol. 11 (1914), and Pannell and Higgins Vol. 13 (1916). This is hereafter called the "N. P. L." data and curves.

¹⁵ Since this paper in preliminary form was presented at the Chicago meeting of the American Chemical Society (September 1920) an article by A. C. Preston has appeared in *Chemical and Metallurgical Engineering*, for September 29 and October 6, 1920, which presents some of these results in graphic form. The Kinney Manufacturing Company and the King-Knight Company have also published two editions of an excellent booklet of the flow of oils which makes use of these N. P. L. data and method of presentation. Buckingham also discusses these data mathematically in the *Trans. Am. Soc. Mech. Eng.*, 37 (1915), 263.

⁸ Math. and Phys. Papers, Vol. III (1850), 17.

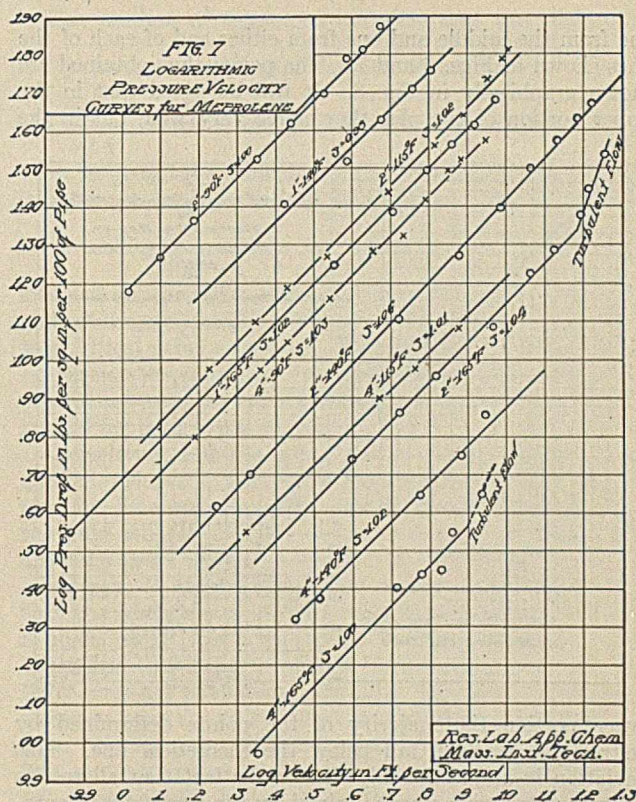
⁹ Reynolds, *Trans. Roy. Soc. London*, 1883, 935; Helmholtz, "Wissenschaftliche Abhandlungen," I (1873), 158; Rayleigh, *Phil. Mag.*, 48 (1889), 321; Lamb, "Hydrodynamics of Fluids," Cambridge Univ. Press, 4th Ed., 656.

In making use of the fortunate fact that f in Fanning's equation is a function of $\frac{D v s}{z}$ rather than of all the variables independently, the obvious way to present experimental data is to plot the values of f , calculated from Fanning's equation for a given set of observations, against the corresponding value of $\frac{D v s}{z}$.

At first sight this method of presentation would seem applicable only in the region of turbulent flow, since a different law, Poiseuille's (where $p = 0.000668 \frac{l v z}{D^2}$), is known to hold for the region of viscous flow. However, by comparing this equation with Fanning's ($p = 0.323 \frac{f l s v^2}{D}$), it will be noted (as pointed out by Blasius) that if $f = 0.00207 \frac{z}{D v s}$, the two equations become identical. Furthermore, values of f which fulfil the latter equation must all lie on a line (straight on a logarithmic plot) on the above-mentioned plot of f against $\frac{D v s}{z}$. It is therefore possible to calculate all experimental results, regardless of the type of flow, on the basis of Fanning's equation, and plot the resulting values of f , which should approximate the above-mentioned line if Poiseuille's law holds for a given case. Conversely, by referring to such a diagram for the values of f corresponding to a given value of $\frac{D v s}{z}$, it becomes

possible to calculate the pressure drop for any condition of flow using only a single formula (Fanning's).

This method of presenting data is therefore used throughout the following discussion. It may be well at this point for the reader to refer to Fig. 12, which shows the value of f (plotted logarithmically) over substantially the entire range of conditions met with commercially. For convenience in the presentation of experimental results, this curve has been enlarged, divided into three sections, and the data pertaining to each one discussed separately.

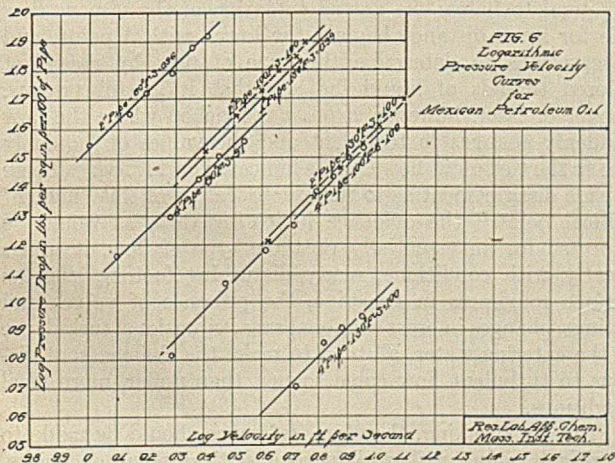


The individual observations on the first two oils are most definitely shown in Figs. 6 and 7, where the logarithm of the velocity is plotted against the logarithm of the pressure drop in each series of runs in which the viscosity and pipe size were kept constant. This is a convenient method of checking up on the variability of individual results and showing a large number of points in which all the data with regard to a given run are evident from an inspection of the plot (which is not true when the observed value of f is merely plotted against $\frac{D v s}{z}$, as in Fig. 8).

Through each of these series of points the best representative line has been drawn and the slope is indicated in the figures. According to Poiseuille's law the pressure drop should be proportional to the velocity and these slopes should equal 1.00. Actually they are found to vary from 0.95 to 1.06, with an average of 1.01. As far as the velocity-pressure drop relationships are concerned, therefore, Poiseuille's formula appears to hold within the limit of error of the experiments, which is rather high in case of the heated oils in viscous flow because of the nonuniform distribution of temperature throughout the pipe. It will be noted that the concordance of the individual points with the line is satisfactory in substantially all cases. Data on the Mexican petroleum in 1-in. lines are omitted because (on account of the high frictional resistance) the temperature of the oil rose as much as 10° or 12° in passing through the pipe and it was impossible to get reproducible or concordant results.

It will also be noted that two of the lines show breaks in the slope, indicating a change from viscous to turbulent flow in the cases of the 2-in. and 4-in. pipes with the hottest oil (165° F.).

Since the number of individual observations in this range was so large, the method of checking up the results as a whole (as to the effect of viscosity and pipe size as well as velocity) by plotting the calculated values of f was not applied to each individual observation, but to three points—



DATA IN VISCOUS FLOW REGION—Three sets of runs have been made by this Laboratory in the viscous flow region—one with Mexican crude in the highest viscosity region; one with Meprolene over a wide intermediate range of viscosities obtained by varying the temperature; and a few results with modified Port Arthur in the smaller sizes of pipe.

one from the middle and one from either end of each of the lines shown in Figs. 6 and 7. The points thus obtained are shown graphically in Fig. 8. It will be noted that in the upper portion of the plot they agree very well, but in the

communicated by the Standard Oil Company, correcting the data given in the booklet.

Considering the results as a whole, while there is considerable variation both above and below the line, due to factors such as frictional heating in the pipe and variations in temperature between the inside and the outside, there can be no real doubt as to the essential validity of Poiseuille's formula for viscous flow in pipes of commercial size and roughness. Since the same law has been checked up very closely for all types of liquids in extremely smooth glass and metal tubes, it is evident that the roughness of the pipe is a comparatively small factor in determining the resistance to viscous flow—as might indeed be anticipated on theoretical grounds, since there is in any case a practically stationary and fairly thick film of oil on the inside surface of the pipe. It will be noted that this conclusion is quite different from that drawn from results obtained in the turbulent flow region.

DATA IN CRITICAL AND UPPER TURBULENT FLOW REGIONS—Possibly the most interesting, and at the same time the most troublesome, portion of the subject of the flow of fluids is the critical region between viscous and turbulent flow. Fig. 8a brings out the essential facts as they appear from a careful study of the various experiments (usually in small tubes) described in the literature.¹⁶ The solid lines are the portions of the viscous and turbulent flow curves about which there is little doubt; the turbulent flow line extended to the left intersects the viscous flow line at Point 1 frequently referred to as the "minimum" critical point. The weight of evidence seems to indicate that these two intersecting lines represent the most stable conditions of flow, it being noteworthy that the type of motion giving the largest value of f (and hence the greatest dissipation of energy) for a given value of $\frac{D v s}{z}$ is the one which tends to prevail.

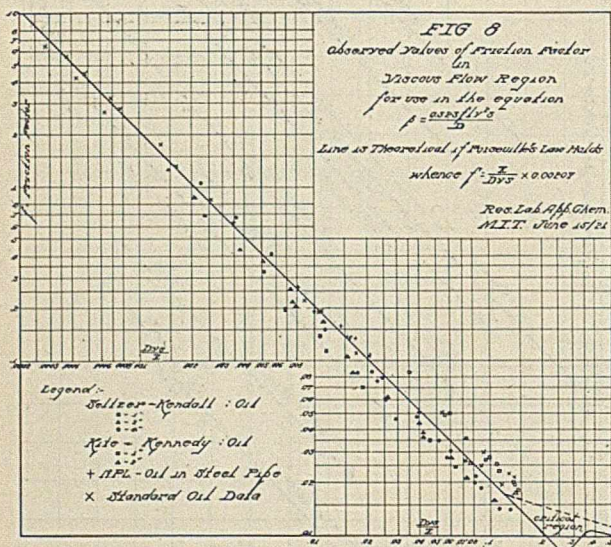
Actually, however, it is observed in careful laboratory experimentation that viscous flow has a marked tendency to perpetuate itself under conditions where turbulent flow would be expected, while the opposite tendency has never been noted. If, for a given liquid flowing through a given pipe, the velocity (and hence $\frac{D v s}{z}$) is gradually increased

and no disturbing influences are present, the observed values of f tend to follow the dotted extension of the viscous flow line for some distance beyond the lower critical point, and observations to determine the type of flow by means of colored threads of liquid indicate that it is still viscous. Sooner or later, however, a point is reached where the flow suddenly changes to turbulent and the values of f quickly rise to the turbulent flow line, as indicated on Fig. 8a. There is wide disagreement as to the exact location of this "higher" critical point,¹⁷ the evidence indicating that, as would be expected for an essentially unstable type of flow, it varies greatly with conditions; many disturbing factors, such as surface roughness in the pipe, the presence of valves and fittings, changes in cross-sectional area, vibrations, turbulence of the entering water, all tend to make the change from viscous to turbulent flow come sooner than under more ideal conditions.

Properly speaking, therefore, reference should be made to a critical region, rather than to a critical point or points. Furthermore, most authorities state that if this critical region is entered by gradually lowering the velocity from the

¹⁶ Lamb, "Hydrodynamics," 4th Ed. (1916), Cambridge Univ. Press, 651; Russell, "Textbook of Hydraulics" (1908), 110; Reynolds and Osborne, Proc. Roy. Soc. London, 35 (1883), 94; Barnes and Coker, *Ibid.*, 74 (1904-5), 341.

¹⁷ There is also some disagreement in the literature as to whether Point 2 or 3 should be called the higher critical point.



lower portion the majority of the points determined by Seltzer and Kendall fall below the theoretical line. This deviation is unquestionably due to the fact that all results lying in this region were obtained by the use of the Meproline heated to a fairly high temperature. In such cases there is a very wide temperature gradient between the warm center and the cold outside of the pipe, due to the absence of any convection or mixing currents in viscous flow, and it is practically impossible to make an accurate measurement or calculation of the effective average temperature. The temperatures used in the calculations were measured by thermometers in wells in the 4-in. pipe line just beyond the entrance and exit of the 2-in. and 1-in. lines, as indicated in Fig. 2. The thermometer therefore recorded a temperature nearer to that of the pipe and the outside cool layers of the oil than to the true average effective temperature, since most of the flow was undoubtedly taking place in the hot center core. The theoretical values of the friction factor corresponding to these high values for the viscosity were, therefore, higher than the observed points in the region where measurements were made on hot oil. The deviation averaged about 17 per cent in the highest temperature runs, and was worst, as might be expected, in the 1-in. pipe, where the velocity through the 4-in. exit line was extremely low. An error of only 3° or 4° in the effective average temperature would account for the above divergence.

In order to obtain some further data another brief series of runs was made by Kite and Kennedy covering the lower portion of this region, using the modified Port Arthur oil at ordinary temperatures. For some unexplained reason (possibly an error in the viscosity determinations) the results of this series of runs (hollow squares on Fig. 8) were about as much above the theoretical line as the other series were below, the average of the two checking the theoretical line very closely.

The only other satisfactory data on viscous flow of heavy oils through commercial pipes appear to be the single set of experiments of the N. P. L., and some results of the Standard Oil Company of California on pipes up to 12-in. diameter, published in their bulletin on the California Oil Pipe Line. Representative points from both of these sources are also recorded on Fig. 8. In calculating over the latter results use was made of a table of viscosities, privately com-

turbulent flow side, the tendency is to follow the dotted turbulent flow line clear over to the point of intersection, without any abnormal dip in the observed values of f . Experimental results seem to indicate, however, that while turbulent

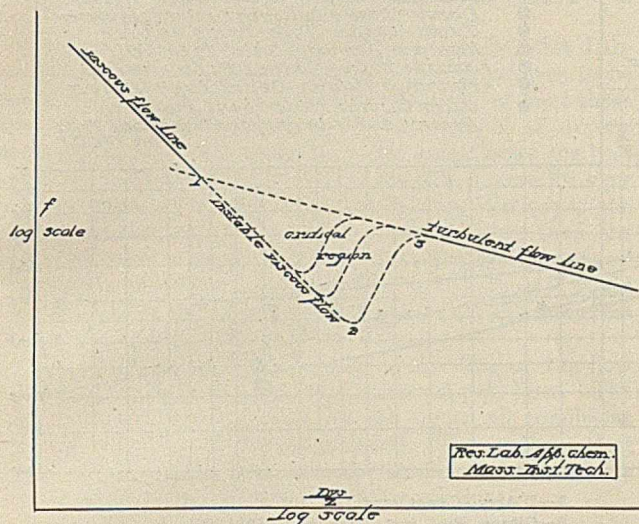


FIG. 8a—DIAGRAMMATIC REPRESENTATION OF DIFFERENT FLOW CURVES OBTAINED IN THE CRITICAL FLOW REGION

flow tends to persist longer under these conditions, it may nevertheless return to viscous flow before Point 1 is reached.

The N. P. L., working with extremely smooth tubes, have obtained the most consistent series of data in this region which has thus far been available, practically all their points falling within 3 or 4 per cent of the curve shown in Fig. 9. (The number of points determined by the N. P. L. is so large that reference must be made to the original article for such details.) The recalculated data of Saph and Schoder¹² also check this curve very well, showing that, with very smooth pipe, even the critical region gives fairly consistent values of f when plotted against $\frac{Dvs}{z}$. The abnormal dip in the curve as determined by them is both wider and deeper than would be indicated by a few experiments under commercial conditions, though it is less pronounced than has been found by some experimenters under ideal conditions in glass tubes.

In view of the almost complete lack of accurate data for commercial pipes in this region, this Laboratory undertook a rather extensive investigation of the phenomenon in 1-in., 2-in., and 4-in. pipes, with the Port Arthur light crude and modified Port Arthur oils, the results of which are shown in Fig. 9. Since the observed points indicate a much smaller dip in the critical region for commercial pipe than is found by the N. P. L. (undoubtedly due to surface roughness, the presence of couplings, vibrations, etc.) and furthermore, since the presence of other disturbing factors or special operating conditions are at any time likely to bring the pressure drop up to the theoretical line for turbulent flow, it appears to the authors that the proper treatment of this region for practical purposes in commercial pipe lines is to assume the turbulent flow line as extending straight over to the viscous flow line, thus simplifying the treatment and being on the safe side in all calculations. This would, of course, lead to slight errors if the pressure drop through a commercial pipe line were used as a measuring system in this region of flow, but no such method of measurement, regardless of the friction factors assumed, can give reliable and reproducible results in this unstable region.

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This method of treatment indicates that the critical velocity for commercial pipes occurs when $\frac{Dvs}{z} = 0.12$ or

$$v = \frac{0.12 z}{D s}$$

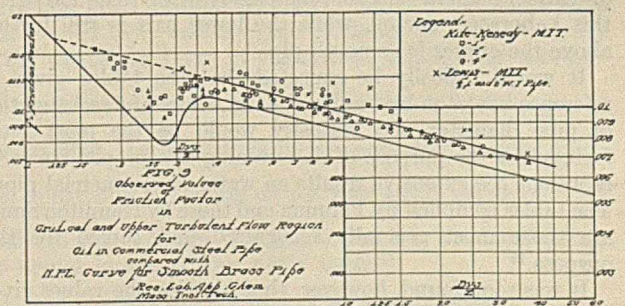
which is much lower than the values based on work in glass tubes, which are the ones customarily quoted in reference books. As indicated above, however, the flow

is variable and uncertain for values of $\frac{Dvs}{z}$ between 0.12

and 0.4 (or possibly even higher under ideal conditions) and reference should be made to a critical region rather than to a critical point or points. Fortunately, in the method of calculation recommended hereinafter there is no need whatever of knowing the critical velocity, since the same formula is used for both types of flow.

Considering next the upper part of the turbulent flow region, also shown in Fig. 9, the data obtained in this Laboratory by Kite and Kennedy, and by Lewis,¹³ appear to be the only reliable data for commercial pipes in this region, although there are a considerable number available in the lower part of the turbulent flow region. It will be noted that the concordance of the points (except a few of Lewis') is much better than it was in the viscous flow region, owing to the fact that in turbulent flow the temperature is substantially constant throughout the pipe, and that variations in viscosity have much less effect in turbulent than in viscous flow. Furthermore, there is no consistent difference between 2-in. and 4-in. pipes, though the 1-in. results appear to average very slightly higher. The results are, however, consistently higher than those obtained by the N. P. L. on smooth pipe in the same region—the divergence averaging about 15 per cent. Unfortunately, practically no other data are available to serve as a check upon these results, but as will be noted later from a consideration of Fig. 10, the results are entirely consistent with those obtained by many observers in the lower part of the region.

DATA IN LOWER TURBULENT FLOW REGION—This Laboratory has secured no original data in the lower turbulent flow region, primarily because this appeared to be well covered by the results of a number of other experimenters both in very smooth and in commercial pipe.

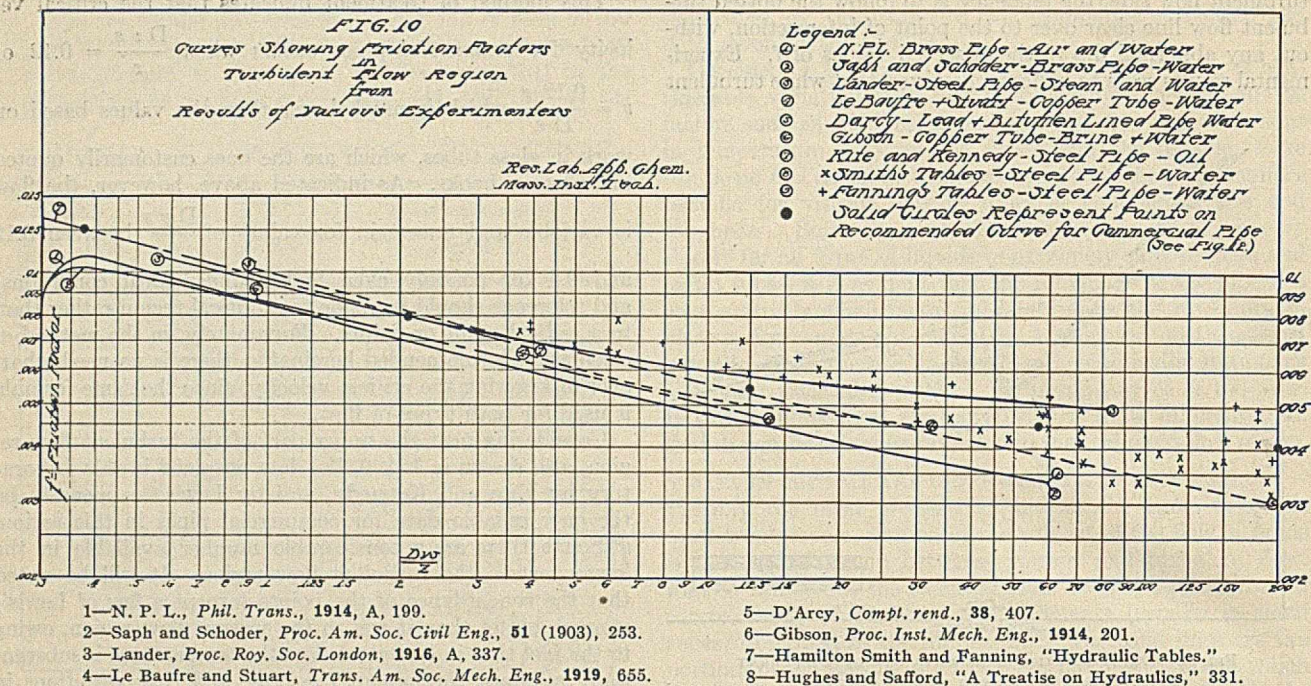


Again, for very smooth pipe, the lower line in Fig. 10 represents very well the accurate and highly satisfactory data of the N. P. L., which are substantially identical with the curve obtained on recalculating the results of Saph and Schoder in smooth brass pipe.

There are certain other experimenters whose data appear to be thoroughly reliable and can be satisfactorily represented by a smooth curve in plotting f against $\frac{Dvs}{z}$. It should be

understood that most of these data were not presented in this form by the original authors, but have been recalculated

¹³ THIS JOURNAL, 8 (1916), 627.



either by the N. P. L. or by this Laboratory to put it in this more convenient form. Curves are in no cases drawn unless there is a reasonably good concordance among the points when thus calculated and plotted.

Considering briefly the other lines on Fig. 10, the results of Gibson with brine solutions in smooth copper tubing are also only slightly above the N. P. L. curve. The work of Le Baufre and Stuart on condenser tubes of Admiralty metal is still slightly higher than these results.

Undoubtedly, the best results on commercial steel pipes are the comparatively recent and extensive results of Lander, in England, who used steam and water flowing through steel pipe and obtained a very concordant series of results when

plotted against $\frac{Dv_s}{z}$. It will be noted that the upper part

of Lander's curve checks very closely with that derived in this Laboratory for oil, while the lower part is still further above the curves for smooth pipe.

It would logically be expected that the tables given in reference books on hydraulics for the values of f as a function of pipe diameter and viscosity would be the most satisfactory for the purpose of determining the proper curve to represent the extensive results on water in commercial pipes. The tables compiled by Fanning and those by Hamilton Smith are those most generally recognized and copied for this purpose.¹⁹

It was soon found, however, that plotting the values given by these authors against $\frac{Dv_s}{z}$ gave widely scattering points, as is shown in Fig. 9. Furthermore, deviations between the values given by the two authors were sometimes as great as 30 per cent (mostly in large pipes). A careful consideration of the results indicated further that, if these tables are correct, f is not a function of $\frac{Dv_s}{z}$ for very large pipes such as are used in water mains.

Being somewhat reluctant, however, to accept this conclusion, the authors made an effort to resurvey the original data on which Fanning and Hamilton Smith based their

¹⁹ For both sets of tables see Hughes and Safford, "A Treatise on Hydraulics," p. 331.

tables. This inspection readily showed the difficulties encountered in attempting to work out these tables for very large pipes. In practically every case the data obtained by a given experimenter covered only one size of pipe, and, furthermore, no attempt was made to measure the temperature of the water. Since the viscosity of water varies about 25 per cent for a variation of 20° F. it is undoubtedly an important cause of the discordant results reported. Other variations were undoubtedly caused, even in comparatively new pipes, by wide variations in roughness due to tuberculations, etc., on the surface of the pipes. Being compelled to derive formulas from this kind of scattered and unreliable data, especially for the larger pipes, it is obvious that considerable errors might be made in interpolating and extrapolating results to cover the whole field.

The authors therefore reached the conclusion that the tables derived by Fanning and by Hamilton Smith were as good as could be worked out, considering the type of data which was available to them, but that the wide scattering

of the values of f when plotted against $\frac{Dv_s}{z}$ does not in any

sense prove that f is not a function of $\frac{Dv_s}{z}$. Typical in-

dividual points from the tables of these two authors are shown in Fig. 10. While the deviations are obviously large, their average deviation from the recommended curve for f is no greater than that between the two tables themselves in the cases of the larger pipes. The results also indicate clearly that for commercial pipes, especially for high values of $\frac{Dv_s}{z}$, the values of f are very much higher than those obtained by the N. P. L. in smooth pipe.

It should be pointed out that for a given value of $\frac{Dv_s}{z}$ both tables tend to give higher f 's for pipes of smaller diameter working at correspondingly higher velocities. This might appear to indicate that for very large pipes the effect of a given degree of surface roughness became relatively less, and that all large pipes gave results similar to the N. P. L. for very smooth pipe; on the other hand, it might merely be due to the fact that the large pipes were usually bitumen-

covered wood and hence somewhat smoother than ordinary cast iron or steel. These results cannot, however, be given as much weight as those of Lander, which were obtained under much more carefully controlled conditions, although not in such very large sizes of pipe.

From a careful consideration of these results, this Laboratory has determined (see Fig. 12) what it believes to be the best values of f for clean commercial pipes, at least those from 1 in. to 8 in. in diameter, in the light of all experimental data at present available. For larger pipes the best value of f probably deviates toward the lower curve for very smooth pipes. For very rough or tuberculated pipes the friction factors may, of course, be much higher than the values given for commercially smooth steel or cast-iron pipes. The recommended line is not drawn in Fig. 10 because it would tend to obscure the other lines, but the solid circle indicates its location as drawn in Fig. 12.

This completes the consideration of the data on the flow of all fluids in both smooth and commercial pipe lines. The recommended friction factors for use under all conditions are shown in Fig. 12, as above noted. The mathematical significance of these lines, and the recommended methods of calculation, are discussed in later sections.

RESISTANCE TO FLOW THROUGH ELBOWS—The subject of the flow through elbows is another on which the data are very incomplete. The most convenient method of expressing the frictional resistance due to an elbow of given size is in terms of the equivalent length of straight pipe which will give the same resistance to the flow of a given liquid. The published results on this subject have indicated that the equivalent length of pipe in feet was nearly independent of velocity, but was almost directly proportional to the size of the elbow, and it has therefore become customary to express this equivalent length in terms of pipe diameters, rather than feet, so that the figure will be substantially the same for all sizes of pipe.

Expressed on this basis, the customary recommendation of handbooks is to allow from 30 to 50 pipe diameters for each elbow in a line. An inspection of the data indicates that this rule is fairly well justified for the case of water (though the figure of 50 pipe diameters is well on the safe side of most of the results). There are, however, comparatively few data in the upper part of the turbulent flow region, and apparently none whatever in the critical or viscous flow regions.

Fig. 11 presents in graphic form the results of the experimental runs in this Laboratory, in which the equivalent length of straight pipe in pipe diameters is plotted against $\frac{D v s}{z}$. For reasons discussed in the next section, the resistance of the equivalent length of straight pipe was calculated from the recommended average line on Fig. 12, and not from the observed value in the simultaneous reading on the straight pipe in a particular experiment. A considerable proportion of the observed data had to be omitted from Fig. 11 to prevent the points from becoming crowded, but the points as given are strictly representative of all the results. In the lower turbulent flow region data are also added from other investigators which are quite consistent with the points determined by this Laboratory.

Of the points determined in this Laboratory, the results by Kite and Kennedy in 4-in. pipes at fairly high velocities appear to be distinctly lower than the results for 1-in. and 2-in. pipes, which agree very well. This effect is almost certainly due to the fact that the distance between the two elbows of the 4-in. line (see Fig. 2) was too small to permit the full disturbing influence of the first elbow to manifest itself, and the average pressure drop per elbow was

therefore low, especially at high velocities, compared with that in 1-in. and 2-in. lines where the distance between the two elbows was comparatively large. This would also indicate that the resistance of a standard return bend would be distinctly less than that of two elbows placed some distance apart.

From a careful consideration of these results it appears to be fairly conclusive that the elbow correction, like f , is a

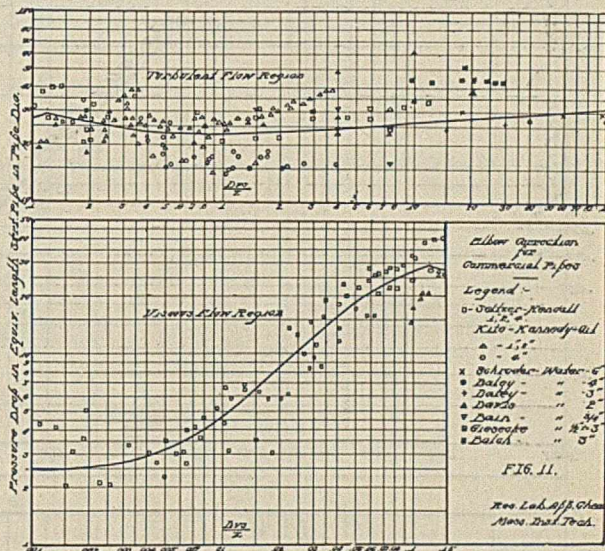


FIG. 11

- 1—Balch, University of Wisconsin, *Bull. Eng. Series*, 7, No. 3, 253, Paper No. 578.
- 2—Gieseecke, University of Texas, *Bull.* 1759 (Oct. 20, 1917).
- 3—Daly, Schoder and Bain, *Cornell Civil Eng.*, 20 (1911-12), 107.
- 4—Davis, University of Wisconsin, *Bull. Eng. Series*, 6, No. 4, 115.

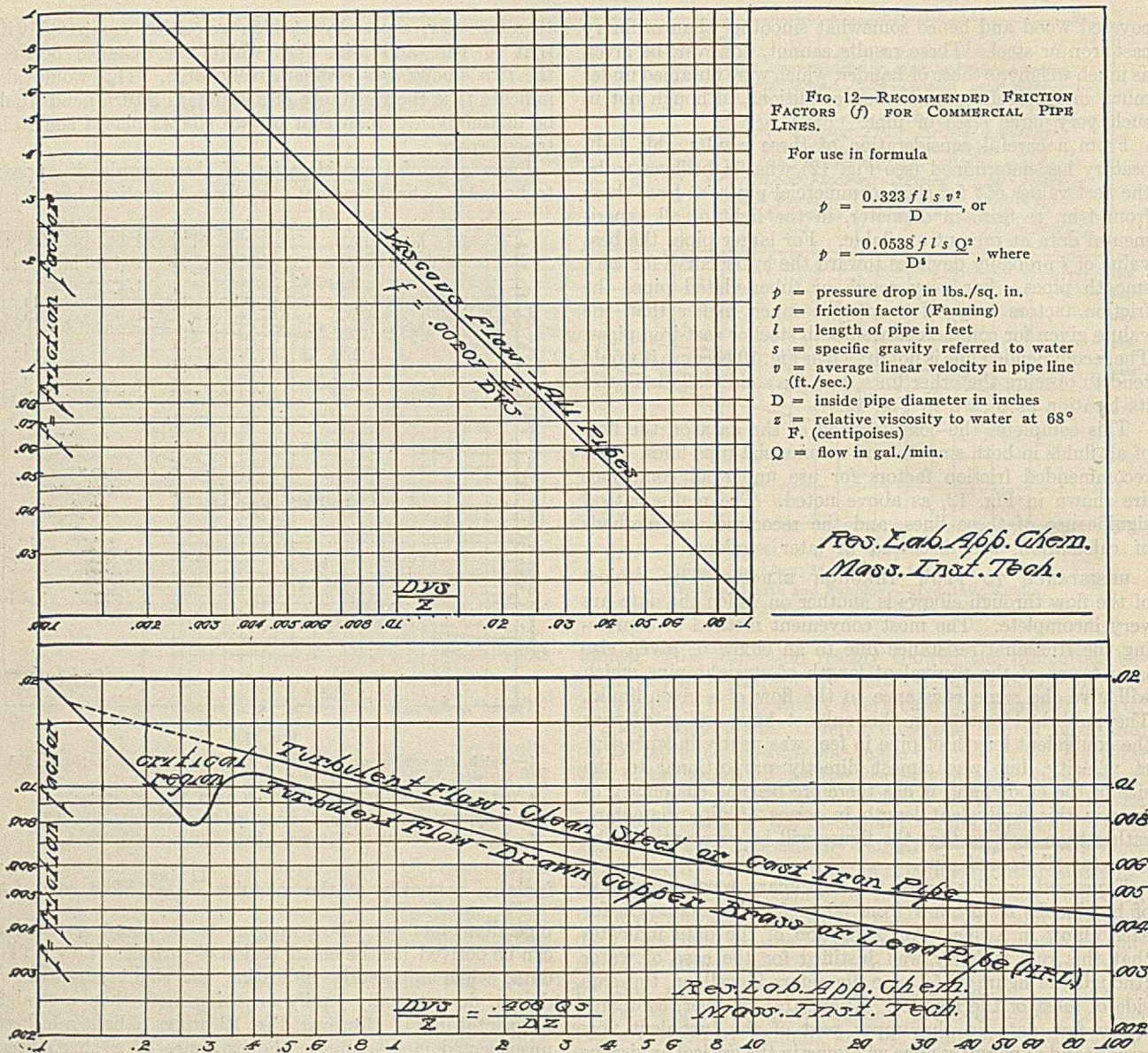
function primarily of the modulus $\frac{D v s}{z}$. The rule of 30 pipe diameters per elbow appears to be about as good as can be derived for the entire region of turbulent flow. (The data, while apparently indicating the slight curvature as drawn, do not really justify anything more than a straight horizontal line.) However, Fig. 12 brings to light a hitherto unsuspected fact—namely, the existence of a sharp break in the correction curve at the critical velocity for commercial pipes beyond which, as $\frac{D v s}{z}$ decreases into the region of viscous flow, the magnitude of the correction rapidly grows less, apparently flattening off for very small values of $\frac{D v s}{z}$ to about 2 or 2.5 pipe diameters, which is little more than the actual length of the elbow itself.²⁰

THEORETICAL ASPECTS OF THE RESULTS

In the course of evolving the method of presentation given in the previous sections and recommended for practical use in the following section, a number of interesting points of theoretical importance have come to light and seem to justify at least passing comment. In most cases they amount to alternative methods of presentation of the same results, which need not concern one interested merely in the practical aspects of the problem.

The preceding results show clearly that for a very wide range of conditions f is a function of $\frac{D v s}{z}$. What function?

²⁰ The complete tabulated data on the 400 odd runs are obviously too bulky for reproduction, but are available for inspection at any time in the files of this Laboratory.



This important point and its significance have scarcely been mentioned.

Referring to Fig. 12, since the line for the viscous flow region is straight and at an angle of 45° (slope = -1) it can readily be shown that its equation is

$$f = 0.00207 \frac{z}{D v s}$$

Substituting this value of *f* in Fanning's equation, it is possible to derive a general equation for flow for this region which is, as noted previously, simply the modified Poiseuille's equation,

$$p = \frac{0.000668 z l v}{D^2}$$

Deriving an equation for the curved line in the turbulent flow region is not, however, such a simple matter. The best form for the equation appears to be

$$f = a + b \left(\frac{D v s}{z} \right)^n$$

where *n* is a negative exponent. Using this form of equation and deriving the constants, it is found that the best equation

for turbulent flow in smooth pipes (as already worked out by Lees²¹) is:

$$f = 0.0018 + 0.00662 \left(\frac{z}{D v s} \right)^{0.355}$$

Applying the same method to the recommended line for commercial pipe gives the new equation of the form:

$$f = 0.0035 + 0.00594 \left(\frac{z}{D v s} \right)^{0.424}$$

Substituting the latter value of *f* in the Fanning equation gives as the most accurate general equation for turbulent flow in commercial pipes the following:

$$p = \frac{0.323 l s v^2}{D} \left[0.0035 + 0.00594 \left(\frac{z}{D v s} \right)^{0.424} \right]$$

A similar equation can readily be derived for turbulent flow in smooth pipes. It is obvious, however, that this equation is too complicated for any practical calculations—or indeed for giving a clear picture as to the comparative effects of the different variables. In order to secure such a semiquantitative visualization for the case of commercial pipes, it is

²¹ Proc. Roy. Soc. London, 1914, 406.

possible to draw a straight line which is fairly representative of the turbulent flow curve for commercial pipes in Fig. 12, which has the equation:

$$f = 0.01 \left(\frac{D v s}{z} \right)^{0.2}$$

Substituting this value for f in the Fanning equation, we obtain

$$p = \frac{0.00323 s^{0.3} z^{0.2} / v^{1.8}}{D^{1.2}}$$

which is a reasonably accurate formula for the middle range of turbulent flow in commercial pipes. Actually, of course, the slope and the intercept of the curved line are continually changing, which changes the value of the constant in the above equation for f from 0.01 to 0.007, while the exponent varies from 0.13 to 0.26. This accounts for the fact that many investigators studying a comparatively narrow range of data have proposed formulas with fractional exponents similar to that given above, but each writer gives different values for the constant and for the exponent, depending on the particular part of the region and condition of pipe surface with which they were working. When working with water alone, as in most of the experiments, z and s have both been erroneously assumed to be constant and therefore became part of the proportionality constant.

There are also certain matters of interest in connection with the flow through elbows. As noted in that section, the resistance through an elbow was figured in terms of the equivalent resistance of straight pipe as *calculated* from the straight line in Fig. 12, rather than in terms of the resistance of a straight pipe as *measured* in the same run. This made little difference, except in the critical region, but when the equivalent length of pipe was figured in terms of the abnormally low resistances actually measured in this critical region, the points in this vicinity formed a sharp hump for values of $\frac{D v s}{z}$ between 0.12 and 0.35, as compared with the smooth curve obtained when using the theoretical line as a basis. The latter method of presentation was not used merely on account of this fact, however, but because if the recommended line is used in making the calculations for the straight pipe, the elbow effect should also be figured in terms of that line. Furthermore, although in straight pipe there is unquestionably a tendency toward perpetuating viscous flow into the turbulent flow region, this unstable tendency is undoubtedly less pronounced during flow through an elbow and the pipe immediately beyond it, which will very probably force the liquid into turbulent motion. The method of presenting the results is therefore sound on theoretical grounds and confirms the belief that elbows tend to diminish the importance of the dip in the critical flow region.

RECOMMENDED METHODS OF CALCULATION

GENERAL PROCEDURE FOR CALCULATING PRESSURE DROP IN ANY PIPE LINE—With the data and charts previously presented, the calculation of the pressure drop through a pipe line under any specified set of conditions is a very simple matter. The steps involved may be outlined as follows:

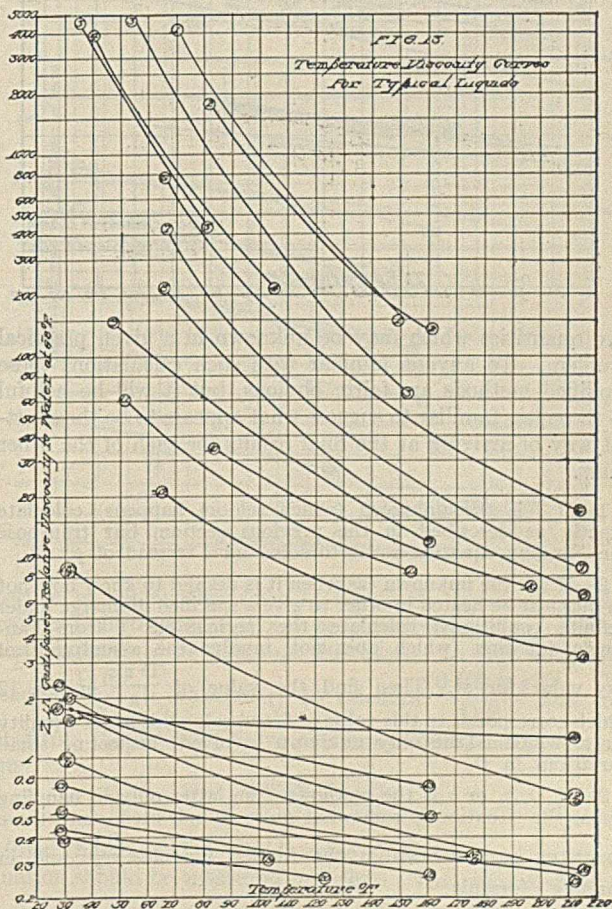
1—Calculate the value of $\frac{D v s}{z}$ (or its equivalent, $\frac{0.408 Q s}{D z}$, if Q is known rather than v) for the fluid and pipe in question. If there is any uncertainty as to the measurement or estimation of any of the quantities, see the subsequent section on determination of the known quantities.

2—By referring to Fig. 12 find the value of f which corresponds to this value of $\frac{D v s}{z}$, using the curve corresponding to the degree of roughness of the pipe in question. (See previous

discussion of Fig. 12.) For values of $\frac{D v s}{z}$ less than 0.002, extrapolations on the straight 45° line for viscous flow may readily be made by *dividing* the abscissae by 10 (or 100) and simultaneously *multiplying* the ordinates by 10 (or 100).

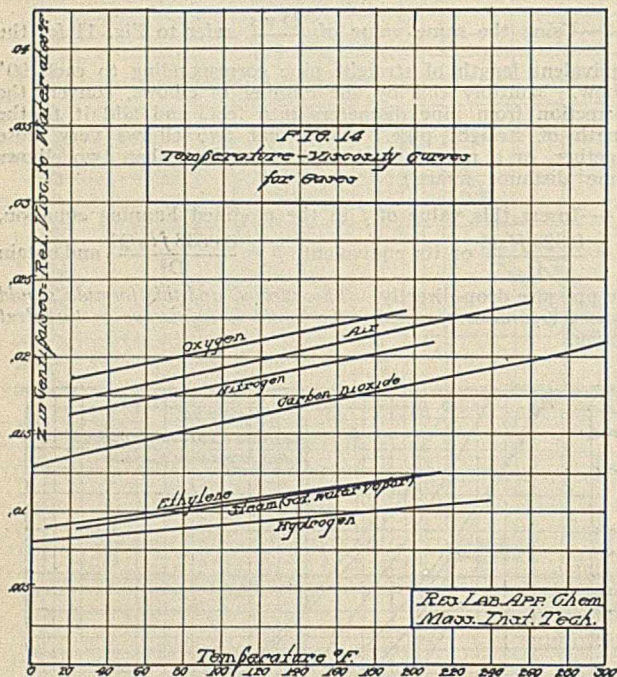
3—Using the same value of $\frac{D v s}{z}$, refer to Fig. 11 for the equivalent length of straight pipe corresponding to each 90° elbow. Multiply this by the number of elbows, convert the correction from pipe diameters into feet, and add it to the length of straight pipe. (Note that two elbows very close together, or a return bend, have less effect than two elbows some distance apart.)

4—Insert this value of f in the modified Fanning equation, $p = \frac{0.323 f l s v^2}{D}$ or its equivalent, $p = \frac{0.0538 f l s Q^2}{D^2}$, and obtain the pressure drop directly. *This method and this formula should be used regardless of whether the liquid is in viscous or turbulent motion.*



- 1—Mexican petroleum (Mex. Pet. Co.) (See Fig. 5)
- 2—Meprolene (Parks-Cramer Co.) (See Fig. 5)
- 3—Cal. heavy crude, 15.2° Bé. (Std. Oil Co.)
- 4—Castor oil (Smithsonian Tables)
- 5—Glycerol (Smithsonian Tables)
- 6—Mobiloil B (Vacuum Oil Co.)
- 7—Mobiloil A (Vacuum Oil Co.)
- 8—Texas engine oil (Vacuum Oil Co.)
- 9—Olive oil (Smithsonian Tables)
- 10—Linseed oil (Smithsonian Tables)
- 11—Cal. light crude 24.4° Bé. (Std. Oil Co.)
- 12—Nonviscous neutral (Vacuum Oil Co.)
- 12A—Amyl alcohol (Opt. inactive) (Smithsonian Tables)
- 13—Mercury (Smithsonian Tables)
- 14—Turpentine (Smithsonian Tables)
- 15—Ethyl alcohol (Smithsonian Tables)
- 16—Water (Smithsonian Tables)
- 16A—Benzene (Smithsonian Tables)
- 17—Octane (Smithsonian Tables)
- 18—Heptane (Smithsonian Tables)
- 19—Carbon disulfide (Smithsonian Tables)
- 20—Hexane (Smithsonian Tables)

GENERAL PROCEDURE FOR CALCULATING OTHER QUANTITIES—The foregoing procedure must, of course, be slightly modified in case the permissible or available pressure drop is known and it is desired to calculate any one of the other



five quantities which may be unknown in a given practical problem. To anyone familiar with such calculations these modified methods are fairly obvious, but it will be helpful to those less familiar to suggest what appears to be the shortest way of arriving at the final results for each of the other cases.

1—If l is the unknown (which seldom happens) calculate exactly as described in the previous section, but transpose the Fanning equation so as to solve for l instead of p .

2—If z is the unknown (as when it is desired to know how hot an oil must be heated in order to give a specified discharge under definite conditions) calculate the permissible f from Fanning's equation (which does not involve the assumption of any value for z). Then find the value of $\frac{D v s}{z}$ in Fig. 12 which corresponds to this value of f , and solve this latter equality for z , which is the only unknown involved (neglecting small variations in s).

3—If D , v , or s is the unknown (the latter only in handling gases) the situation is somewhat more complicated, since these quantities appear both in the friction modulus $\frac{D v s}{z}$ and in Fanning's formula.

These cases may be treated by the customary method of trial and error used by hydraulic engineers, starting with a reasonable value for f , but experience with classes in chemical engineering indicates that for various reasons it is usually preferable to assume a value for the unknown and calculate the resulting pressure drop in the ordinary way. If this comes too high or too low, assume a new value for D , v , or s which will give more nearly the proper pressure drop. By remembering that, for a given Q , p varies inversely as the fourth or fifth power of the diameter, the correct solution can very quickly be obtained. If the first approximation indicates that the value is in the viscous flow region, the simplest way to solve for one of these three variables is to substitute the known quantities directly in Poiseuille's equation,

$$p = \frac{0.000668 z l v}{D^2}$$

or its equivalent,

$$p = \frac{0.000273 z l Q}{D^4}$$

METHODS OF DETERMINING THE KNOWN FACTORS—Six separate variables— D , v , s , p , l , and z —are involved in making the foregoing calculations, five of which must be known in order to solve for the sixth. The determination of the precise values and proper units of these five known quantities sometimes involves difficulties, and it seems desirable to outline the best procedure for determining them in any given case, and to present certain data and conversion charts which will aid in the solution of practical problems.

Viscosity—For use throughout this paper viscosity, z , is expressed in centipoises, which may be more readily visualized as the viscosity relative to water at 68° F., at which temperature water has a viscosity of one centipoise. Data in literature are frequently expressed in poises; these results should be multiplied by 100 to give the viscosity in centipoises.

For many definite chemical compounds entirely satisfactory viscosity data are available in the literature, and data for a number of these and for some commercial oils are presented graphically in Fig. 13. For most commercial purposes, however, it is desirable to make an independent determination of the viscosity of the fluid. To determine this directly in absolute units is difficult and time consuming, but it is possible, for liquids that are distinctly more viscous than water, to employ one of the standard instruments familiar in the oil trade, such as the Saybolt Universal viscosimeter, which measures the time of efflux of a given volume of liquid. For reasons discussed in several papers by the Bureau of Standards, this does not measure the true

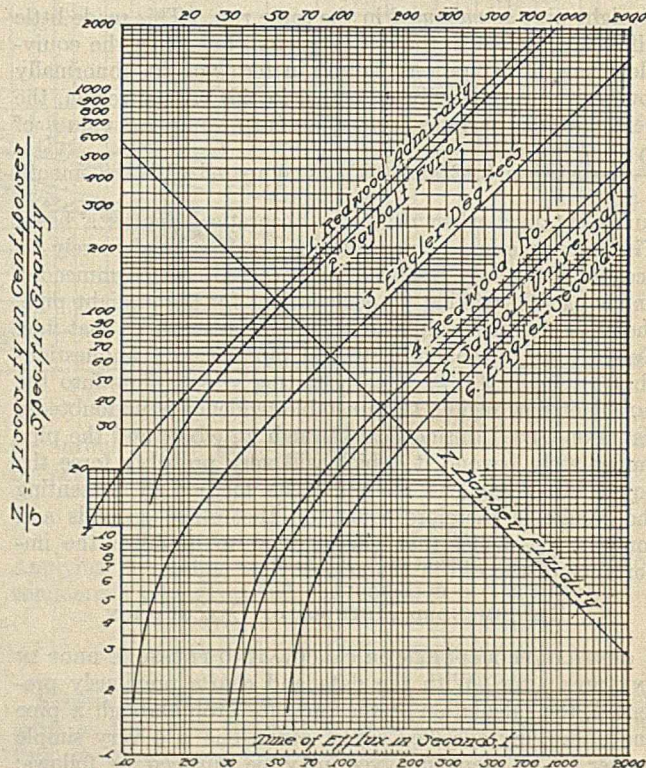


FIG. 15—CONVERSION DIAGRAM FOR VISCOSIMETERS

NOTE: For line 3, Abscissa, scale gives 10 × Engler degrees = 10(t/2). For line 7, Time, $t = 600$, and scale gives flow in cc./hr.

viscosity directly and is not applicable to liquids having a viscosity near that of water, but by the use of the conversion charts presented in Fig. 15²² it is possible to determine the

²² Modified slightly from a chart drawn up by W. H. Herschel (Bureau of Standards). Method due to N. MacCull, of the Texas Co.

correct value of $\frac{z}{s}$ from the readings on any standardized type of viscosimeter. The reciprocal of this ratio may be inserted directly into the expression $\frac{D v s}{z}$, or if z alone is desired it can readily be obtained by multiplying this ratio by s , the specific gravity of the liquid at the temperature in question.

Since the same method of calculation is applicable to most problems involving the flow of gases, data are also appended (Fig. 14) for a number of common gases, including steam. It will be noted that whereas the viscosity of liquids decreases rapidly with increase in temperature, the viscosity of gases increases. It is also important to remember that the viscosity of gases is practically independent of the pressure, though of course the latter factor does affect the density, s , in direct proportion, and hence changes the value of $\frac{D v s}{z}$, as would be expected.

It will be noted that the viscosities of the gases are far lower than those of the liquids, but it so happens that the effect is roughly counterbalanced by other factors—particularly their lower density—so that the values of $\frac{D v s}{z}$ used in handling gases commercially are not far distant from those most used in the flow of liquids.

It will be noted that the data on the viscosity of various fluids are plotted on semi-logarithmic paper, which tends to give rather flat curves and makes it possible to present data on liquids whose viscosities vary greatly and yet get equal percentage accuracy in all parts of the plot. For purposes of extrapolation or of interpolation from two observed points it is preferable to use a method of plotting which gives still flatter curves, and the one which the authors recommend²³ for this purpose is to plot the fluidity (the reciprocal of the viscosity) against the temperature on an ordinary scale. Most oils give nearly a straight line on this type of plot, unless they approach the point where paraffin begins to separate out or other disturbing factors enter into the determination.

Specific Gravity—The value of the specific gravity, s , must be expressed in units relative to water at 39° F. (temperature of maximum density). In other words, it is equivalent to the true density in grams per cc. Specific gravity figures are frequently given relative to water at some other temperature than 39° F. (4° C.) and hence are subject to some slight correction to give the proper value of s for use in the foregoing equations.

To convert Baumé readings to specific gravity use the formula $s = \frac{140}{130 + B\acute{e}}$ ²⁴ for liquids lighter than water.

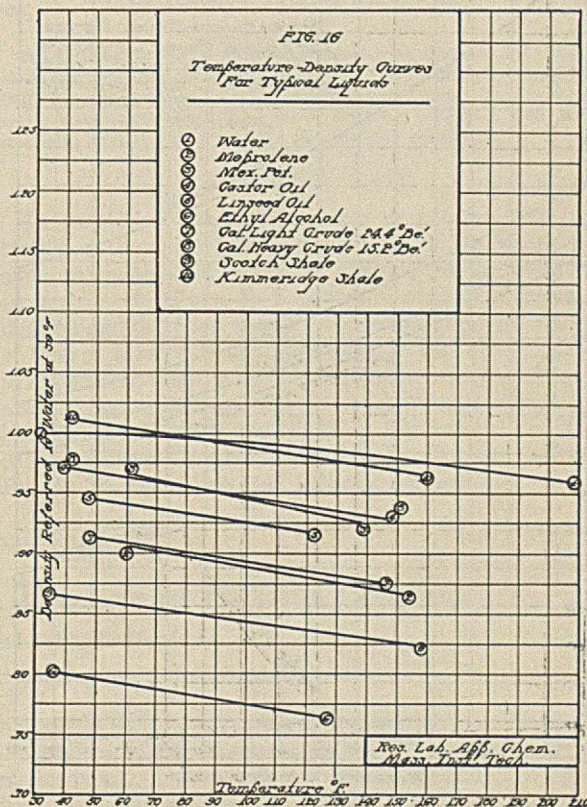
For convenience, Fig. 16 gives typical density curves for various liquids as a function of temperature, and Fig. 17 gives the same data for the commoner gases. In dealing with gases, care should be taken to use an average value if the pressure drop through the line is enough to cause appreciable variations in this factor.

Length of Pipe—This is, of course, measured in feet and the only precaution to be observed is to add to the actual length the equivalent length of pipe due to elbows, as found by using Fig. 11. For pipes less than 500 diameters long consideration must be given to entrance and exit losses, as pointed out later under "limitations."

²³ More exact methods have been proposed, but are too complicated for most practical purposes.

²⁴ While this is the official B. of S. Baumé scale, the great bulk of the oil trade uses instruments calibrated on a scale which gives 141.5 instead of 140 for this figure.

Velocity—Velocity should be expressed in ft. per sec., and means the effective average velocity in the pipe, obtained by dividing the rate of discharge in cu. ft. per sec. by the cross-sectional area of the pipe in sq. ft. Data may be transposed from gal. per min. to velocity in ft. per sec., or vice versa, by the conversion formula, $v = \frac{0.408 Q}{D^2}$. It is also



possible to use another form of Fanning's equation, which involves Q instead of v if any considerable number of calculations have to be made on this basis. In this case, instead of $\frac{D v s}{z}$, it is necessary to calculate $\frac{0.408 Q s}{D z}$ and to substitute the resulting value of f from Fig. 12 in the equation

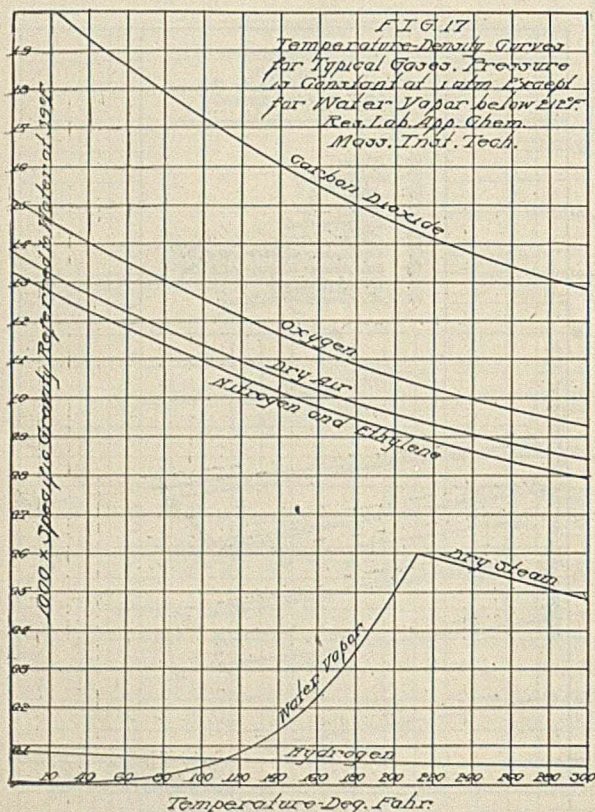
$$p = \frac{0.0538 f l s Q^2}{D^5}$$

Pipe Diameter—The inside pipe diameter used in this equation should be measured in inches. The nominal diam-

TABLE II—DIAMETER FUNCTIONS OF STANDARD IRON AND STEEL PIPE

Nominal Diameter In.	D Actual Inside Diameter In.	D ²	D ⁴	D ⁵	Actual Internal Cross-section Area Sq. In.
0.5	0.622	0.3869	0.1497	0.09310	0.3039
0.75	0.824	0.6790	0.4610	0.3799	0.5333
1.0	1.049	1.100	1.211	1.270	0.8639
1.5	1.610	2.592	6.719	10.82	2.036
2.0	2.067	4.272	18.25	37.73	3.356
2.5	2.469	6.096	37.16	91.75	4.786
3.0	3.068	9.413	88.60	271.8	7.392
4.0	4.026	16.21	262.7	1058.0	12.73
6.0	6.065	36.78	1353.0	8206.0	28.89
8.0	8.071	65.14	4243.0	34250.0	51.15
8.0	7.981	63.70	4057.0	32380.0	50.02
10.0	10.192	103.8	10790.0	109980.0	81.55
10.0	10.136	102.7	10560.0	106990.0	80.75
10.0	10.020	100.4	10080.0	101000.0	78.82
12.0	12.090	145.9	21370.0	258300.0	114.80
12.0	12.000	144.0	20736.0	248800.0	113.10
14.0	13.250	175.5	30750.0	407500.0	137.7
16.0	15.250	232.5	54200.0	825100.0	182.7
18.0	17.250	297.2	88500.0	1526000.0	224.0
20.0	19.250	370.5	137300.0	2640000.0	291.1
24.0	23.250	540.0	291900.0	6777000.0	424.5

eters used to identify commercial pipes do not correspond to actual inside diameters, but their exact dimensions have been quite well standardized within recent years, and the accepted figures for each nominal size of pipe are given in Table II. For precise work the diameters should be measured accurately, as this factor enters to the fourth or fifth power in some of the equations used.



Pressure Drop—The pressure drop should be expressed in lbs. per sq. in. If the data are given in any other form they may be converted by the use of Table III. If it is desired to calculate the theoretical horse power required, the following formula can be used:

$$H. p. = \frac{19.2 \times \text{gal./min.} \times \text{press. drop in lbs./sq. in.}}{33,000}$$

The actual horse power required equals this figure divided by the efficiency of the pump as a whole.

TABLE III

x	To Convert x to Lbs./Sq. In. Multiply by	To Convert Lbs./Sq. In. to x Multiply by
Lbs./sq. ft.	0.00695	144.
Cm. mercury	0.1934	5.171
Atmospheres	14.70	0.06804
Liquid head expressed in ft. ¹	0.4332 s	$\frac{2.309}{s}$

¹ This equals pressure drop in lbs. per sq. ft. divided by the liquid density at that point, which = 62.3 s.

LIMITATIONS TO APPLICATION OF RECOMMENDED METHOD OF CALCULATION—The data and methods of calculation given in this article cover substantially the entire field of the flow of all fluids, including gases and dry vapors, through commercial pipe lines. There are, however, a few exceptions which should be carefully noted before attempting to use the formula in certain special cases. These may be specified as follows:

1—The method is not directly applicable to the flow of gases where the drop in pressure along the pipe line is more than 10 or 15 per cent of the final absolute pressure, because the density

and velocity of the fluid are thereby changed. If, however, average values are used for the density and velocity, instead of the initial or final values, this formula may be used for pressure drops up to 40 or 50 per cent without serious error. To make calculations for compressed air lines with still larger drops in pressure, it is necessary to use an approximate integrated form of the equation, which has previously been discussed by Lewis.²⁵ The regular method of calculation may, however, be used for all ordinary problems of handling air through circular ducts or steam in pipes lines.

2—The method is not applicable to flow through short sections of pipe opening into large chambers where the entrance and exit losses are appreciable in comparison with the friction losses through the pipe. These losses become inappreciable when the pipe is more than 1000 diameters long, and may generally be neglected for approximate calculations for lines longer than 300 diameters. For shorter tubes the reader is referred to the recent comprehensive treatment of Herschel.²⁶

3—The method is not applicable to the flow of semisolid plastic materials, such as asphalt, clay suspensions, very viscous colloidal solutions, etc., where the laws of flow are modified by the tendency of the material to behave like a solid under certain conditions.

4—Precautions must be observed, and highly accurate results cannot be expected in cases: (a) where the pipe is badly corroded or tuberculated, and the apparent value of f may increase to double that given in the formula, owing partly to a decrease in the effective cross-sectional area; (b) where a hot oil is passing through a pipe line in straight line flow, and the existence of a large temperature gradient from the inside to the outside makes accurate calculations practically impossible; and (c) where there is any tendency to precipitate out solids (such as paraffin wax) on the walls or in the bottom of the pipe lines.

With these exceptions it is believed that the recommended method of calculation is applicable to an entirely satisfactory degree of accuracy to all commercial problems involving the flow of fluids through pipe lines.

ILLUSTRATIVE EXAMPLES

To illustrate the practical utilization of the foregoing charts and tables, two typical examples are appended herewith.

EXAMPLE 1—CALCULATION OF REQUIRED PRESSURE DROP

It is desired to transmit 20 U.S. gal. per min. (686 oil bbls. per 24 hrs., based on 1 oil bbl. = 42 U.S. gal.) of a very viscous oil at 70° F. through a standard 6-in. steel pipe line. What will be the pressure drop as lbs. per sq. in. per mi.?

DATA—The oil at 70° F. has a time of 9050 sec. in a Saybolt Universal viscosimeter and a gravity corresponding to 15.2° Bé.

SOLUTION—From Table II, one sees that $D = 6.07$ in. and $D^2 = 36.78$.

Since the average velocity = $\frac{0.408 Q}{D^2}$, $v = \frac{0.408 \times 20}{36.78} = 0.222$ ft. per sec.

From Fig. 15 it is seen that the value of $\frac{z}{s}$, corresponding to a time of 9050 Saybolt sec., is 1990.

Hence the numerical value of

$$\frac{D v s}{z} = \frac{6.07 \times 0.222}{1990} = 0.000677,$$

and the value of f corresponding (Fig. 12) is 3.06 (extrapolation made by multiplying ordinate and dividing abscissae scales by 10).

The specific gravity at 70° F. = $\frac{140}{130 + 15.2} = 0.964$.

The value of p is figured from the modified Fanning equation:

$$p = \frac{0.323 f l s v^2}{D} = \frac{0.323 \times 3.06 \times 5.280 \times 0.964 \times 0.222^2}{6.07} = 40.8 \text{ lbs. per sq. in.}$$

Thus it is found that this oil flowing at an average velocity of 0.222 ft. per sec. gives a pressure drop of 41 lbs. per sq. in. per mi.

EXAMPLE 2—CALCULATION OF DIAMETER REQUIRED

Dry compressed air at 80° F. must be delivered through 200 ft. of straight steel pipe connected by means of three standard elbows at a rate equivalent

²⁵ THIS JOURNAL, 8 (1916), 1133.

²⁶ "The Flow of Liquids through Short Tubes," *Proc. Am. Soc. Civil Eng.*, 84 (1921), 527.

to 1000 cu. ft. of "free" air per min. The initial air is at a pressure of 150 lbs. per sq. in. What size of standard steel pipe must be used in order that the drop in pressure shall not exceed 10 lbs. per sq. in.?

SOLUTION—From Fig. 14, $s = 0.0188$ at 80° F.

From Fig. 17, $s = 0.00118$ at 80° F. and 1 atm. Since the average pressure is $\frac{150 + 140}{2 \times 14.7} = 9.87$ atm., $s = 9.87 \times 0.00118 = 0.01165$.

Since free air refers to air at 1 atm. and 70° F. the actual volume at 80° F. (540° F. absolute) and 9.87 atm. pressure is

$$\frac{1000 \times 540}{9.87 \times 530} = 103.2 \text{ cu. ft. per min.,}$$

and $v = \frac{103.2 \times 144}{60 \times 0.785 D^2} = \frac{315}{D^2}$ ft. per sec. at 80° F. and a mean pressure of 9.87 atm.

$$\text{Then } \frac{D v s}{z} = \frac{D \times \frac{315}{D^2} \times 0.01165}{0.0188} = \frac{195}{D} \quad (a)$$

Taking the equivalent length of each elbow as 30 pipe diameters,

$$1 = 200 + \frac{3 \times 30 D}{12} = 200 + 7.5 D.$$

$$\text{But } p = \frac{0.323 f l s v^2}{D^5}$$

$$\text{so } p = \frac{0.323 f [200 + 7.5 D] 0.01165 \times (315)^2}{D^5}$$

$$p = \frac{374 f [200 + 7.5 D]}{D^5} = \frac{\text{Lbs.}}{\text{Sq. in.}} \quad (b)$$

As noted above, one may assume a value of D actually obtainable, find

from Fig 12 the corresponding value of $\frac{D v s}{z}$, and calculate p . The result of such procedure is shown below.

Nominal Dia.	Actual Dia. (D)	(From Eq. a)	f (From Fig. 12)	D^5 (Table II)	p (From Eq. b)
1.5	1.61	121 ¹	0.0041	10.82	30.1
2	2.07	94.3	0.0043	37.7	9.2

¹ The friction factor for this case was taken from Fig. 10, as Fig. 12 does not show f for values of $\frac{D v s}{z}$ beyond 100.

It should be noted that although the first trial diameter (1.61 in.) called for a pressure drop of 30 lbs. per sq. in., a diameter only slightly larger (2.07 in.) gave practically the desired pressure drop. This is because p varies inversely as the fifth power of diameter. Hence a 2-in. standard steel pipe must be used to meet the specified conditions.

ACKNOWLEDGMENT

In conclusion the writers desire to express their appreciation of the many helpful suggestions of Dr. W. K. Lewis, at whose instigation this work was first undertaken; of the accurate work of Mr. V. V. Kendall, who aided in the conduction and direction of much of the experimental work; and of that of Messrs. Kite and Kennedy, who made the runs in the turbulent and critical flow regions. Acknowledgments are also due to the various cooperating companies mentioned in the introduction; and to Mr. R. S. Danforth of The Kinney Manufacturing Company, and Dr. W. H. Herschel of the Bureau of Standards, for valuable suggestions.

The Determination of Carbon Dioxide in Baking Powder^{1,2}

By C. S. Robinson³ and Selma L. Bandemer

MICHIGAN AGRICULTURAL COLLEGE EXPERIMENT STATION, EAST LANSING, MICHIGAN

The gasometric method for the determination of carbon dioxide in baking powder is as accurate as the absorption methods. It is much more rapid and requires but a single piece of apparatus. It can be used for the determination of both total and residual carbon dioxide.

At the 1920 meeting of the Association of Official Agricultural Chemists the senior author suggested, as a substitute for the present official methods for determining total carbon dioxide in baking powder, a modification of the gasometric method originally devised by Van Slyke for the determination of carbon dioxide in blood plasma.⁴

Its use has since been extended to the estimation of residual carbon dioxide. The object of the present paper is to describe this procedure and report the results obtained with it.

PROCEDURE

TOTAL CARBON DIOXIDE—The procedure for the determination of total carbon dioxide in baking powder is identical with that for the analysis of marl and limestone as given in the original description of the method, except that 100-mg. samples are used.

RESIDUAL CARBON DIOXIDE—A 2-g. sample of the well-mixed material is weighed into a small beaker and 20 cc. of distilled water are added. The mixture is thoroughly stirred, allowed to stand for 20 min. at room temperature, and set in a bath of boiling water for the same length of time. Fi-

nally it is boiled for 1 min. The addition of a drop or two of octyl alcohol to reduce foaming is sometimes advisable at this point. One sample is diluted to 25 cc. in a volumetric flask, and 1-cc. samples are used for the determination.

The accompanying table shows the results obtained with this method and with the two official methods. They are typical of the agreement of results which have been obtained in this laboratory with all sorts of carbonates during the past year.

COMPARISON OF OFFICIAL AND GASOMETRIC METHODS FOR DETERMINING CARBON DIOXIDE IN BAKING POWDER

	Total Carbon Dioxide				
	Ia	IIa	IIIa	IVa	Va
	(CaCO ₃)				
Official method	43.34	13.54	13.48	16.73	14.62
	43.81	13.29	13.11	17.03	14.35
	43.70	13.30	13.48	16.90	14.29
Gasometric	43.78	13.55	13.34	17.03	14.52
	43.70	13.52	13.31	16.89	14.52
	43.78	13.52	13.29	16.92	14.53
	Residual Carbon Dioxide				
	Ib	IIb	IIIb	IVb	Vb
Official method, Heidenhain	0.73	1.15	1.74	5.51	1.27
Knorr	0.85	1.26	1.51	5.26	1.39
Gasometric	0.75	1.16	1.63	5.45	1.35
	0.75	1.31	1.59	5.62	1.27

In order to test the method when a product contained a water-insoluble carbonate, Sample IVb was made up by mixing Sample Vb and calcium carbonate. Duplicate results agreed as closely as did those with other products.

Only one source of trouble has been encountered. It has been found necessary to lubricate the stopcocks of the apparatus rather frequently with a heavy grease to prevent leakage during the maintenance of the high vacuum used. If the carbon dioxide is absorbed each time and the residual air measured instead of being calculated from the table, this source of error is avoided. With proper attention to stopcocks, however, this is unnecessary.

¹ Received November 3, 1921.

² Published as Journal Article No. 20 from the Chemical Laboratory of the Michigan Agricultural College Experiment Station. Published by permission of the Director of the Experiment Station.

³ Research Associate in Chemistry.

⁴ *J. Biol. Chem.*, **30** (1917), 347; *Soil Sci.*, **10** (1920), 41.

eters used to identify commercial pipes do not correspond to actual inside diameters, but their exact dimensions have been quite well standardized within recent years, and the accepted figures for each nominal size of pipe are given in Table II. For precise work the diameters should be measured accurately, as this factor enters to the fourth or fifth power in some of the equations used.

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$$p = \frac{0.323 f l s v^2}{D} = \frac{0.323 \times 3.06 \times 5.280 \times 0.964 \times 0.222^2}{6.07} = 40.8 \text{ lbs. per sq. in.}$$

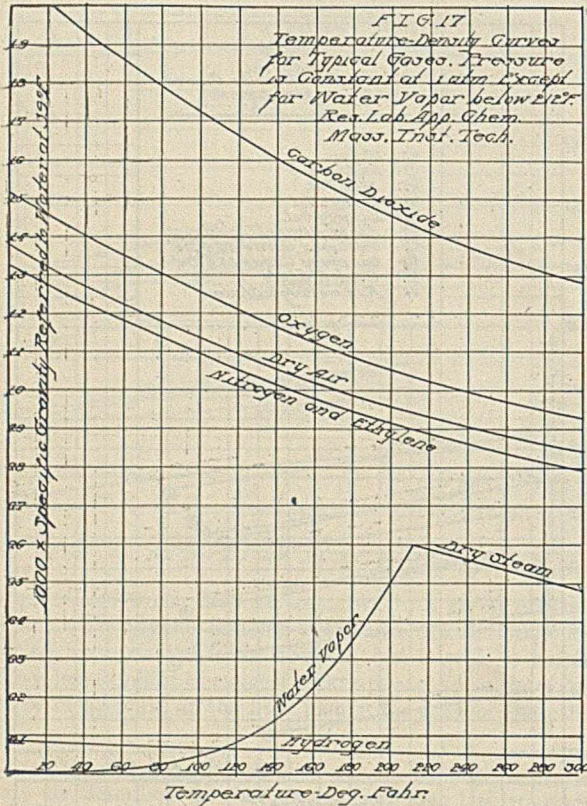
Thus it is found that this oil flowing at an average velocity of 0.222 ft. per sec. gives a pressure drop of 41 lbs. per sq. in. per mi.

EXAMPLE 2—CALCULATION OF DIAMETER REQUIRED

Dry compressed air at 80° F. must be delivered through 200 ft. of straight steel pipe connected by means of three standard elbows at a rate equivalent

²⁵ THIS JOURNAL, 8 (1916), 1133.

²⁶ "The Flow of Liquids through Short Tubes," Proc. Am. Soc. Civil Eng., 84 (1921), 527.



Pressure Drop—The pressure drop should be expressed in lbs. per sq. in. If the data are given in any other form they may be converted by the use of Table III. If it is desired to calculate the theoretical horse power required, the following formula can be used:

$$H. p. = \frac{19.2 \times \text{gal./min.} \times \text{press. drop in lbs./sq. in.}}{33,000}$$

The actual horse power required equals this figure divided by the efficiency of the pump as a whole.

TABLE III

<i>x</i>	To Convert <i>x</i> to Lbs./Sq. In. Multiply by	To Convert Lbs./Sq. In. to <i>x</i> Multiply by
Lbs./sq. ft.	0.00695	144.
Cm. mercury	0.1934	5.171
Atmospheres	14.70	0.06804
Liquid head expressed in ft. ¹	0.4332 <i>s</i>	$\frac{2.309}{s}$

¹ This equals pressure drop in lbs. per sq. ft. divided by the liquid density at that point, which = 62.3 *s*.

LIMITATIONS TO APPLICATION OF RECOMMENDED METHOD OF CALCULATION—The data and methods of calculation given in this article cover substantially the entire field of the flow of all fluids, including gases and dry vapors, through commercial pipe lines. There are, however, a few exceptions which should be carefully noted before attempting to use the formula in certain special cases. These may be specified as follows:

1—The method is not directly applicable to the flow of gases where the drop in pressure along the pipe line is more than 10 or 15 per cent of the final absolute pressure, because the density

to 1000 cu. ft. of "free" air per min. The initial air is at a pressure of 150 lbs. per sq. in. What size of standard steel pipe must be used in order that the drop in pressure shall not exceed 10 lbs. per sq. in.?

SOLUTION—From Fig. 14, $s = 0.0188$ at 80°F .

From Fig. 17, $z = 0.00118$ at 80°F . and 1 atm. Since the average pressure is $\frac{150 + 140}{2} = 9.87$ atm., $s = 9.87 \times 0.00118 = 0.01165$.

Since free air refers to air at 1 atm. and 70°F . the actual volume at 80°F . (540°F . absolute) and 9.87 atm. pressure is

$$\frac{1000 \times 540}{9.87 \times 530} = 103.2 \text{ cu. ft. per min.,}$$

and $v = \frac{103.2 \times 144}{60 \times 0.785 D^2} = \frac{315}{D^2}$ ft. per sec. at 80°F . and a mean pressure of 9.87 atm.

$$\text{Then } \frac{D v s}{z} = \frac{D \times \frac{315}{D^2} \times 0.01165}{0.0188} = \frac{195}{D} \quad (a)$$

Taking the equivalent length of each elbow as 30 pipe diameters,

$$l = 200 + \frac{3 \times 30 D}{12} = 200 + 7.5 D.$$

$$\text{But } p = \frac{0.323 f l s v^2}{D^5}$$

$$\text{so } p = \frac{0.323 f [200 + 7.5 D] 0.01165 \times (315)^2}{D^5}$$

$$p = \frac{374 f [200 + 7.5 D]}{D^5} = \frac{\text{Lbs.}}{\text{Sq. in.}} \quad (b)$$

As noted above, one may assume a value of D actually obtainable, find

from Fig 12 the corresponding value of $\frac{D v s}{z}$, and calculate p . The result of such procedure is shown below.

Nominal Dia.	Actual Dia. (D)	$\frac{D v s}{z}$ (From Eq. a)	f (From Fig. 12)	D^5 (Table II)	p (From Eq. b)
1.5	1.61	121 ¹	0.0041	10.82	30.1
2	2.07	94.3	0.0043	37.7	9.2

¹ The friction factor for this case was taken from Fig. 10, as Fig. 12 does not show f for values of $\frac{D v s}{z}$ beyond 100.

It should be noted that although the first trial diameter (1.61 in.) called for a pressure drop of 30 lbs. per sq. in., a diameter only slightly larger (2.07 in.) gave practically the desired pressure drop. This is because p varies inversely as the fifth power of diameter. Hence a 2-in. standard steel pipe must be used to meet the specified conditions.

ACKNOWLEDGMENT

In conclusion the writers desire to express their appreciation of the many helpful suggestions of Dr. W. K. Lewis, at whose instigation this work was first undertaken; of the accurate work of Mr. V. V. Kendall, who aided in the conduction and direction of much of the experimental work; and of that of Messrs. Kite and Kennedy, who made the runs in the turbulent and critical flow regions. Acknowledgments are also due to the various cooperating companies mentioned in the introduction; and to Mr. R. S. Danforth of The Kinney Manufacturing Company, and Dr. W. H. Herschel of the Bureau of Standards, for valuable suggestions.

The Determination of Carbon Dioxide in Baking Powder^{1,2}

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The gasometric method for the determination of carbon dioxide in baking powder is as accurate as the absorption methods. It is much more rapid and requires but a single piece of apparatus. It can be used for the determination of both total and residual carbon dioxide.

.....

At the 1920 meeting of the Association of Official Agricultural Chemists the senior author suggested, as a substitute for the present official methods for determining total carbon dioxide in baking powder, a modification of the gasometric method originally devised by Van Slyke for the determination of carbon dioxide in blood plasma.⁴

Its use has since been extended to the estimation of residual carbon dioxide. The object of the present paper is to describe this procedure and report the results obtained with it.

PROCEDURE

TOTAL CARBON DIOXIDE—The procedure for the determination of total carbon dioxide in baking powder is identical with that for the analysis of marl and limestone as given in the original description of the method, except that 100-mg. samples are used.

RESIDUAL CARBON DIOXIDE—A 2-g. sample of the well-mixed material is weighed into a small beaker and 20 cc. of distilled water are added. The mixture is thoroughly stirred, allowed to stand for 20 min. at room temperature, and set in a bath of boiling water for the same length of time. Fi-

nally it is boiled for 1 min. The addition of a drop or two of octyl alcohol to reduce foaming is sometimes advisable at this point. One sample is diluted to 25 cc. in a volumetric flask, and 1-cc. samples are used for the determination.

The accompanying table shows the results obtained with this method and with the two official methods. They are typical of the agreement of results which have been obtained in this laboratory with all sorts of carbonates during the past year.

COMPARISON OF OFFICIAL AND GASOMETRIC METHODS FOR DETERMINING CARBON DIOXIDE IN BAKING POWDER

	Total Carbon Dioxide				
	Ia (CaCO ₃)	IIa	IIIa	IVa	Va
Official method	43.34	13.54	13.48	16.73	14.62
	43.81	13.29	13.11	17.03	14.35
	43.70	13.30	13.48	16.90	14.29
Gasometric	43.78	13.55	13.34	17.03	14.52
	43.70	13.52	13.31	16.89	14.52
	43.78	13.52	13.29	16.92	14.53
	Residual Carbon Dioxide				
	Ib	IIb	IIIb	IVb	Vb
Official method, Heidenhain	0.73	1.15	1.74	5.51	1.27
	0.85	1.26	1.51	5.26	1.39
Knorr	0.75	1.16	1.63	5.45	1.35
	0.75	1.31	1.59	5.62	1.27
Gasometric					

In order to test the method when a product contained a water-insoluble carbonate, Sample IVb was made up by mixing Sample Vb and calcium carbonate. Duplicate results agreed as closely as did those with other products.

Only one source of trouble has been encountered. It has been found necessary to lubricate the stopcocks of the apparatus rather frequently with a heavy grease to prevent leakage during the maintenance of the high vacuum used. If the carbon dioxide is absorbed each time and the residual air measured instead of being calculated from the table, this source of error is avoided. With proper attention to stopcocks, however, this is unnecessary.

¹ Received November 3, 1921.

² Published as Journal Article No. 20 from the Chemical Laboratory of the Michigan Agricultural College Experiment Station. Published by permission of the Director of the Experiment Station.

³ Research Associate in Chemistry.

⁴ *J. Biol. Chem.*, **30** (1917), 347; *Soil Sci.*, **10** (1920), 41.

Phthalic Anhydride. V—The Preparation of Phthalic Anhydride by the Catalysis of the Vapor Phase Reaction between Naphthalene and Atmospheric Air^{1,2}

By Courtney Conover and H. D. Gibbs

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So far as revealed by the literature, phthalic acid and phthalic anhydride always have been prepared on a commercial scale by the oxidation of naphthalene or some of its simpler derivatives. In the methods used up to the last few years of the nineteenth century comparatively expensive chemicals, such as nitric acid or chromic acid, were used as the oxidizing agents.³ During the last decade of the nineteenth century the growing demand for phthalic anhydride for use in the preparation of xanthene and the indigoid dyes led to research toward the discovery of cheaper processes for its manufacture. A method for converting naphthalene to phthalic anhydride, using sulfuric acid as the oxidizing agent in the presence of a mercury salt as a catalyst, was discovered by E. Sapper, and was patented by the Badische Anilin und Soda Fabrik⁴ in 1896. From then until now this process has been commonly described as the commercial method for making phthalic anhydride. It is said to have been employed on an enormous scale by the Badische Anilin und Soda Fabrik in connection with their manufacture of synthetic indigo, and it is interesting to note that the present contact process for producing sulfuric acid is a result of efforts to utilize the sulfur dioxide formed during the process.⁵

When importations of phthalic anhydride from Germany were interrupted during the war, many attempts were made in this country to prepare phthalic anhydride by this sulfuric acid oxidation process as described in the patents and in chemical literature. The difficulties discovered in its application and the disappointing yields resulting from its use have been mentioned by Gibbs.⁶ Even when most successfully put into practice, the method is unsuitable for small-scale operation. The large quantities of sulfur dioxide evolved create a nuisance or must be converted into sulfur trioxide by means of expensive apparatus.

Other processes for the manufacture of phthalic anhydride have been patented or described in the literature in recent years by Prochazka,⁷ Imray,⁸ Ditz,⁹ and others,¹⁰ while improvements on the sulfuric acid and mercury process have

been patented by Greenley¹¹ and Takahashi.¹² So far as known these processes have not been found in practice to have any great advantage over the older sulfuric acid process.

In studying the sulfuric acid oxidation process, the writers soon realized its many disadvantages, and, of other possible methods, it was concluded that the direct oxidation of naphthalene with air in the presence of a catalyst, if feasible, would be ideal in simplicity and cheapness. The possibility of the successful development of a process of this nature was suggested by the oxidation of toluene to benzaldehyde and benzoic acid with air in the presence of catalysts, which had been successfully carried out by Gibbs.⁶ Vanadium pentoxide and molybdenum trioxide had been found to be the best catalysts in this process.

In the first attempts to prepare phthalic anhydride by the catalytic oxidation of naphthalene in the gas phase, a crude form of apparatus was assembled which permitted the mixing of naphthalene vapor with oxygen or air in approximately known proportions and bringing the mixed gases in contact with the catalyst at temperatures up to about 500°. The temperatures were measured roughly. In the few experiments where oxygen was used it was found that with vanadium pentoxide at temperatures around 275° and with molybdenum trioxide at temperatures around 325° there was some darkening of the naphthalene which condensed, some formation of carbon dioxide, and some development of acidity. But if the temperature rose above 300°, in the case of vanadium pentoxide, or 350°, in the case of molybdenum trioxide, ignition of the naphthalene vapor took place, sometimes with violent explosions. If the temperature was kept at a safe point the development of acid was very slight. When air was substituted for oxygen it was found that the temperature could be raised to nearly 500° without ignition of the vapors and that at these higher temperatures the product condensed contained considerable quantities of acid. It was demonstrated that phthalic anhydride was present in this condensate.

COMPARISON OF CATALYTIC EFFECT OF VARIOUS SUBSTANCES FOR CONVERSION OF NAPHTHALENE TO PHTHALIC ANHYDRIDE

PLAN OF TESTS—Since it had been shown that naphthalene was converted to phthalic anhydride when naphthalene vapor and air were brought into contact with certain catalysts at temperatures above 350°, it was planned to test each of a number of possible catalysts under fairly uniform conditions in order to discover the substance most suitable for the catalysis of this reaction. It was planned to mix a known weight of naphthalene vapor with a known volume of air, to keep the two gases in proportions practically the same as those required by theory for the oxidation of naphthalene to phthalic anhydride, to carry out the reaction at the highest temperature which could be maintained without ignition, to condense all the solid and liquid products of the reaction, and to determine the total acid formed and the total naphthalene recovered.

Since the object of the experiments was to develop a practical process for the manufacture of phthalic anhydride rather than to study the catalytic action of the substances

¹ Received September 28, 1921.

² Published as Contribution No. 53 from the Color Laboratory of the Bureau of Chemistry, U. S. Department of Agriculture.

³ H. Lüddens, *Chem.-Zig.*, **15** (1891), 585; *J. Soc. Chem. Ind.*, **10** (1891), 758.

⁴ D. R. P. 91,202 (1896); Brit. Patent 18,221 (1896). See *Chem. Zentr.*, **68** (1897), I, 1040; *J. Soc. Chem. Ind.*, **16** (1897), 676.

⁵ "The History of the Development of the Manufacture of Indigo." Lecture delivered by Brunck on the dedication of the Hofmann Memorial in Berlin, October 20, 1900.

⁶ "Phthalic Anhydride. I—Introduction," *THIS JOURNAL*, **11** (1919), 1031.

⁷ *Ber.*, **30** (1897), 3108. Naphthalene is oxidized to phthalic acid by means of permanganate in boiling water.

⁸ Brit. Patent 15,527 (1901). Naphthols and other naphthalene derivatives are oxidized to phthalic acid by heating in alkaline solution with various metallic oxides or peroxides. The same processes are described in D. R. P. 138,790 (1903), 139,956 (1903), and 140,999 (1903). A similar process is described in D. R. P. 136,410 (1902). See *J. Chem. Soc. (Abstr.)*, **84** (1903), 487, 561; *J. Soc. Chem. Ind.*, **20** (1901), 1139; *Chem. Zentr.*, **73** (1902), II, 1371; **74** (1903), II, 1106.

⁹ *Chem.-Zig.*, **29** (1905), 581; *J. Chem. Soc. (Abstr.)*, **88** (1905), 516. Naphthalene is oxidized by sulfuric acid in the presence of salts of the rare earths, mainly Ce salts. The process is described in D. R. P. 158,609 (1905). See *Chem. Zentr.*, **76** (1905), I, 841.

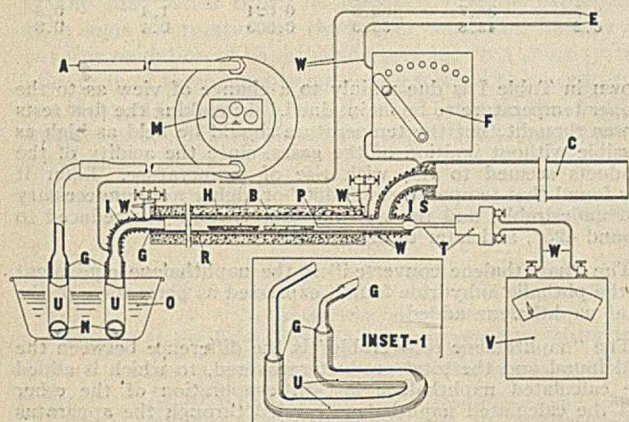
¹⁰ D. R. P. 152,063 (1904). Naphthalene is oxidized electrolytically to naphthoquinones or phthalic acid in an acid solution, using a Ce salt as a catalyst.

¹¹ U. S. Patent 1,261,022 (1918); *C. A.*, **12** (1918), 1558.

¹² *Jap. Patent* 31,387 (1917); *C. A.*, **12** (1918), 157.

as a matter of scientific interest, no great care was taken to prepare absolutely pure chemical compounds for use as catalysts, to attain any great precision in quantitative measurements, or to hold the conditions under which the experiments were made absolutely uniform in the different tests.

PREPARATION OF CATALYSTS—Most of the substances selected as possible catalysts were metallic oxides. Oxides, such as those of arsenic, antimony, lead, and zinc, which might volatilize or form volatile products under the condition of the experiment, were believed to be impracticable and were not tested. The state of oxidation of the metallic oxides selected for testing was felt to be of little importance, since the final state of oxidation undoubtedly would depend upon the conditions of the experiment.



The metallic oxides were in some cases purchased as such. Several were prepared by igniting nitrates of the metals, and a few from other salts by common methods. Vanadium pentoxide was made by heating ammonium metavanadate at about 200° until the hot material no longer smelled of ammonia. Chromium sesquioxide and manganese sesquioxide were prepared from chromium trioxide and manganese dioxide, respectively, by heating these oxides to low redness and adding naphthalene in small portions to the hot material until there was no ignition. Platinum was deposited in a finely divided form upon magnesium oxide by mixing solutions of platinum chloride and magnesium nitrate, evaporating the mixture to dryness, igniting the residue, treating the product with ammonia water, drying, and igniting again. The product contained about 5 per cent of platinum.

Some of these catalysts were prepared from chemicals supposed to be of the very highest purity, but most of them were made from C. P. chemicals which had been examined and passed as suitable for use as analytical reagents.

APPARATUS—A great deal of trouble was experienced in discovering a form of apparatus which would permit the desired control of conditions and measurements of results, and which would endure the temperature desired. The form finally developed is shown in the figure. Apparatus of this general form was used not only for this series of experiments but for numerous others in connection with the development of the process described in this paper. It was found to be of fairly general application in making tests of catalytic gas-phase reactions.

A is the air supply and M is a dry gas meter which measures the air. In U the naphthalene is volatilized and the vapor mixed with air. It is a U-tube with the ends bent at right angles to the plane of the U so that it will lie on the bottom of the oil bath O, with the ends of the tube above the surface of the oil. Its form can be seen in the inset. Outlet and inlet tubes are fitted into it with ground-glass joints, G. The tube is of Pyrex glass and has an inside diameter of about

2 cm. It is charged with naphthalene, N, in such quantity that the portion of the tube lying on the bottom of the oil bath is not quite filled. Hence the air passes over the melted naphthalene but does not bubble through it.

The outlet of the U-tube is covered with a thin sheet of asbestos, I, and is heated with a few turns of resistance wire, W, so that it will not be closed by the solidification of naphthalene on the walls. This outlet is connected to the reaction tube R by a ground-glass joint, G.

The reaction tube R is made of Pyrex glass. It is 65 cm. in length and has an inside diameter of about 2 cm. It branches at the rear end, a thermocouple being inserted through the straight branch while the effluent gases are led off through the side branch. The catalyst is placed in the reaction tube in porcelain combustion boats, B, which are about 75 mm. long, 15 mm. wide, and 8 mm. high.

The condenser C is simply an air-cooled glass tube of about 5 cm. inside diameter. A tube of this diameter and about 80 cm. long, with a plug of cotton wool in the open end, was found adequate to collect all visible solid reaction products when the production of phthalic anhydride was high. In other cases two connected tubes with a total length of 175 cm. were used. The condenser C is fitted on to the reaction tube R by means of a built-up asbestos stopper.

The reaction tube R lies in a copper heating tube, H, which is heated by the resistance wire W. The copper tube is covered with a thin layer of sheet asbestos, the resistance wire is wound upon this, and the whole is heavily insulated with asbestos. The current which heats tube H also passes through sections of resistance wire wound upon the outlet of tube U and upon the side branch of the reaction tube. These sections of resistance wire are connected by means of binding posts, so that the connections can be broken readily. This allows the reaction tube to be withdrawn from the heating tube and the U-tube to be disconnected from the reaction tube. The current is controlled by the resistance F.

The temperature of the reaction tube at the point P is measured by means of a platinum-rhodium thermocouple, T. The wires of the thermocouple are inserted in a special protecting tube made of Pyrex glass.

CONTROL OF GAS MIXTURE—It was thought that the proportion of naphthalene vapor in the gas mixture could be controlled simply by controlling the temperature of the bath in which the U-tube rested. It was found, however, that the quantity of naphthalene carried out of the U-tube depended not only upon the temperature of the bath but also on several other conditions, such as the temperature of the parts of the tube above the surface of the oil and the velocity of the air through the tube. At a given temperature in the bath a rapid stream of air would emerge from the U-tube, containing a greater proportion of naphthalene than would a slowly moving stream of air. Since all the conditions involved could not be controlled easily it was difficult in all experiments to keep the ratio of naphthalene vapor to air as nearly constant as was desired.

ANALYTICAL PROCEDURE—Before and after each experiment the U-tube was wiped free from oil, washed with a cloth saturated with ether, and, after standing for a few minutes in the air, was weighed on an analytical balance, the weight being recorded to the nearest centigram. The major part of the product in the condenser was scraped out and placed in a desiccator. The product remaining in the condenser was rinsed out with ether into a small weighed beaker. This beaker was placed in a vacuum desiccator where the ether was evaporated by directing upon its surface a rapid stream of air which had been dried by passing through sulfuric acid. In this way the ether could be evaporated without condensation of moisture on the beaker and in the residue. The beaker

TABLE I—TESTS OF VARIOUS SUBSTANCES AS CATALYSTS FOR THE CONVERSION OF NAPHTHALENE TO PHTHALIC ANHYDRIDE

EXPT. No.	Substance Tested	Vol. Air per 1 G. Naphthalene Liter	Time of Contact Sec.	Specific Time of Contact	Temperature ° C.	Naphthalene			Anhydride Produced per Hr. Gram	Acid in Product as Anhydride Per cent	Yield of Anhydride on Naphthalene Attacked Per cent
						Converted Per cent	Recoverable Per cent	Lost Per cent			
256	MgO	5.1	4.06	2.65	413	Trace	84.6	15.4	Trace	Trace	..
434	Al ₂ O ₃	4.3	2.39	2.39	400	0.2	56.1	43.7	0.013	0.1	0.1
258	SiO ₂	4.2	3.72	2.43	397	0.1	78.9	21.0	0.007	0.2	0.6
411	TiO ₂	5.1	2.57	2.57	419	0.3	57.8	41.9	0.009	0.5	0.6
188	ZrO ₂	3.9	2.03	2.21	450	0.2	51.2	48.6	0.019	0.6	0.6
183	CeO ₂	3.2	1.96	2.14	455	0.2	61.1	38.7	0.017	0.4	0.5
197	V ₂ O ₅	4.7	2.44	2.66	450	3.7	42.9	53.4	0.191	9.4	7.5
189	Co ₂ O ₃	4.1	2.02	2.20	455	0.3	89.6	10.1	0.025	0.5	3.9
432	Cr ₂ O ₃	4.0	2.45	2.45	401	Trace	52.5	47.5	Trace	Trace	..
271	MoO ₃	4.5	2.90	1.85	426	10.2	62.2	27.6	0.590	16.2	31.1
182	WO ₃	3.6	2.01	2.19	428	2.7	63.0	34.3	0.226	4.9	8.6
415	UO ₂	5.2	2.73	2.73	427	1.3	47.3	51.4	0.049	3.3	3.0
278	Mn ₂ O ₃	4.8	3.87	2.54	401	1.8	46.0	52.2	0.100	4.3	3.8
181	Fe ₂ O ₃	3.2	1.97	2.15	456	0.3	64.8	34.9	0.020	0.4	0.7
184	NiO	5.2	1.97	2.15	455	0.2	51.7	48.1	0.019	0.5	0.5
416	Co ₂ O ₃	4.5	2.67	2.67	410	0.1	21.5	78.4	0.005	0.6	0.2
187	Cu ₂ O	5.0	2.13	2.32	445	0.5	35.7	63.8	0.024	1.4	0.8
184	5% Pt; 95% MgO	5.1	2.20	2.40	431	0.2	43.8	56.0	0.009	0.4	0.3

and residue were further dried for several hours in a desiccator over sulfuric acid. The quantity of ether used was noted. The amount of naphthalene lost during the evaporation of a known quantity of ether by this method had been determined by experiment. Hence allowance could be made in each experiment for the loss of naphthalene due to the evaporation of ether. The beaker and the total product recovered were weighed. A measured quantity of standard alkali was then added, followed by water sufficient to cover the solid matter in the beaker. The beaker was next immersed in a steam bath until the naphthalene was melted and the acid products were dissolved. When this had taken place, the mixture was vigorously agitated from time to time and allowed to digest for several minutes. The residual alkali was then titrated with standard acid, using a solution of thymolsulphalein as an outside indicator.¹³

OBSERVATIONS MADE AND CALCULATED VALUES RECORDED—The following explanations are offered in connection with the results obtained (Tables II-V):

The "volume of air per 1 g. naphthalene" is the ratio between the total volume of air used (in liters), as shown by the gas meter, and the total naphthalene used, as shown by the loss in weight of the U-tube.

The "time of contact" is the theoretical average time during which a gas molecule may come in contact with the catalyst bed; that is, the time required for the column of gas over the catalyst to move the length of the catalyst bed. It is calculated by the following formula:

$$\text{Vol. mixed gases added per sec.} \times \frac{\text{Vol. gas over catalyst bed}}{\text{temp. in tube} + 273} = \frac{\text{Time of contact in seconds}}{\text{temp. in room} + 273}$$

The volume of mixed gases includes the air (measured at room temperature) and the calculated volume of naphthalene vapor at 25°. No account is taken of the penetration of the catalyst bed by the gases.

The "specific time of contact" is the time of contact divided by the volume of gas over 1 sq. cm. of catalyst surface, that is, the time in seconds required for supplying 1 cc. of mixed gases for each sq. cm. of catalyst surface. The purpose of calculating this value is to make the results obtained in tubes of different caliber comparable. The following is the formula used:

$$\text{Vol. mixed gases added per sec.} \times \frac{\text{Area of catalyst bed}}{\text{temp. in tube} + 273} = \frac{\text{Specific time of contact}}{\text{temp. in room} + 273}$$

The "temperature" is an average of the pyrometer readings taken at intervals of 10 or 15 min. It represents the average temperature of the gases immediately after leaving the catalyst—*i. e.*, at point P in the figure. The wide variation in temperature

shown in Table I is due mainly to a change of view as to the proper temperature to be maintained. In making the first tests it was thought that the temperature should be held as high as possible without ignition of the gases, since the acidity of the products seemed to rise with rise of temperature. Later it was found that temperatures of 450° or higher were unnecessary and undesirable, and the working temperature was reduced to around 425°, and later to around 400°.

The "naphthalene converted" is the naphthalene equivalent to the phthalic anhydride found, expressed as percentage of the total naphthalene added.

The "naphthalene recoverable" is the difference between the acid found and the total product recovered, to which is added the calculated naphthalene lost in evaporation of the ether and the calculated naphthalene carried through the apparatus with the waste gases. The naphthalene lost during the evaporation of 100 cc. of ether as carried out in the analytical work was determined by experiment to be approximately 0.05 g. Since the amount of ether used was ordinarily around 50 cc., the correction generally amounted to 0.02 or 0.03 g. The naphthalene lost with the waste gases was calculated from the vapor pressure of naphthalene, which is given in the literature as 0.064 mm. at 20°, 0.164 mm. at 30°, and 0.378 mm. at 40°.

It was calculated that at 25°, 0.0007 g. of naphthalene would be carried away with each liter of waste gases. The "naphthalene recoverable" is expressed as percentage of the total naphthalene added.

The "naphthalene lost" is the naphthalene not converted and not recoverable, expressed as percentage of the total naphthalene added.

The "acid in product" is the acid found, calculated as phthalic anhydride and expressed as percentage of the total product recovered.

The "yield of anhydride on naphthalene destroyed" is the acid found, calculated as anhydride, and expressed as percentage of the sum of the naphthalene converted and naphthalene lost.

RESULTS OF SEARCH FOR THE BEST CATALYST. DISCUSSION OF TABLE I—The results of the first tests of various substances as catalysts are given in Table I.

Of the 18 substances tested, the oxides of vanadium, molybdenum, tungsten, uranium, manganese, and copper produced more highly acid products than did the other substances, while the oxides of vanadium, columbium, molybdenum, tungsten, uranium, and manganese gave the highest yields. The results show no definite relations between the position of an element in the periodic system and the behavior of the oxide as a catalyst in the reaction under discussion. It is worthy of note, however, that the six substances giving the highest yields were oxides of metals of the fifth, sixth, and seventh groups.

Under the conditions of the experiments, molybdenum trioxide obviously was the best catalyst. It was decided, however, to make further tests of five of the six oxides giving the highest yields. Columbium oxide was eliminated because it was thought to be too rare to be used in a commercial

¹³ This indicator was preferred because the color change taking place is very marked and is not obscured by the dark brown color present in the solution titrated. Furthermore, it is water-soluble, which makes it convenient for use on a spot plate. For description of this compound and its uses, see *J. Am. Chem. Soc.*, 15 (1918), 1443. Phenolphthalein can be used for the titration, but with less convenience and accuracy.

TABLE II—BEST RESULTS OBTAINED IN EXPERIMENTS IN WHICH VARIOUS GAS MIXTURES, TIMES OF CONTACT, AND TEMPERATURES WERE TRIED FOR EACH OF THE CATALYSTS TESTED

EXPT. No.	Catalyst	Naphthalene			Anhydride Produced per Hour Gram	Acid in Product as Anhydride Per cent	Yield of Anhydride on Naphthalene Attacked Per cent
		Converted Per cent	Recoverable Per cent	Lost Per cent			
10	V ₂ O ₅	54.8	19.0	26.2	0.99	80.6	78.5
270	MoO ₃	18.8	62.6	18.6	0.66	26.2	57.9
279	W ₂ O ₇	10.5	39.9	49.6	0.22	24.3	20.1

process. In the additional tests it was planned to vary the ratio of air to naphthalene vapor, the time of contact, and the temperature of the reaction chamber in different experiments with the same catalyst in order to determine whether by changing the conditions of the tests results superior to those of the first series could be obtained. These experiments gave some information on the proper conditions for carrying out this oxidation of naphthalene, and led to a more systematic study of these conditions aiming toward the discovery of the best gas mixture, the best time of contact, and the best temperature. The results of this study will be reported in a subsequent paper.

TABLE III—TESTS OF THE CATALYTIC PROPERTIES OF VANADIUM PENTOXIDE IN DIFFERENT PHYSICAL CONDITIONS

EXPT. No.	DESCRIPTION OF EXPERIMENTS ¹	Naphthalene			Anhydride Produced per Hr. Grams	Acid in Product as Anhydride Per cent	Yield of Anhydride on Naphthalene Attacked Per cent
		Converted Per cent	Recoverable Per cent	Lost Per cent			
327	Catalyst; light, fluffy V ₂ O ₅ made from ammonium metavanadate by heating; not heated above 450°	50.6	14.9	34.5	0.98	84.0	68.8
328	Same catalyst used as in Expt. 327 but after heating to 560° and slightly sintering	55.6	21.7	22.7	1.15	76.0	81.8
331	Catalyst; V ₂ O ₅ made from same sample of ammonium metavanadate as catalyst used in Expt. 327 but completely fused and afterwards powdered	61.2	11.7	27.1	1.46	88.0	80.1
334	Catalyst; light V ₂ O ₅ powder—method of preparation unknown	47.4	13.0	39.6	0.84	83.2	63.0
336	Same catalyst used as in Expt. 334 but after heating until slightly sintered	55.1	26.7	18.2	1.13	72.3	87.2
345	Catalyst; V ₂ O ₅ of unknown origin, fused, and then powdered	61.9	14.5	23.6	1.24	86.9	83.5

¹ The conditions with respect to gas mixture, time of contact, and temperature were approximately uniform for the group of experiments.

DISCUSSION OF TABLE II—In tests of uranium trioxide and manganese sesquioxide under varied conditions no yields better than those resulting from the first tests (Table I) were obtained. This was not the case, however, in tests of the oxides of vanadium, molybdenum, and tungsten, of which some results are given in Table II. With these oxides as catalysts it was found that by varying the conditions of the tests, yields much better than those obtained in the first series of experiments could be obtained. For instance, with the same vanadium pentoxide as that used in Expt. 197 (Table I) a yield of 78.5 per cent was obtained, given suitable conditions of gas mixture, time of contact, and temperature. No combination of conditions which would give yields equal to this when molybdenum trioxide was used as a catalyst could be found, notwithstanding the fact that under some conditions (Expt. 271, Table I) this catalyst gave better yields than vanadium pentoxide. Tungsten trioxide was found to be a very poor catalyst in comparison with the oxides of vanadium and molybdenum.

The best yields obtained with each of the three oxides under discussion are shown in Table II. In each test the sample of oxide used was the same as that used to obtain the results reported in Table I.

Molybdenum trioxide not only failed to give yields as high as the best obtained with vanadium pentoxide, but also showed the rather serious fault, from a practical point of view, of being slightly volatile at the reaction temperature. The conclusion was drawn that vanadium pentoxide was the best catalyst, and subsequently in the development of a commercial method for the manufacture of phthalic anhydride this catalyst was used exclusively.

SOME PROPERTIES OF VANADIUM PENTOXIDE AS A CATALYST

FORMS OF VANADIUM PENTOXIDE—When prepared from ammonium metavanadate at temperatures below 300°, vanadium pentoxide is a light, fluffy, chocolate-colored powder. When heated to about 550° it grows somewhat darker and apparently sinters enough to become less fine and fluffy. At a higher temperature (given in the literature as 658°) it fuses, and when cooled again solidifies to a crystalline mass.

In a series of experiments in which at first light, fluffy vanadium pentoxide was used as a catalyst, this oxide was overheated. Apparently it gave better results than when used in the light state. It was found that the oxide had been sintered by the overheating. Further experiments showed that in its catalytic properties light vanadium pentoxide differs somewhat from the sintered or fused forms. It is not known whether this change in catalytic properties is due to physical changes alone or whether chemical changes also occur. It is quite possible that deleterious substances might be volatilized by heating, but this point was not investigated.

DISCUSSION OF TABLE III—The results of a few experiments

recorded in Table III furnish some basis for a comparison of the catalytic properties of the oxide in the three forms. With respect to gas mixture, time of contact, and temperature, the conditions were approximately uniform for the whole group of experiments.

It will be noticed that the light oxide and the fused oxide attacked a greater proportion of the naphthalene added and gave a more highly acid product than did the sintered oxide. But the oxide after sintering or fusion gave higher yields than did the oxide in the light state. It must be concluded that it generally is advisable to sinter or fuse vanadium pentoxide for use as a catalyst.

EFFECT OF CERTAIN FOREIGN SUBSTANCES ON CATALYTIC PROPERTIES OF VANADIUM PENTOXIDE

As will be shown in a later article, a great many substances, when present in the reaction chamber with the catalyst during the oxidation of naphthalene to phthalic anhydride, reduce the yield of the anhydride. Substances in the reaction chamber in chemical combination with the catalyst might be expected also to have a deleterious effect. This proved to be true in the case of two substances tested, cobalt metavanadate and vanadium pentoxide containing sodium compounds.

DISCUSSION OF TABLE IV—The results of the test of the two substances mentioned are given in Table IV. The same table shows the results of tests on the effect of sulfur dioxide and of arsenic trioxide on the catalyst. The effect of sulfur dioxide was studied because it was thought that the small amounts of this compound present in the air in industrial centers might poison any vanadium pentoxide catalyst used

TABLE IV—TESTS OF THE EFFECT OF FOREIGN SUBSTANCES ON CATALYTIC PROPERTIES OF VANADIUM PENTOXIDE

EXPT. No.	DESCRIPTION OF EXPERIMENT ¹	Naphthalene			Anhydride Produced per Hr. Grams	Acid in Product as Anhydride Per cent	Yield of Anhydride on Naphthalene Attacked Per cent
		Converted Per cent	Recoverable Per cent	Lost Per cent			
335	Test of cobalt metavanadate as a catalyst	19.4	18.5	62.1	0.53	56.5	27.8
340	Test of a sample of V ₂ O ₅ which was found to contain about 4 per cent of sodium	15.3	47.7	36.9	0.23	27.7	33.1
345	Control experiment, V ₂ O ₅ catalyst	61.9	14.5	23.6	1.24	86.9	83.5
346	Test of effect of SO ₂ . Same catalyst used as in Expt. 345. Enough SO ₂ was added to the air used to smell strongly in the effluent gases ²	61.6	20.4	18.0	1.57	80.3	89.3
347	Test of effect of SO ₂ . Same catalyst used as in Expts. 345 and 346. Before the experiment, the catalyst was exposed at a temperature of 400° to an atmosphere of undiluted SO ₂ for about 1 hour. No SO ₂ was added during the experiment	60.4	13.2	26.4	1.48	86.8	80.4
348	Test of effect of SO ₂ . Same catalyst used as in Expts. 345-347; treated as in Expt. 347 except that treatment was continued for 3 hrs. No SO ₂ was added during the experiment	60.9	12.9	26.2	1.42	87.1	80.7
349	Test of effect of As ₂ O ₃ . Same sample of V ₂ O ₅ used as catalyst as in Expt. 345, but mixed with 0.1 per cent of its weight of As ₂ O ₃	65.2	11.2	23.6	1.21	90.4	84.9
350	Test of effect of As ₂ O ₃ . Same catalyst used as in Expt. 349 but mixed with an additional 0.2 per cent of its weight of As ₂ O ₃ ³	63.0	14.3	22.7	1.16	86.5	85.2

¹ The conditions with respect to gas mixture, time of contact, and temperature were approximately uniform for the group of experiments.

² Some sulfuric acid was formed during the experiment. The quantity was determined and taken into account in calculating the results of the experiment.

³ Some of the As₂O₃ sublimed out of the catalyst before the test was begun.

for a long period in contact with such contaminated air. The effect of arsenic trioxide was tested because this compound is known to act as a poison in other catalytic reactions.

Neither sulfur dioxide nor arsenic trioxide seems to exert any unfavorable influence upon the catalyst and apparently neither substance interferes with the normal course of the reaction. On the contrary, sulfur dioxide actually seems to aid the catalyst, judging from the results of the one experiment (Expt. 346) in which the gas was introduced during the progress of the reaction.

PRODUCTS OF CATALYTIC OXIDATION OF NAPHTHALENE

It has been shown (Expts. 331 and 345, Table III) that naphthalene may be oxidized in the presence of a catalyst under such conditions that the principal solid product obtained will be phthalic anhydride. Some naphthalene generally passes through the reaction chamber unchanged and in addition there are always some brown material and some substance or substances giving the condensate a very sharp, irritating odor. Both the brown coloring matter and the irritating substance are produced most abundantly under certain working conditions which do not yield large proportions of the anhydride.

The by-products of the reaction under discussion have not been carefully studied because, in the laboratory, they are formed only in minute quantities. Some information concerning them has been gathered, however, and methods for their separation from the anhydride have been developed.

The presence of benzoic acid was indicated in all condensates examined by a positive reaction to Mohler's¹⁴ test and by the presence of acid which could be extracted by chloroform from aqueous solutions. In the product resulting from experiments with factory-scale apparatus this acid was found in proportions amounting to about 1 per cent of the total product.

Positive reactions for α - and β -naphthols have been obtained when large quantities of crude condensate made on a factory scale were available for testing. These compounds seem to be present in very small proportions of the whole.

The irritating substance is not much in evidence when the reaction is proceeding smoothly. It is volatile enough to be driven off almost completely when the condensate is dissolved in ether and the ether evaporated, as in the collection of the condensate for analysis. Its vapor, in very moderate concentrations, causes an abundant flow of tears.

The brown coloring matter is soluble in alkaline solution and in the common organic solvents. In chloroform solution

it has a bright cherry-red color. It is less volatile than phthalic anhydride.

Both the irritating fumes and the brown coloring matter suggest naphthoquinones, and it seems reasonable to suppose that these compounds, as well as phthalaldehydes, would be formed in the reaction.

Carbon dioxide is the main gaseous product of the reaction, but it is not found in quantities sufficient to account for the total naphthalene destroyed. Carbon monoxide is not found in the gases given off. The conclusion must be drawn that a portion of the naphthalene attacked is broken down into gaseous compounds other than carbon dioxide and carbon monoxide.

SEPARATION OF PHTHALIC ANHYDRIDE FROM BY-PRODUCTS

Fortunately phthalic anhydride can be separated with ease from all of the other substances formed in the catalytic oxidation of naphthalene. One means for accomplishing this separation is fractional sublimation. In the process of sublimation, water, whether free or combined, and naphthalene pass over at lower temperatures than the anhydride does and may be separated quite sharply from it. The anhydride, in turn, may be sublimed away from the colored material, and with proper regulation of conditions may be condensed in a high state of purity, while the colored material is retained in the retort.

The anhydride can also be separated from the crude condensate by crystallization from organic solvents, the color being removed from the solution by means of an adsorbent. For instance, the crude product may be dissolved in warm carbon tetrachloride and a decolorizing charcoal added to remove the color. If the charcoal is then filtered out and the solution cooled in successive stages, successive crops of phthalic anhydride crystals may be recovered while naphthalene is left in the solution.

SUMMARY

1—Naphthalene is oxidized to phthalic anhydride when a mixture of naphthalene vapor and air is passed through a heated tube in the presence of certain catalysts.

2—Vanadium pentoxide is an excellent catalyst for bringing about this reaction; MoO₃ is a fairly good catalyst; while MgO, Al₂O₃, SiO₂, TiO₂, ZrO₂, CeO₂, Cb₂O₅, Cr₂O₃, WO₃, UO₃, Mn₂O₃, Fe₂O₃, NiO, Co₂O₃, Cu₂O, and finely divided Pt mixed with MgO are poor or worthless catalysts.

3—Vanadium pentoxide, fused and then finely powdered, is a better catalyst for this reaction than is the light powder prepared by decomposing ammonium metavanadate at low temperatures.

4—The value of vanadium pentoxide as a catalyst in the reaction under discussion is not sensibly lowered by arsenic trioxide or sulfur dioxide. The presence of sodium compounds in vanadium pentoxide lowers its efficiency as a catalyst for this reaction.

5—When naphthalene is oxidized under favorable conditions with vanadium pentoxide as a catalyst, phthalic an-

hydride is the main solid reaction product. Other unidentified solid substances are produced in small quantity. Benzoic acid has been found in the product and naphthols probably are present as a very small proportion of the whole. Carbon dioxide is the main gaseous product, although other unidentified compounds are formed. Carbon monoxide is not found in the gaseous products.

The Nature of Acid Water from Coal Mines and the Determination of Acidity^{1,2}

By W. A. Selvig and W. C. Ratliff

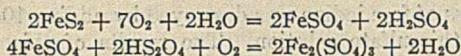
BUREAU OF MINES EXPERIMENT STATION, PITTSBURGH, PENNSYLVANIA

In connection with an investigation of the corrosive action of acid mine water from coal mines on various types of iron and steel, conducted by the Bureau of Mines for the American Society for Testing Materials, the chemical laboratory of the Bureau determined over an extended period of time the degree of acidity of mine water from a bituminous coal mine in western Pennsylvania. Satisfactory results were not obtained in determining acidity due to free mineral acids by the usual titration method,³ on account of the presence of a large amount of iron and aluminium sulfates. A general study was accordingly made of the nature of acid mine water from coal mines and of the bearing of sulfates of iron and aluminium on acidity determinations.

NATURE OR COMPOSITION OF MINE WATER

SOURCE OF SULFURIC ACID—Water from coal mines is usually decidedly acid, containing free sulfuric acid and ferrous, ferric and aluminium sulfates, in addition to sulfates of calcium, magnesium, sodium, and potassium, together with silica and usually some chlorides.

The occurrence of iron sulfates and free sulfuric acid is due to the action of water and air on the pyrite or marcasite associated with coal. These substances are oxidized to ferrous sulfate, ferric sulfate, and sulfuric acid:



NATURAL PRECIPITATE—When acid mine water stands a short time a considerable precipitation of iron-bearing compounds usually occurs. Campbell⁴ gives the following typical composition of the natural precipitate, commonly called "sulfur mud:"

	Dry Per cent	Wet Per cent
Moisture	70.50
Silica (SiO ₂)	0.70	
Alumina (Al ₂ O ₃)	3.97	
Lime (CaO)	Nil	
Magnesia (MgO)	Nil	
Alkalies (Na ₂ O + K ₂ O)	Not determined	
Iron oxide (Fe ₂ O ₃)	63.43	
Loss on ignition	31.82	
Sulfur trioxide (SO ₃)	14.44	

The composition and character of the colloidal precipitates resulting from the hydrolysis of iron salts have been given considerable study by different investigators.⁵ As no definite

¹ Presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

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

³ "Standard Methods for the Examination of Water and Sewage," American Public Health Association, 1920, 41.

⁴ Discussion, "Sulfur in Coal and Coke," *Proc. Eng. Soc. Western Penn.*, 36 (1920), 629.

⁵ F. K. Cameron and W. O. Robinson, "Ferric Sulfates," *J. Phys. Chem.*, 11 (1907), 641; Eugen Posnjak and H. E. Merwin, "The Hydrated Ferric Oxides," *Am. J. Sci.*, 47 (1919), 339; Harry B. Weiser, "Hydrous Oxides," *J. Phys. Chem.*, 24 (1920), 277.

basic ferric salt has been established with certainty, it is probable that the yellow-brown precipitate consists of hydrous ferric oxides. The presence of sulfur in the natural precipitate is probably due to adsorption of sulfate ions by the colloidal hydrous oxides.

IRON COMPOUNDS—The iron may be considered to exist as soluble ferrous and ferric sulfates together with hydrous ferric oxides in suspension and colloidal solution. On standing, dilution, aeration or warming, insoluble iron compounds tend to precipitate, principally as hydrous ferric oxides.

TYPICAL ACID WATER FROM A BITUMINOUS COAL MINE OF WESTERN PENNSYLVANIA. *Collection of samples*—Samples of water were collected from a bituminous coal mine in the vicinity of Calumet, Pa., the water from which was considered typical of the acid mine water region. The water was collected above ground after it had been pumped from the mine, and contained considerable entrapped air. Before the stoppers were inserted the filled sample bottles were allowed to stand a few minutes to permit the air bubbles to escape. Samples were taken at regular intervals over a period of 6 mo.

Acidity determinations—The unfiltered water was titrated with 0.02 *N* sodium carbonate on the day following collection. The raw water was diluted 1 to 10 before titrating on account of the high concentration of sulfates of iron, which by partial precipitation obscured the end-point when the undiluted water was used. The results obtained by titrating for free mineral acids with methyl orange were unquestionably high, as the result of partial hydrolysis and liberation of free sulfuric acid by aluminium and ferric sulfates. This was confirmed by experimental work in which the ferric sulfate was reduced to ferrous sulfate, before titration, thus eliminating the readily hydrolyzed ferric sulfate. Acidity due to free mineral acids plus sulfates of iron and aluminium was determined by titrating the diluted water at a boiling temperature with 0.02 *N* sodium carbonate in the presence of phenolphthalein. The maximum, minimum, and average acidity of the water during the 6-mo. period are given in Table I.

TABLE I—ACIDITY OF TYPICAL WATER FROM BITUMINOUS COAL MINE OF WESTERN PENNSYLVANIA
Acidity (p. p. m.) in terms of H₂SO₄

No. of Samples Collected	Acidity Due to Free Sulfuric Acid ¹			Acidity Due to Free Sulfuric Acid Plus Sulfates of Iron and Aluminium		
	Max.	Min.	Av.	Max.	Min.	Av.
19	825	590	695	2070	1495	1690

¹ Acidity due to free sulfuric acid is unquestionably too high, as the result of hydrolysis of ferric and aluminium sulfates.

Ferrous and ferric iron—The amount of ferrous and ferric iron present in the unfiltered raw water was determined at different times. The ferrous iron determination was made at the mine on the fresh water, and the total iron determina-

tion was made in the laboratory on the day following collection.

Ferrous iron was determined on 50-cc. portions of the unfiltered water by adding 40 cc. of sulfuric acid (1:3) and titrating at once to a faint pink with 0.1 *N* potassium permanganate. Ferric iron was calculated from the difference between the total iron and the ferrous iron in the water. The total iron was determined by treating 50-cc. portions of the unfiltered water in a 300-cc. Erlenmeyer flask with 40 cc. of sulfuric acid (1:3) and 5 g. of granulated zinc. The flask was covered with an inverted porcelain crucible lid, and warmed. When the zinc was practically all dissolved the contents of the flask were quickly cooled and filtered through glass wool, washed with distilled water, made up to about 200 cc. with cold distilled water, and titrated at once with 0.1 *N* permanganate. A blank was run with the same amounts of zinc and sulfuric acid. The ferrous and ferric iron content of the water is given in Table II.

TABLE II—FERROUS AND FERRIC IRON CONTENT OF UNFILTERED WATER

Date of Collection	Ferrous Iron P. p. m.	Ferric Iron P. p. m.
October 1, 1920	122	237
October 15, 1920	91	251
October 29, 1920	116	243
November 12, 1920	105	294

As ferrous sulfate oxidizes very readily to ferric sulfate, a number of determinations were made for ferrous iron at the mine and also on the same water the day following collection. In all cases an appreciable oxidation of ferrous iron occurred, although the bottles were completely filled with water and tightly stoppered. This oxidation may be accounted for by the presence of dissolved oxygen in the water.

TABLE III—FERROUS IRON CONTENT OF MINE WATER AT MINE AND AFTER STANDING

Date of Collection	At Mine P. p. m.	After Approx- imately 24 Hrs. P. p. m.	Decrease of Fer- rous Iron after 24 Hrs. P. p. m.
October 1, 1920	122	94	28
October 6, 1920	91	66	25
October 29, 1920	116	55	61
November 12, 1920	105	89	16

Mineral analysis of water—The mine water as collected was yellow-brown in color and contained some suspended matter. After a short time a considerable precipitation of iron oxides took place. One of the samples was analyzed for mineral content the day following collection and was thoroughly shaken before removing portions for analysis so as to include all mineral matter in solution and suspension. Another sample was allowed to stand in a tightly stoppered glass bottle for about 1 mo., and filtered, and a mineral analysis made on the filtrate. The precipitated matter from this sample amounted to 761 p. p. m. when dried at 105° C. The analytical results on these two samples are given in Table IV.

TABLE IV—MINERAL ANALYSIS OF MINE WATER

CONSTITUENT	Unfiltered Water Analyzed Day Following Collection	Filtrate from Water Al- lowed to Stand 1 Mo.
	P. p. m.	P. p. m.
SiO ₂	60	56
Fe ⁺⁺	101	3
Fe ⁺⁺⁺	283	263
Al	101	91
Ca	221	224
Mg	87	93
K	5	5
Na	49	53
Cl	9	6
SO ₄	2282	2246

The results show that the ferrous sulfate was practically completely removed on standing. After standing, the water contained considerable ferric sulfate in solution, and without doubt an acid concentration had been reached which prevented any further hydrolysis of ferric sulfate and precipitation of hydrous ferric oxides.

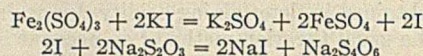
DETERMINATION OF ACIDITY

SPECIAL METHODS FOR ESTIMATION OF FREE ACID—The amount of free sulfuric acid in mine water is frequently calculated by making a complete mineral analysis of the filtered water and combining the bases as normal sulfates, the excess SO₄ being figured to free H₂SO₄. This involves much work and is not satisfactory because the value obtained is subject to an error equal to the algebraic sum of the individual errors of the mineral analyses.

Ferric and aluminium sulfates hydrolyze very readily, and waters containing appreciable amounts of these salts invariably give high results when an attempt is made to determine free mineral acids by direct titration with standard alkali and methyl orange.

Capps and Boies⁶ removed ferric sulfate by reducing it to ferrous sulfate by means of cadmium amalgam, the air dissolved in the water also being replaced by hydrogen.

Rankin⁷ recommends a very simple method of reducing the ferric sulfate to ferrous sulfate by adding an excess of potassium iodide solution to the water and subsequently converting the liberated iodine to sodium iodide by the addition of a slight excess of sodium thiosulfate, measured by the disappearance of the yellow color due to free iodine. The reactions are as follows:



The method requires no special apparatus and is extremely simple. It was subjected to experimental tests as to its suitability for the determination of free acid in mine water from coal mines.

DETERMINATION OF FREE ACIDITY—Five samples of water from the Calumet mine were collected at different times, and the acidity due to free mineral acids was determined with and without reducing the ferric sulfate to ferrous sulfate. In the first case, the unfiltered water was diluted and titrated against 0.1 *N* sodium hydroxide, with methyl orange as an indicator. In the reduction method an excess of 10 per cent potassium iodide solution was added to the unfiltered, undiluted water until a yellow color of free iodine appeared; the water was then diluted and titrated. Before the titration the excess of free iodine was destroyed by adding 10 per cent sodium thiosulfate solution. The results of this series of tests are given in Table V.

TABLE V—TITRATION OF FREE MINERAL ACIDS WITH AND WITHOUT REDUCTION OF FERRIC SULFATE

Sample No.	Acidity (p. p. m.) in terms of H ₂ SO ₄	
	Ferric Sulfate not Reduced	Reduced to Ferrous Sulfate
1	665	324
2	688	320
3	865	458
4	715	372
5	670	487

A marked decrease in free acidity after reducing the ferric sulfate is noted in each sample. However, the value obtained must still be considered too high, owing to the presence of aluminium sulfate.

Five synthetic waters with varying amounts of free sulfuric acid were prepared. Ferrous and ferric sulfates and aluminium sulfate were added in approximately the amounts which were found in the acid Calumet mine waters:

	P. p. m.
FeSO ₄	275
Fe ₂ (SO ₄) ₃	1000
Al ₂ (SO ₄) ₃	640

The acid water was titrated before the addition of the salts in order to determine the exact acidity due to added sulfuric

⁶ *J. Phys. Chem.*, **19** (1915), 65.

⁷ "Acidity Determination in Water, Leach Liquors, Mine Waters, Etc.," *Chem. Met. Eng.*, **18** (1918), 96.

acid. Portions of the water were then diluted and titrated for free acidity with and without previous reduction of ferric to ferrous sulfate. The results of the determinations are given in Table VI.

TABLE VI—TITRATION OF FREE SULFURIC ACID IN SYNTHETIC MINE WATERS
Acidity (p. p. m.) in terms of H_2SO_4

Sample No.	Acidity Due to Added H_2SO_4	Acidity by Titration $Fe_2(SO_4)_3$ Not Reduced	Acidity by Titration $Fe_2(SO_4)_3$ Reduced
1	None	461	294
2	460	1,003	772
3	909	1,403	1,237
4	4,724	4,954	4,782
5	10,025	10,368	10,045

The excess of acidity shown in the unreduced samples apparently consists of free sulfuric acid liberated by the unreduced ferric sulfate. Sample 1, which contained no added acid, showed 294 p. p. m. free acid after the reduction of the ferric sulfate. Doubtless this can be accounted for by the hydrolysis of the aluminium and ferric sulfates during the short interval between the preparation of the water and the reduction of the dissolved ferric sulfate. The excess of free acid determined by titration, after reduction of the ferric sulfate, over that actually added is fairly uniform in Samples 1, 2, and 3, ranging from 294 to 328 p. p. m. Samples 4 and 5, which contained a very large excess of added sulfuric acid, gave by titration after reduction of the ferric sulfate only slightly more free acid than was added. In these waters the very high concentration of free acid apparently prevented hydrolysis of the iron and aluminium sulfates during the interval of time between the preparation of the water and the titration for acidity, and the excess acid shown is probably largely due to hydrolysis of aluminium sulfate during titration. The acid concentration of Samples 4 and 5 is considerably higher than that of acid mine water from bituminous coal mines.

To determine the excess acidity due to hydrolysis of aluminium sulfate, a sample of the Calumet mine water was analyzed for ferrous, ferric, and aluminium sulfates. The first two were determined by titration with standard permanganate as previously described, and aluminium sulfate was determined by a mineral analysis of the water. The calculated acidity due to the sulfates of iron and aluminium was subtracted from the total acidity due to sulfates of iron and aluminium plus free sulfuric acid as determined by titration in the presence of phenolphthalein as an indicator. The difference was considered to represent the true free acidity of the water, due to free sulfuric acid.

Titrations for free acidity due to free sulfuric acid were made on the clear filtered water with and without previous reduction of the ferric sulfate to ferrous sulfate. The results are given in Table VII.

TABLE VII

Sulfates of iron and aluminium, determined by analysis:	Calculated Acidity in Terms of H_2SO_4	
	P. p. m.	P. p. m.
$FeSO_4$	9	6
$Fe_2(SO_4)_3$	966	711
$Al_2(SO_4)_3$	575	494
Calculated acidity due to sulfates of iron and aluminium	...	1211
Total acidity, sulfates of iron and aluminium plus free sulfuric acid	...	1510
Difference acidity due to free sulfuric acid	...	299
Titrated free acidity after reduction of ferric sulfate	...	372
Titrated free acidity without reduction of ferric sulfate	...	715

The mine water had stood for some time in the laboratory after collection and considerable deposition of iron compounds had occurred. The ferrous iron had been practically entirely oxidized to ferric iron.

If 299 p. p. m. be taken as the true acidity due to free sulfuric acid, the titration method with previous reduction of the ferric sulfate gave results only 73 p. p. m. too high, while

the titration without previous reduction of the ferric sulfate gave results 416 p. p. m. too high. This indicates clearly that fairly satisfactory results for free acidity can be obtained if the ferric sulfate is reduced previous to titration. If extreme accuracy is desired, a correction can be made for the water in question by calculating the effect of the aluminium sulfate present and deducting this from the value for free acidity determined by reduction of the ferric sulfate and subsequent titration. With waters of unknown aluminium sulfate content, the degree of free acidity can best be calculated from the total acidity determined by titration in the presence of phenolphthalein, and the acidity due to sulfates of iron and aluminium, as calculated from the analysis of the water. In a series of acidity determinations on the same water, if the aluminium sulfate content does not vary greatly from time to time, a correction for the water in question could be calculated and deducted from the titrated free acidity after previous reduction of the ferric sulfate.

As this method of calculation of free sulfuric acid in mine water assumes that the ferrous and ferric iron determined by titration are present as normal sulfates, it is necessary to filter the water to remove any insoluble suspended hydrous ferric oxides.

DETERMINATION OF TOTAL ACIDITY—The total acidity due to free mineral acids plus sulfates of iron and aluminium can be determined satisfactorily by a direct titration at a boiling temperature with standard alkali in the presence of phenolphthalein as an indicator. The indicator shows an acid reaction until the free acid has been neutralized, and sulfates of iron and aluminium have been converted to hydroxides.

Mine water usually contains appreciable amounts of calcium sulfate in solution. A saturated solution of calcium sulfate in water was titrated at a boiling temperature to a faint pink with both $NaOH$ and Na_2CO_3 solutions with phenolphthalein as an indicator; no difference in results was obtained. The amount of sodium hydroxide or carbonate required was the same as with the same quantity of distilled water.

Precipitation of insoluble calcium carbonate will occur if a considerable excess of sodium carbonate is added. This excess, however, is considerably greater than that necessary to give a pink end-point after the neutralization of free acid and sulfates of iron and aluminium.

Probably, for all practical purposes, the determination of total acidity due to free mineral acids plus sulfates of iron and aluminium is of as great importance as the actual free acid present in the mine water. As the free acid is neutralized or the water diluted, the sulfates of iron and aluminium will hydrolyze and liberate more acid. These sulfates may be considered as latent sources of free acid and play a very important role in the corrosive action of mine water.

SUMMARY

Direct titration of acid mine water for free sulfuric acid with alkali solutions in the presence of methyl orange will give too high results, on account of hydrolysis of ferric and aluminium sulfates. Reduction of ferric sulfate previous to titration gives more nearly correct free acid values. A correction for the hydrolysis of the aluminium sulfate can be applied.

ACKNOWLEDGMENTS

The authors are indebted to Mr. A. C. Fieldner, Supervising Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, for many helpful suggestions, and to Mr. J. R. Campbell, Chief Chemist, H. C. Frick Coke Co., for much valuable information on mine water.

A Preliminary Study of the Activated Sludge Process¹

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In October 1920, an investigation was begun in this laboratory to determine the cause of periodic recurrences of difficulties in filter-pressing sewage sludge from the activated sludge process. Our first experiments showed that the variation in rate of filtration with the hydrogen-ion concentration of the sludge is so great as to make the control of this factor essential to the efficient operation of the plant. In fact it was found that adding sufficient sulfuric acid to the sludge to reduce its pH value from 8 to 3 generally reduced the time required to filter a given quantity by 80 per cent. The increase in efficiency in the big plant is even greater because the rapidly filtering sludge leaves the filter bags in the press clean enough to be used again without washing, which is not the case with untreated sludge. Later it was found that the use of aluminium sulfate and similar salts in conjunction with hydrogen-ion control gave rates of filtration about twice as great as were possible by change of acidity alone. Some of these experiments have already been reported in earlier papers.^{2,3}

Careful studies of the effect of hydrogen-ion concentration upon the rate of filtration of sludges obtained throughout the year made it evident that hydrogen-ion control, tremendously important in itself, is not the only factor vital to the efficient operation of the plant. Sludge obtained during February, when the temperature of the raw sewage was 12°, required eighteen times as long to filter as sludge obtained during August, when the temperature had risen to 21°, even though each sample was brought to its optimum acidity before filtering. It became clear that an entirely satisfactory solution of the filter-pressing problem involved a reasonably complete investigation of the entire activated sludge process. A search of the literature revealed that very little has been accomplished towards an explanation of the mechanism of the process, and we have therefore begun an investigation with this object in view. While the work is still incomplete, it has seemed desirable to take advantage of this occasion to present what has been accomplished in the hope of stimulating other activities along these lines.

The most trying period of the year is the first quarter, when the temperature of the raw sewage is lowest. But even during this period it is possible to make the purity of the effluent discharged into the lake meet the requirements set, although the condition of the sludge for dewatering is then very poor.

METHOD OF DEFINING THE CONDITION OF SLUDGE

An important discovery in this investigation was the fact that the condition of a sludge can be defined satisfactorily by the curve representing its rate of filtration under fixed conditions as a function of the hydrogen-ion concentration. In making this determination in this work, we first dilute the sludge to contain 1 per cent of solid matter. The filtering equipment consists of 20 Büchner funnels set in filter flasks all connected with one pump furnishing a high and practically constant vacuum. Twenty portions of sludge, of 450 cc. each, are treated with 50 cc. of sulfuric acid solutions of different concentrations so as to give a range of

pH values from 2 to 8. All samples are thrown on the filters at the same time, the number of minutes required for complete filtration is noted, and the pH values of the filtrates determined. As soon as any sample is completely filtered, its flask is cut off from the main line so as not to reduce the vacuum on the others. The number of minutes required for filtration is plotted against the pH value found. The curve is a measure of the condition of the sludge and indicates not only the efficiency with which it can be filter-pressed, but also the rate at which it is becoming septic. These curves will be referred to hereafter as "condition curves" of the sludge.

CHANGES IN CONDITION OF SLUDGE DURING THE YEAR

Fig. 1 shows condition curves of representative samples of sludge taken during each month of the present year to date. In order to handle the sludge of February, more than eighteen times as many filter presses would be required as would be needed to handle the August sludge, even with the most rigid hydrogen-ion control. The lowest temperature of the raw sewage was 7° on March 8, and the highest was 23° on July 21 and 22. Unfortunately the curves cannot be used as a measure of the effect of temperature alone on the condition of the sludge because of changes in the raw sewage brought about by the industrial depression. During the coldest period, the amount of solid matter in the sewage was unusually low, necessitating a longer time for its collection after the aeration. The condition of the sludge becomes worse the longer it is allowed to stand after aeration, apparently because of septic action.

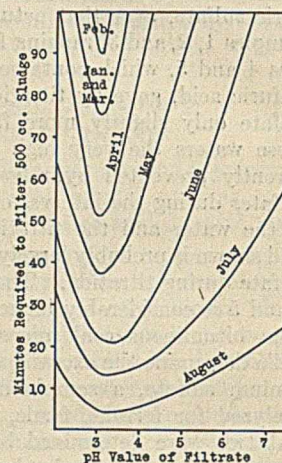


FIG. 1
Showing how the condition of the sludge from the activated sludge process varied from January to August 1921

AERATION vs. SEPTIC ACTION

A sample of July sludge was allowed to stand over night in a warm place. Next day it was quite foul and its condition curve changed from that of July sludge to that of February sludge shown in Fig. 1. Aerating this septic sludge for 2.5 hrs. brought its condition curve almost to that of May sludge, whereas 5 hrs. of aerating brought it almost to that of June sludge. Further experiment showed that the curves in Fig. 1 are all obtainable with any sludge; the lower curves can be raised by allowing the sludge to stand, while the higher curves can be lowered by aerating the sludge sufficiently long, the change apparently being reversible. This fact offers a solution of the filter-pressing problem during cold weather. While the cost of heating 85 million gallons of raw sewage daily during the cold weather would be prohibitive, it is apparently quite feasible to heat the sludge obtained from this amount of sewage and re-aerate it. It is conceivable that this will make for uniform pressing conditions all year round, which would be of enormous value, as the curves in Fig. 1 indicate.

The effect of hydrogen-ion concentration upon the septic action is shown in Fig. 2. A sludge already in very poor con-

¹ Presented before the Division of Water, Sewage and Sanitation Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

² "Role of Acidity in the Dehydration of Sewage Sludge," THIS JOURNAL, 13 (1921), 406.

³ "Application of Colloid Chemistry to the Filter Pressing of Sewage Sludge," J. Am. Water Works Assoc., 8 (1921), 486.

dition was used and condition curves were obtained with only 100-cc. portions of the sludge because of its poor condition. A second series was treated with acid, but was kept

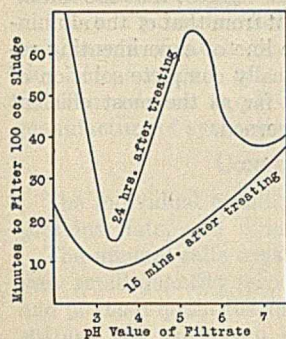


FIG. 2
Showing how septic action is dependent upon hydrogen-ion concentration. A more septic sludge filters more slowly

Further work will soon be under way.

In order to study the effect of temperature upon the re-aeration of sludge, three stoneware cylinders were equipped as aerating tanks. In the bottom of each was placed a Filtros plate having an area of 1 sq. ft. through which air could be

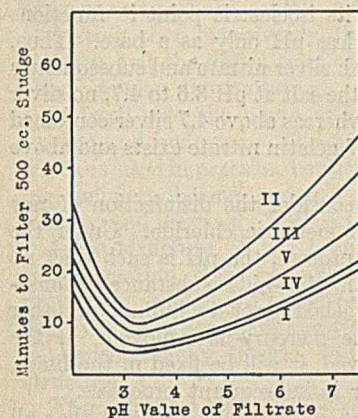


FIG. 3

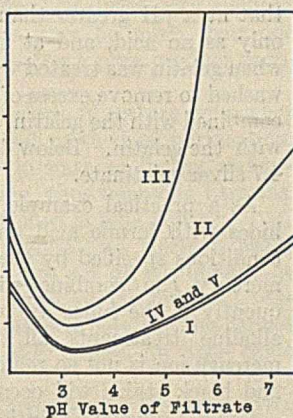


FIG. 4

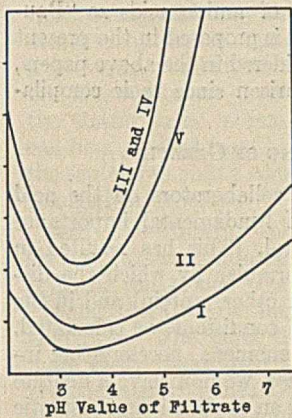


FIG. 5

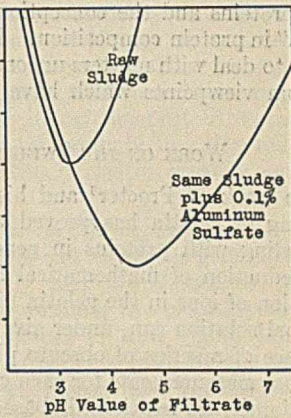


FIG. 6

FIG. 3—Showing the effect of temperature upon the efficiency of re-aerating sludge. I—Fresh sludge. II—Same after standing 45 hrs. III—Same after aerating 5 hrs. at 11°. IV—Same as II, but after aerating 5 hrs. at 22°. V—Same as II, but after aerating 5 hrs. at 34°
FIG. 4—Showing effect of the nature of the gas upon the efficiency of re-aerating sludge. I—Fresh sludge. II—Same after standing over night. III—Same after aerating 4 hrs. with hydrogen. IV—Same as II after aerating 4 hrs. with oxygen. V—Same as II after aerating 4 hrs. with air
FIG. 5—Same as Fig. 4 except that the sludge was covered with xylene during aeration
FIG. 6—Showing the effect of aluminium sulfate upon the condition of sludge

forced. Each cylinder had a diameter of 15 in. For each experiment 66 gal. of sludge containing 1 per cent of solid matter were used and air was forced through at the rate of 0.45 cu. ft. per min. Each cylinder was surrounded by a cooling or warming jacket and the temperature was maintained by means of water warmed with steam or cooled with ice.

A set of experiments is shown in Fig. 3. Curve I represents a sample of August sludge in excellent condition; Curve II this same sludge after standing for 45 hrs. at 20°. Portions of the sludge after standing were put into the 3 cylinders. The temperature of the first was maintained at 11°, the second 22°, and the third 34°. Each was aerated for 5 hrs. Apparently there is an optimum temperature of aeration lying between 11° and 34°, since better results were obtained at 22°. The experiment was repeated with the same result. The work will soon be extended to other temperatures and to sludges in a more septic condition. August sludge does not become septic rapidly at 20°.

The same cylinders were used to study the effect of the nature of the gas employed. During ordinary aeration, oxidation and nitrification of the sludge take place but

whether these are essential to bring the sludge into good condition for pressing is not yet clear. In Fig. 4, Curve I represents a good August sludge and Curve II shows the same sludge after standing over night. This sludge was then put into the cylinders at a temperature at 20°. The cylinders were covered to prevent the entrance of air as much as possible and the samples were aerated for 4 hrs., the first with hydrogen, the second with oxygen, and the third with air. Hydrogen made the sludge worse, while oxygen and air improved it to an equal degree and brought it back almost to its condition before standing over night.

The above experiment was repeated except for covering each sludge during aeration with a layer of xylene. The presence of the xylene entirely altered the results; all gases now made the condition of the sludge worse. Fig. 5 shows that hydrogen and oxygen now behave exactly alike, while air does not do so much harm.

DISCUSSION

Sufficient data are not yet available to form a sound theory of the mechanism of the activated sludge process, but speculation is desirable at this stage as a guide in outlining further experiments. It is generally conceded that putrefaction is usually due to bacteria or enzymes, both of which are present in the sludge. Whether or not bacteria and enzymes

are essential to the aeration process is not so clear. The question may be asked: Is the action aeration vs. putrefaction really a conflict between certain aerobic and anaerobic bacteria? The fact that the aeration action is more effective at 22° than at 34° makes it doubtful that ordinary enzymes are responsible, as these operate more effectively as the temperature is raised to 40°. This would also be borne out by the fact that aeration in one test was as effective at a pH value of 3 as at 8. On the other hand, the action is not merely mechanical, since hydrogen makes the sludge worse, whereas oxygen or air makes it better. But the presence of xylene renders the oxygen of no more value than the hydrogen. Is the action of the xylene to retard the action of aerobic bacteria or does it prevent some chemical action by becoming adsorbed by the surface of the sludge? Mechanical action alone, if sufficiently vigorous, will make the condition of the sludge worse. This constitutes a serious difficulty in attempting to use the centrifuge for dewatering sludge.

Whatever may be the initial cause of the aeration action, the ultimate change appears to be chemical. Good flocks were obtained by adding aluminium sulfate or sodium phos-

phate to the raw sewage, but not by adding sulfuric acid or lime. The cost of such treatment, however, was found to be much greater than aeration, with results not as good. The addition of aluminium sulfate to sludge lowers its condition curve, but at the same time changes its point of optimum hydrogen-ion concentration to a point between the isoelectric point of alumina and that of the sludge before adding aluminium sulfate. This is shown in Fig. 6. Re-aeration of sludge

lowers its condition curve, but not its point of optimum hydrogen-ion concentration. All curves in Fig. 1 have points of minimum at about 3.2. Does this suggest that the fundamental action of aeration is different from that of the aluminium sulfate? It is hoped that the line of experimenting recently begun may lead to a practically complete solution of this complex problem, at least so far as the most efficient chemical control of the plant is concerned.

The Chemical Constituents of Skin¹

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It is the object of this paper to present very briefly a survey of the chemical constituents of skin, regarded, as far as may be possible, as chemical individuals. In recent years two general papers on skin chemistry have appeared, one, written about 1910 but published posthumously, by R. A. Seymour-Jones,^{1*} and the other, published in 1920, by G. L. Terrasse.² These summarize the work on the subject, but deal more particularly with the structure of the hide proteins and the conception of amino acids as "Bausteine" in protein composition. It is proposed in the present paper to deal with matters unconsidered in the above papers, or from viewpoints which have arisen since their compilation.

WORK ON THE SWELLING OF GELATIN

The work of Procter³ and his collaborators on the acid swelling of gelatin has proved of fundamental importance in dealing with proteins in general. This has resulted in the deduction of mathematical formulas by which the distribution of ions in the gelatin (or other protein) and in the external solution can, under given conditions, be calculated. In place of a series of obscure phenomena, necessitating individual measurements for each case, we now have a definite stoichiometrical relationship based on applications of osmotic equilibria and Donnan's theory of membrane equilibria.

This theory of gelatin swelling depends, however, on a definite conception of the molecular structure of gelatin. Procter regards gelatin jellies and solutions as composed of a network of molecular dimensions. This permits the development of osmotic effects, while ions within the jelly remain within the range of molecular attractions. In a protein jelly the term "molecular" may, however, cover a relatively large space. Bütschli has formulated a theory in which the jelly is presumed to have a network of microscopic dimensions, while Quincke considers a jelly to be of two phases, a colloid-poor and a colloid-rich phase, the one dispersed in droplets throughout the other. This last view has met with considerable support, but, on the whole, the evidence favors Procter's view.

WORK ON ISOELECTRIC POINT OF PROTEINS

Arising from the work on gelatin swelling, most important results have been obtained in the researches of Jacques Loeb,⁴ who has clearly shown the importance of taking into account the isoelectric point of proteins and the hydron concentration of solutions employed. The isoelectric point (I. E. P.) has been shown to be, for proteins in general, coincident with the points of minimum swelling, conductivity, osmotic pres-

sure, viscosity, and solubility. For gelatin,[†] determinations vary from pH 4.5-4.7, and the value may be taken as about 4.6. No figures have been published yet for skin proteins in general, but work at Leeds University on hide powder gives the figure 4.8 for collagen.

The importance of this figure lies in the fact that proteins in general are amphoterics. Loeb has shown for gelatin, and the same probably applies to hide proteins in general, that at a pH greater than its isoelectric point it functions only as an acid, and at a less pH only as a base. Thus, when gelatin was treated with silver nitrate and subsequently washed to remove excess of the salt at pH 3.6 to 4.7, no silver combined with the gelatin, whereas above 4.7 silver combined with the gelatin. Below 4.7 gelatin nitrate exists and above 4.7 silver gelatin exists.

As a practical example, consider the disinfection of raw hides with formic acid and mercuric chloride. Under the conditions specified by the process, the pH is such that no mercury can combine with the hide substance. Consequently if the hides are washed prior to liming (or other alkaline treatment) all the mercury is removed. If the mercury ion is not so removed, it will be fixed in the limes, and black stains will occur in subsequent processes.

Using equivalent solutions of bases, Loeb found that all monacid bases gave a swelling, viscosity, and osmotic pressure practically identical, but considerably greater than di-acid bases. The same applies to acids; all functioning as monobasic acids gave practically identical curves, while dibasic acids (*e. g.*, sulfuric, and to a lesser extent oxalic) gave curves of diminished swelling, etc. This identity, however, applies only when plotting pH against the property measured; that is, the amount of acid present may vary considerably, but, provided the pH's be identical, all monobasic acids will swell the protein to the same extent.

In this fact lies the explanation of the mystery of the "Hofmeister" or "lyotrope" series, a curious sequence of ions arranged in the order in which they affect the properties of colloids. In the compilation of this series, the factor of hydron concentration was neglected. Provided all excess of the reacting salt is removed, the various properties of proteins, such as swelling, viscosity, osmotic pressure, etc., are in reality functions of the hydron concentration.

All this is of great importance in considering the effect of any reagent on the hide proteins. To take a case in point: It will have been noticed that the isoelectric point for gelatin, and presumably for collagen, lies decidedly on the acid side of the point of true neutrality. The actual curve for gelatin, where swelling is plotted against pH, shows a fairly sharp rise to a maximum at about 2.4, a fall to a minimum at 4.6, and a slow gradual rise to a maximum at about 12. If a hide is

¹ Presented before the Division of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

* Numbers in the text refer to Bibliography.

[†] Michaelis, 4.7; D. Jordan Lloyd, 4.6; Loeb, 4.7; M. H. Fischer, 4.5.

in a liquor of pH 2, for example,⁸ decreasing the acidity will increase the swelling until a pH of 2.4 is reached, then will decrease the swelling to a pH of 4.6. Similarly, for a hide in liquor of pH 6, increasing acidity will decrease the swelling until a pH of 4.6 is reached. And all this is on the acid side of the neutral point. The importance of the swelling curve in relation to pH is then obvious in tan liquors, the manufacture of synthetic tannins, and the like.

CONSTITUENTS OF HIDE

The individual constituents of hide may be divided into proteins, fats, and mineral salts.

The mineral salts consist of phosphates and aluminates in very small quantity associated with keratin in the epidermis and of small quantities of various mineral substances, chiefly sodium and potassium chlorides, calcium and magnesium phosphates, in the blood. In the latter also occurs hematin, a highly complex organic iron salt. Generally speaking, the mineral constituents of skin are negligible.

The proteins are mainly scleroproteins or albuminoids (*i. e.*, miscellaneous proteins not allotted to any group), but also include some albumins and globulins.

COLLAGEN—Of the proteins, the most important to the tanner is collagen, which forms the constituent of the white fibers of the corium. It contains carbon, hydrogen, nitrogen, oxygen, and perhaps a little sulfur. Analyses vary slightly, indicating that conceivably there may be more than one collagen, but the difficulty of obtaining a pure product probably explains the variations.

In fresh hide the white collagenous fibers are somewhat swollen and hydrated. The normal method of purification, which is used in practice, consists in washing, liming, unhairing, deliming, bating, and scudding, thus removing keratins, mucins, and elastins. Such a collagen is hide powder.

As to structure, it has been argued that collagen has a ring formation, since trypsin will not act on it unless it be previously swollen with acid or alkali, or treated with pepsin. On the other hand, many synthetic polypeptides cannot be hydrolyzed by trypsin, but still possess an open chain structure.

From the fact that boiling collagen with water hydrolyzes it to gelatin, and from the general similarity between the two, it is commonly supposed that collagen is an anhydride of gelatin.⁵ Furthermore, gelatin heated above 100° is gradually converted into an insoluble substance which, apart from its lack of fibrous structure, closely resembles collagen. Since it is impossible to obtain gelatin again from this by mere boiling,⁶ this argument is of doubtful value. It is known that hide dried at 60° for some hours cannot be softened back, and this is similar to the effect of heat on gelatin. Merely as a suggestion, this hardening on heating may be similar in origin to the coagulation of egg albumen. Analysis does not help in determining the question; the similarity in the figures is great. Collagen has a slightly higher carbon content than gelatin, but is lower in nitrogen, the differences being too small for definite conclusions. On the other hand, collagen gives positive Millon and xanthoproteic tests, indicating the presence of tyrosine and phenylalanine, tests which are negative or only very slightly positive with gelatin.

Collagen forms salts, just as gelatin does, and we may have, for instance, collagen chloride and lime collagenate, depending on the pH's of the solutions employed. There can be but little doubt that collagen is appreciably changed during the earlier processes of leather manufacture, and hence the collagen of fresh and delimed hide is not necessarily identical. The slow hydrolysis of collagen, by alkalies or acids, has not been studied.

The formation of salts by collagen is of importance in the theory of tanning. There is now no reason for doubting the

formation of collagen tannates, collagen chromates, or chromium collagenates, as the case may be. But this is not to say that one single theory will explain every type of tannage. So many substances can be used to tan leather that no one explanation can at present cover all. Further, Shorter⁷ found that the electrical reactions of skin varied according to tannage. With raw hide and wool rubbed together, the hide had a negative and the wool a positive charge; the same applied to oil leather and wool, but with vegetable tanned leather and wool, the wool had a negative and the leather a positive charge.

ELASTIN—The most stable protein of hide is elastin, found in the yellow elastic fibers. It also occurs in many tendons of the body, including the *ligamentum nuchae*, the tendon at the back of the ox's head, and it is the elastin from these sources rather than that of the skin which has been most studied. It has extraordinary elastic properties. The writer found that a piece of *ligamentum nuchae* of about 1 cm. square section gave on a testing machine an extension of 150 per cent before breaking, the strain being too small to measure (*i. e.*, less than 5 lbs.). Elastin is not completely dissolved on boiling with water, is scarcely attacked by acetic acid or cold or hot 1 per cent alkali, and apparently does not combine with tannin or chrome. The writer found that *ligamentum nuchae* is, however, slowly digested by lime solutions, though this may be due to bacteria. It is very slightly attacked by pepsin, but more readily by trypsin, especially if previously boiled, or treated with acids or alcohol. The previous treatment of pelts with alkaline solutions may affect the elastin so as to render it less resistant to trypsin. It can be separated from hide by merely boiling after unhairing, the scutch remaining consisting of elastin, possibly somewhat changed in process.

KERATIN—Keratins occur in the epidermis, hair, hair sheaths, walls of sudoriferous and sebaceous glands, and cell walls in the blood. Usually they are classed as "old" or "young" keratin, the latter forming the basal layers of the epidermis. The chief difference is that young keratin is more easily hydrolyzed than is old keratin by the action of proteoclastic enzymes (*e. g.*, trypsin and pepsin) or dilute alkali. Both are insoluble in water, except on boiling under pressure; they are hydrolyzed by concentrated alkali or sodium sulfide solutions. Since dilute acids may be used to unhair,⁸ possibly young keratin is soluble therein.

MUCIN—Mucins occur in the so-called "coriin" or cementing substance. Procter regards this as some substance "nearly identical with, but somewhat more soluble than that of the fibrils themselves."⁹ It is easily soluble in dilute acid or alkali. Van Lier¹⁰ found it was rather a mucoid, and was usually contaminated with nucleoproteins. By repeated extraction of pelt with half saturated lime water, he found no more could be obtained and therefore claimed that it is not a hydrolytic decomposition product of collagen. It is precipitated by 5 per cent acetic acid, but is soluble in excess; the precipitate consists of a mass of stringy fibers. It is soluble in 1 to 2 per cent hydrochloric acid, and, on boiling some time, reduces Fehling solution. Ox, horse, and calf mucoid appear identical, but they differ from mucoid obtained from tendons. Eitner¹¹ states that it is rendered less soluble on drying at a high temperature. Long liming will obviously open up the fibers by dissolving the coriin.

The blood and lymph in skin are responsible for the presence of serum-albumin and globulin, fibrin, and keratins of the cell walls. Albumin combines with tannin, but is usually removed by soaking and liming.

FATS—The fats of the fat cells consist chiefly of lecithins and cholesterol, *i. e.*, mixed triglycerides, in which a com-

plex phosphoric acid-choline radical replaces one hydroxyl, and alcohols. In certain sebaceous glands cetyl and octodecyl alcohols have been reported. Unfortunately our knowledge of the skin fats is still very limited, and other bodies may also be present in the fat cells.

Much yet remains to be done before the chemistry of skin can be considered to be thoroughly understood, but though progress has been slow in the past, each forward step materially widens the path for those who follow. In any case, it is only through a sounder knowledge of the basic raw material that the art and science of leather manufacture can hope to make progress.

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Influence of Sodium Chloride, Sodium Sulfate, and Sucrose on the Combination of Chromic Ion with Hide Substance¹

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Continuation of the authors' work offers evidence that the retarding action of neutral salts in chrome tanning is due to the formation of addition compounds, with hydration as a secondary cause.

The significance of the presence of neutral salts in chrome liquors was first shown by Wilson and Kern,⁴ and several studies of their effects have been published from this laboratory.⁵ Recently Wilson and Kern⁶ made a further investigation of the question and suggested as an hypothesis that the retarding action on the chrome tanning might be due to hydration by the added salt, resulting in an actual increase in the concentration of chromic ion. Since Miss Baldwin⁷ had found that increase in concentration of a chrome liquor over 16 g. Cr₂O₃ per liter resulted in a diminution of the amount of chromium fixed by hide substance, this hypothesis appeared reasonable.

If hydration did take place, the concentration of hydrogen ion should be increased as well as that of the chrome. That this was actually the case with chlorides was shown by Thomas and Baldwin,⁸ but at the same time they demonstrated that sulfates lower the hydrogen-ion concentration of acid solutions, as measured by the hydrogen electrode. Since Wilson and Kern found that sodium sulfate decreased the fixation of chrome, just as sodium chloride and other chlorides did, they were obliged to admit another possible factor, namely, the formation of addition compounds between the chromium salt and added sulfate as well as between the acid present and added sulfate.

With the view of approaching a solution of this question the following experiments were carried out. In addition to sodium chloride and sulfate, the former raising the C_H⁺ and the latter lowering it, sucrose was selected as a hydrating

nonelectrolyte since H. C. Jones⁹ has shown that it hydrates considerably in aqueous solution. Inasmuch as Thomas and Kelly¹⁰ had shown that in a period of 48 hrs.' contact the maximum combination of chrome with hide substance was effected by a chrome liquor containing 15.5 g. Cr₂O₃ per liter, three sets of liquors were selected, one containing 15.5 g. Cr₂O₃ per liter, and two others 3 g. and 100 g. Cr₂O₃ per liter.

MATERIALS AND TECHNIC

1920 and 1921 American Standard Hide Powder served as the source of hide substance. The chrome liquors were prepared by dilution of pure concentrated liquors made by reduction of chemically pure sodium dichromate with sulfurous acid, as described by Thomas and Kelly.¹¹

Portions of hide powder equal to 5 g. of absolutely dry substance were covered with 50 cc. of distilled water in bottles, and allowed to stand over night, when the salts or sugar to give the desired concentrations were added. Finally 150 cc. of chrome liquor were added, of such a concentration that if it were diluted to 200 cc., it would contain 3, 15.5 or 100 g. Cr₂O₃ per liter. The mixtures were rotated in a tumbling machine for 48 hrs., filtered through muslin bags, and washed well with tap water and three times with 200-cc. portions of distilled water. The powder was air-dried at 30° C., then at 100° C., and finally allowed to come to equilibrium with atmospheric humidity. Moisture, nitrogen, and chromium were determined. Multiplication of the per cent nitrogen by 5.614 gave per cent hide substance. All figures in the tables are on the moisture-free basis.

TABLE I (LIQUOR CONTAINED 3 G. Cr₂O₃ PER LITER)

Concentration of Salt	Protein Per cent	Cr ₂ O ₃ Per cent	Mg. Cr ₂ O ₃ per G. Hide Substance
M (NaCl)			
0	83.75	4.44	53
0.5	88.01	3.62	41
1	90.03	3.16	35
2	90.37	3.45	38
3	88.05	3.75	43
4	87.58	4.19	48
(Na ₂ SO ₄)			
0.5	90.71	4.35	48
1	91.27	3.19	35
2	93.12	2.13	23
3	91.82	2.11	23

¹ Presented before the Section of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

² Published as Contribution No. 381 from the Chemical Laboratories of Columbia University.

³ Assistant Professor.

⁴ *J. Am. Leather Chem. Assoc.*, 12 (1917), 445.

⁵ *Ibid.*, 13 (1918), 248; 14 (1919), 10; *J. Am. Chem. Soc.*, 41 (1919), 1981.

⁶ *J. Am. Leather Chem. Assoc.*, 15 (1920), 273.

⁷ *Ibid.*, 14 (1919), 433.

⁸ *J. Am. Chem. Soc.*, 41 (1919), 1981.

⁹ *Carnegie Inst. Publ.*, 60 (1907).

¹⁰ *THIS JOURNAL*, 13 (1921), 31.

¹¹ *J. Am. Leather Chem. Assoc.*, 15 (1920), 665.

Measurements of the hydrogen-ion concentration of the liquors belonging to Table II verified the contrasting effects of sodium chloride and of sodium sulfate previously reported from this laboratory.

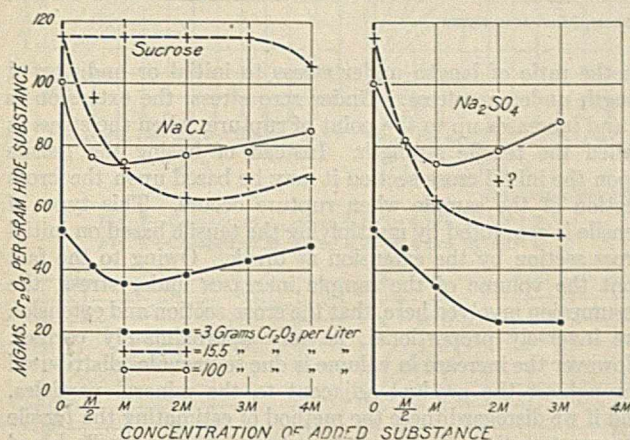


FIG. 1

TABLE II (15.5 G. Cr_2O_3 PER LITER)

Concentration of Salt <i>M</i> (NaCl)	Protein Per cent	Cr_2O_3 Per cent	Mg. Cr_2O_3 per G. Hide Substance
0	77.92	9.01	116
0.5	79.18	7.59	96
1	81.27	5.93	73
2	82.86	5.26	63
3	84.38	5.90	70
4	83.93	5.85	70
(Na_2SO_4)			
0.5	81.07	6.58	81
1	84.32	5.29	63
2	83.48	5.76	69
3	85.44	4.36	51

TABLE III (100 G. Cr_2O_3 PER LITER)

Concentration of Salt <i>M</i> (NaCl)	Protein Per cent	Cr_2O_3 Per cent	Mg. Cr_2O_3 per G. Hide Substance
0	75.57	7.70	101
0.5	80.78	6.17	76
1	82.13	6.15	75
2	82.42	6.35	77
3	81.23	6.35	79
4	79.10	6.77	86
(Na_2SO_4)			
0.5	80.17	6.62	83
1	81.07	6.01	74
2	77.42	6.11	79
3	78.08	6.87	88

The results are plotted in Fig. 1. The curves representing the effect of sodium chloride all proceed to a minimum and show an upward trend similar to the results Wilson and Kern found with magnesium chloride. In all cases sodium sulfate shows greater inhibiting action than sodium chloride, and a minimum with upward slope is obtained only where the liquor is very concentrated. Contrasted to the effect of the electrolytes, we find that sucrose apparently has no effect except at 4 *M* concentration.

TABLE IV (15.5 G. Cr_2O_3 PER LITER)

Concentration of Sucrose <i>M</i>	Protein Per cent	Cr_2O_3 Per cent	Mg. Cr_2O_3 per G. Hide Substance
0	77.47	8.92	115
1	74.76	8.59	115
2	74.72	8.59	115
3	74.83	8.60	115
4	76.74 ¹	8.13	106

¹ This sample appeared to be scorched in spots after drying at 100° C.

TABLE V (LIQUORS CONTAINED 15.5 G. Cr_2O_3 PER LITER)

Concentration of Salt <i>M</i>	Log C_H of Original Liquor	Log C_H of Filtrate
0	-2.78	-2.90
1	-2.54	-2.67
2	-2.39	-2.43
3	-2.20	-2.33
4	-2.10	-2.20
(Na_2SO_4)		
0	-2.80	-2.85
1	-2.91	-2.92
2	-2.91	-3.07
3	-2.67	-3.01

INTERPRETATION OF RESULTS

Since sucrose hydrates in aqueous solution, the inhibition of the fixation of chrome by the lower concentrations of sodium chloride and of sodium sulfate does not appear to be due to hydration. The writers believe that, as Wilson and Kern suggested for sulfates, sodium chloride, as well as the sulfate, forms addition compounds with the constituents of chrome liquor, rendering them less dissociated and consequently less active in combining with the proteins of hide substance. This is like the influence of sodium chloride in inhibiting the adsorption of mercuric chloride by charcoal, which Rona and Michaelis¹² point out is similar to the decrease in toxicity of mercuric chloride in the presence of sodium chloride. They ascribe such effect to the formation of the complex ions HgCl_3^- and HgCl_4^{2-} .

Upon increasing the concentration of salt the hydration effects a virtual concentration of the chrome to such an extent that the retarding action of the addition compound formation is counterbalanced somewhat by the activity of the high chrome concentration, and the curves slope upward. Sodium sulfate does not show the upward slope because, first, owing to mass action it can drive back the ionization of chromic sulfate which represses the activity, as well as causing addition-compound formation, and, second, according to the results of H. C. Jones, it does not hydrate to a large extent. The upward trend with sodium sulfate is shown only where the liquor is very concentrated at the beginning. That the effect of hydration is secondary to addition compound formation is illustrated by sucrose. While it hydrates in aqueous solution, it has no retarding effect on the fixation of chrome. It would seem that since it does not retard the action of the chrome, it must not form the addition compounds, except at concentrations over 3 *M*. The 4 *M* value shows a retardation which we ascribe to a different chemical mechanism. The effect of compounds with several hydroxy groups in forming soluble un-ionizable complexes with the metals, such as tartrate with copper, mannite and glycerol with iron, etc., is well known. The 4 *M* sucrose chrome solution was thick and sirupy in consistency and it seems plausible that a similar compound of chromium and sucrose was formed.

ACKNOWLEDGMENT

We take pleasure in expressing our indebtedness to Messrs. A. F. Gallun and Sons Co., of Milwaukee, for their generous support of this investigation.

¹² *Biochem. Z.*, 97 (1919), 85.

Industrial Alcohol

During the past few months the securing of alcohol for legitimate manufacturing purposes has been made more difficult and new regulations or modifications of existing ones have placed hardships upon those entitled to tax-free use of this necessary chemical raw material. Many protests have been made and the time has now come when manufacturers must be heard and their claims recognized.

The American Chemical Society at the Rochester Meeting appointed a Committee on Industrial Alcohol with the following personnel: R. F. Bacon, Charles Baskerville, F. R. Eldred, Edward Mallinckrodt, Jr., G. D. Rosengarten, M. H. Ittner, *Chairman*, B. R. Tunison, *Secretary*.

This Committee is anxious to know of any and all cases where legitimate manufacturers have had difficulty in obtaining alcohol needed for industrial purposes, and urges that all details available be sent to it. The Committee is ready to cooperate in every way possible and proposes to place the facts before the authorities in Washington in an effort to have them distinguish between beverage and industrial alcohol and to have them carry out the mandatory provisions of the Prohibition Act, which provides not only for national prohibition, but for the extension and development of the use of alcohol in fuels, dyes, medicinal and pharmaceutical preparations, and other lawful industries.

Correspondence should be addressed to any member of the Committee, but preferably to the Secretary, B. R. Tunison, U. S. Industrial Alcohol Co., 27 William St., New York.

Energy Absorbing Capacity of Vulcanized Rubber¹

By H. P. Gurney and C. H. Tavener

BOSTON BELTING CO., BOSTON, MASSACHUSETTS

It is the purpose of this paper to indicate some relations which exist between the capacity of vulcanized rubber to absorb or to store up in a potential form and partially to transform or degrade kinetic energy into heat when subjected to single or repeatedly applied stresses, and factors of construction, such as type of crude rubber, rubber content, and particularly the temperature and duration of cure or heat treatment.

Lieut. J. C. Hunsaker² has pointed out that airplane shock absorbers are more serviceable when constructed of a high rubber content product than of a low rubber content product (by compounding with larger amounts of mineral fillers). While the energy absorbed in the first stress cycle to which the shock absorber is subjected when an airplane lands is not so great where the rubber content is high, the rate of diminution in successive cycles is not so rapid. To express this in terms of human qualities, a product of high rubber content possesses more endurance and is less rapidly fatigued. The importance of these considerations lies in the fact that the greatest stresses which occur to the airplane structure depend upon the rate of stress increase per unit of energy input into the material which absorbs the landing shocks.

When an airplane lands, there is imposed upon the shock absorbers, an intermittent oscillation of stresses between a minimum and decreasing maxima. In the first cycle, the entire downward energy component of the airplane is largely absorbed as work of extension in the shock absorbers. Immediately following the extension, the absorbed potential energy partly reconverted into an upward kinetic energy component, causing the airplane to bound upward from the earth. On the next return to earth, most of the energy of contraction of the first cycle reappears as energy of extension of the second cycle, minus, of course, whatever portion of this energy has been lost through air friction, and through hysteresis in the tires.³

An ideal machine for observing the operation of airplane shock absorbers would measure not only the load-extension relation but, by means of some integrating device, the amount of energy absorbed and returned in successive cycles. By making the energy of extension of any cycle equal to (or a large fraction of) the energy of contraction of the previous cycle, a very accurate comparison could be made between the energy absorbing capacities of different shock absorbers.

METHOD AND CALCULATIONS

In the present investigation, samples of vulcanized rubber 0.1 in. thick, 0.5 in. wide, with marks placed initially 2 in. apart, were subjected to different types of fluctuating stresses in a calibrated tensile testing machine, so arranged that loads are recorded both when decreasing or increasing. Recorded strains were read to the nearest 0.1 in. and divided by 2 to convert into extension ratios. To convert loads into stresses, they were divided by the width and thickness of the samples, the widths being measured in 0.01 in. and the thickness in 0.001 in. Thus, approximately, loads multiplied by 20 gave stresses in lbs. per sq. in. All stresses therefore are expressed in lbs. per sq. in. of initial or undistorted cross section unless otherwise noted. The extensions under stress are expressed

as the ratio of length under stress to initial or undistorted length under no stress. Under zero stress, the extension is 1 and increases up to the point of rupture, when the stress is called the tensile strength. Instead of basing the tensile upon the initial cross section it may be based upon the cross section of the sample when rupture occurs. This type of tensile is computed by multiplying the tensile based on initial cross section by the extension at break. Owing to the fact that the volume of the sample increases under stress, the assumption involved here, that the cross section and extension are inversely proportional, is only approximately correct. However the increase in volume is due to vacuoles distributed throughout the product adjacent to the mineral particles, and if we disregard these the method of estimating the tensile per cross section at rupture is correct. If the tensile based on the actual cross section at rupture be divided by the proportion of rubber by volume, the resulting tensile thereby becomes based on the actual rubber cross section at rupture.

Even this does not take into account micro-inequalities of stress in the rubber portion. These undoubtedly vary from point to point and are doubtless due to the nature, size, concentration, and degree of dispersion of the filling media.

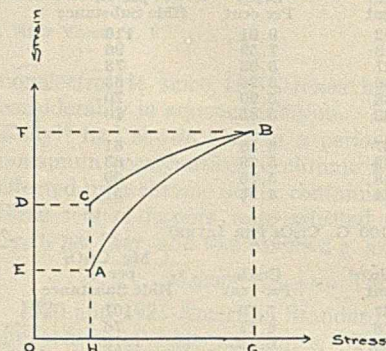


FIG. 1

The work or energy involved in stressing is referred to a unit volume (hence will have the same dimensions as stress). This unit of energy per unit volume is expressed in ft. lbs. per cu. in. This work or energy is of three types.

1—The work of extension, which is the work done upon the vulcanized rubber in increasing the stress from a minimum value to a maximum, whereby kinetic energy is converted into potential energy of stress.

2—The work of contraction, which is the energy released as the stress is reduced from the maximum to minimum value, whereby a portion of the potential energy of stress reappears as kinetic energy.

3—The energy of hysteresis, which is the difference between the energy of extension and contraction.

This may be made clearer by referring to Fig. 1. The condition of the vulcanized rubber is represented by A, the stress being OH or EA, the elongation (extension minus unity) by OE or HA. Let the elongation be increased from OE to OF by an increase of stress of OH to OG. The amount of work done upon a unit volume of rubber by this change is proportional to the area ABFE, since

$$\text{Energy of extension} = \int_E^F (\text{Stress varying EA to FB}) \times (\text{Infinitesimal strain increases}) = ABFE.$$

If, thereupon, the stress be reduced from OG to OH, the elongation is not reduced from OF to OE but from OF to OD. The energy liberated is proportional to the area CBED.

$$\text{Energy of contraction} = \int_F^D (\text{Stress varying FB to CD}) \times (\text{Infinitesimal strain decreases}) = CBFE.$$

¹ Received July 13, 1921.

² "Notes on Aeroplane Shock Absorbers of Rubber," *Aviation and Aeronautical Eng.*, September 1, 1916.

³ This matter is amply treated from a standpoint of practical design by Prof. A. Klemm, in "Course in Aerodynamics and Airplane Design," in *Aviation and Aeronautical Eng.*, June 1, 1917.

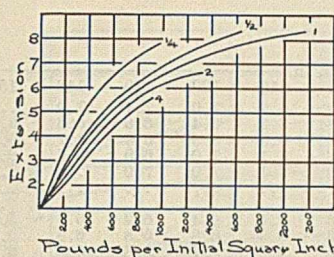


FIG. 2

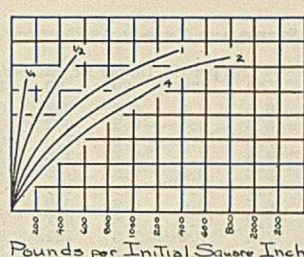


FIG. 3

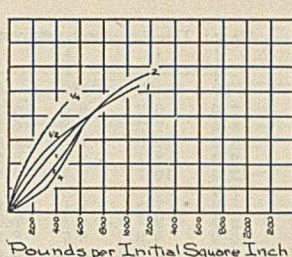


FIG. 4

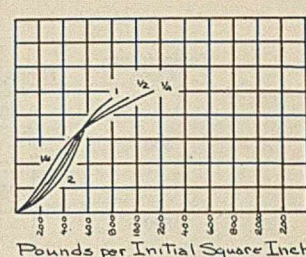


FIG. 5

RELATION BETWEEN STRESS AND STRAIN

Fig. 2—Compound A, cured 0.25 to 4 hrs. at 300° F
Fig. 3—Compound B, cured 0.25 to 4 hrs. at 300° F.

Fig. 4—Compound C, cured 0.25 to 4 hrs. at 280° F.
Fig. 5—Compound C, cured 0.25 to 2 hrs. at 300° F.

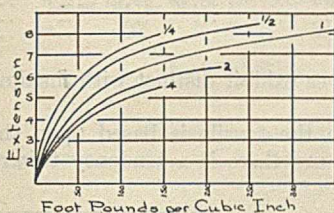


FIG. 6

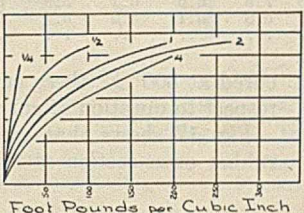


FIG. 7

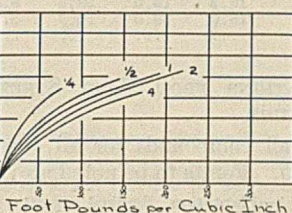


FIG. 8

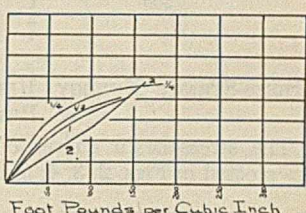


FIG. 9

RELATION BETWEEN STRAIN AND ENERGY ABSORBED PER UNIT VOLUME

Fig. 6—Compound A, cured 0.25 to 4 hrs. at 300° F.
Fig. 7—Compound B, cured 0.25 to 4 hrs. at 300° F.

Fig. 8—Compound C, cured 0.25 to 4 hrs. at 280° F.
Fig. 9—Compound C, cured 0.25 to 2 hrs. at 300° F.

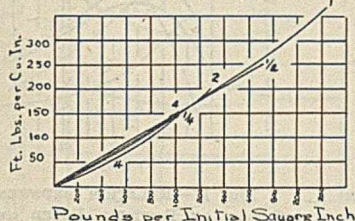


FIG. 10

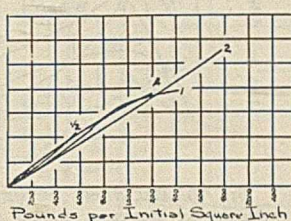


FIG. 11

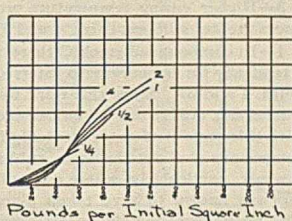


FIG. 12

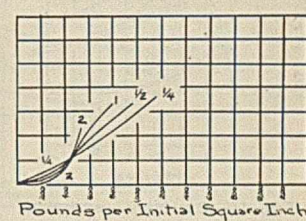


FIG. 13

RELATION BETWEEN ENERGY ABSORBED PER UNIT VOLUME AND STRESS

Fig. 10—Compound A, cured 0.25 to 4 hrs. at 300° F.
Fig. 11—Compound B, cured 0.5 to 4 hrs. at 300° F.

Fig. 12—Compound C, cured 0.25 to 4 hrs. at 280° F.
Fig. 13—Compound C, cured 0.25 to 2 hrs. at 300° F.

The difference between the energy of extension and the energy of contraction is the energy of hysteresis and is proportional to the area ABCDE.

$$ABFE - CBFD = ABCDE$$

If the sample starts from zero stress the points O, A, and E coincide and the energy of hysteresis is proportional to the area ABC. In all work involved in this paper the stress-strain curves were plotted on coordinate paper and the energies of extension and hysteresis determined by planimetry the areas involved and multiplying by a suitable constant.

Referring again to Fig. 1, another cycle may start at C and the process be repeated. The corresponding curves and areas will differ on each successive cycle, although they may approach asymptotically toward definite values and loci.

For the investigation three rubber compounds were employed using a wide range of cures or heat treatments. Compounds A and B in Table I were commercially designated as pure gum stocks, while C was a "compounded" stock. The only difference between A and B was that Plantation Smoked Sheet was used in A, while Upriver Fine Para was used in B. B and C differed in rubber content. In all compounds the ratio of sulfur to rubber was 7 per cent by weight.

Since difference in working has a marked influence upon stress-strain curves, particularly where the stock is heavily compounded, all the mixing and milling of the three compounds took place under as nearly as possible identical conditions and all of each compound was sheeted out at the same time. Even the temperature of breakdown has a

bearing; the colder the temperature, the more intense the breakdown effect. Hence as far as possible the temperature during the mixing and milling was kept as uniform as possible throughout.

TABLE I—PROPORTIONS OF INGREDIENTS AND PROPERTIES OF COMPOUNDS (On volume basis, in parts per thousand)

INGREDIENTS	COMPOUNDS		
	A	B	C
Crude rubber: Fine Para	0	940	0
Smoked sheet	940	0	630
Vulcanizer: Sulfur	30	30	20
Accelerator: Magnesia	10	10	10
Fillers: Whiting	0	0	320
Carbon black	20	20	20
Specific gravity	1.00	1.00	1.52
Per cent of rubber by weight	87	87	38
Ratio of sulfur to rubber by weight	7	7	7
Estimated specific volume heat	0.4	0.4	0.45

Compounds A, B, and C were each cured for 0.25, 0.5, 1, 2, and 4 hrs. at 300° F. In addition, Compound C was cured for the same durations of time at 280° F. In all figures the curves obtained from these cures are designated by the numbers 1/4, 1/2, 1, 2, and 4.

The behavior of these vulcanized rubber samples to stresses will be treated in two general ways, (1) stress increasing from zero to rupture, and (2) stress alternating between definite maxima and minima.

Throughout the work no sample was subjected to more than one test. All samples were allowed to rest several weeks before any tests were started and each series of tests where comparisons are made were performed on the same afternoon.

TABLE II—RELATION BETWEEN STRESS AND ENERGY ABSORPTION

Compound	Temperature Cure ° F.	Hours of Cure	Lbs. per Sq. In. per Ft. Lb. per Cu. In.													
			20	30	40	50	60	70	80	90	100	110	120	130	140	150
A	300	0.25	7.0	6.7	6.5	6.4	6.5	6.6	6.6	6.7	6.8	6.9	7.0	7.1	7.0	...
		0.5	8.5	7.3	7.0	6.8	6.5	6.5	6.3	6.2	6.4	6.3	6.4	6.6	6.6	6.7
		1	8.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	6.8	6.8	6.8	6.8	6.7	6.7
		2	9.0	8.7	8.0	8.0	7.9	7.7	7.5	7.3	7.3	7.1	7.0	6.9	6.7	6.6
		4	12.5	10.7	9.7	9.0	8.3	8.0	7.8	7.6	7.3	7.1	7.0	7.0
B	300	0.25	7.5	
		0.5	8.0	7.3	7.0	6.6	6.7	6.4	6.3	5.9	
		1	9.9	9.7	8.8	7.6	7.2	7.0	6.8	6.7	6.6	6.4	6.4	6.2	6.0	5.9
		2	10.0	9.8	8.7	8.2	7.8	7.0	7.3	7.1	7.0	6.9	6.8	6.8	6.8	6.7
		4	6.5	6.0	6.8	5.6	5.7	5.6	5.5	5.4	5.5	5.6	5.7	5.8	5.9	6.0
C	280	0.25	10.0	9.7	9.0	8.8	8.3	
		0.5	12.0	10.7	9.2	8.8	8.3	7.6	7.3	7.1	6.9	
		1	13.0	11.0	9.5	8.8	8.3	7.4	7.1	6.8	6.5	
		2	15.0	12.0	10.0	9.0	7.7	6.9	6.4	6.0	5.7	
		4	18.0	13.4	10.7	9.0	7.7	6.6	5.9	5.7	5.4	
	300	0.25	13.5	10.7	9.5	8.6	8.0	7.7	7.5	7.3	7.1	
		0.5	15.0	11.7	10.8	8.6	7.7	7.0	6.4	6.0	5.9	
		1	16.5	13.0	10.5	8.8	7.5	6.6	6.1	5.8	5.6	
		2	18.0	13.0	10.9	8.0	6.8	6.1	5.6	5.2	5.0	
		4	

STRESS-STRAIN ENERGY RELATIONS FROM ZERO STRESS TO RUPTURE

The stress-strain curves of all compounds for all cures are plotted in Figs. 2, 3, 4, and 5. Points to be noted are:

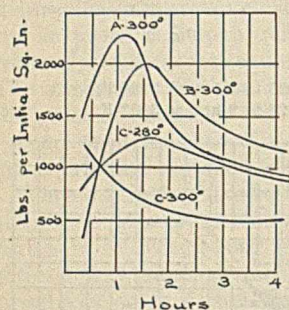


FIG. 14—RELATION BETWEEN STRESS AT RUPTURE AND TIME OF CURE

1—Plantation Smoked Sheet is quicker curing and produces stiffer curves than Fine Para (Figs. 2 and 3).

2—For slight stresses the compounded stock C is stiffer than the purer stocks A and B (Figs. 2 and 4).

3—Higher curing temperature produces greater stiffness (Figs. 4 and 5).

4—In compounded stock C there is a tendency for the curves to intersect (Figs. 4 and 5). Since this work was carried out (1917) one of us has met with this same tendency repeatedly in compounds of about the same rubber content, particularly where overmilling was known to have taken place. The phenomena may have some relation to the softening tendency noted by Gurney in an earlier paper.⁴

The relations between the extension ratio and ft. lbs. per cu. in. are plotted in Figs. 6, 7, 8, and 9. Points to be noted are:

1—A general resemblance to Figs. 2, 3, 4, and 5 except for the absence of a point of intersection.

2—Plantation Smoked Sheet shows less extension for the same energy absorption than Fine Para (Figs. 6 and 7).

3—Stocks A and B are more extensible for equal energy absorptions than the compounded stock C (Figs. 6 and 8).

The relations of stress to energy absorption are plotted in Figs. 10, 11, 12, and 13. The following may be noted:

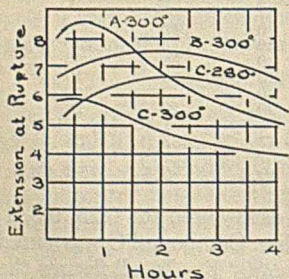


FIG. 15—RELATION BETWEEN STRAIN AT RUPTURE AND TIME OF CURE

1—The relation for A and B is nearly linear for all cures (Figs. 10 and 11).

2—With compounds A and B the direction of slope is nearly constant and independent of the time of cure.

3—With compounded stock C for a given energy absorption:

a—For low energy absorption the stress is greater the longer the cure.

b—For high energy absorptions the stress is lesser the longer the cure. (Figs. 12 and 13.)

4—As a corollary to the above there is a point of intersection or reversal of curvature.

In Table II are given the relations between stress per unit energy absorption and energy absorption for the different compounds and the different cures.

The relations between stresses based on initial, actual, and rubber cross sections, extensions, and energy absorption at rupture and the durations of cure are brought out in Figs. 14, 15, 16, 17, and 18. Except for the curve of Compound C

cured at 300° F., these curves exhibit distinct maxima with respect to duration of cure.

Fig. 17 shows that when the tensile is based upon the rubber cross section at rupture there is a tendency toward

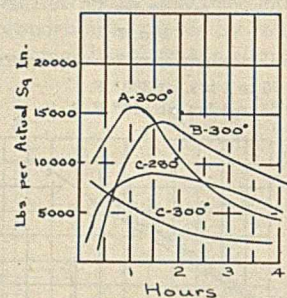


FIG. 16—RELATION BETWEEN STRESS AT RUPTURE BASED ON ESTIMATED RUBBER CROSS SECTION AND TIME OF CURE

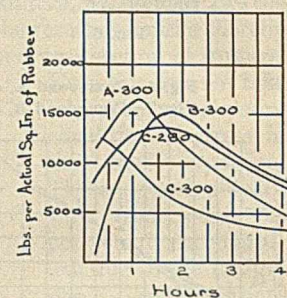


FIG. 17—RELATION BETWEEN STRESS AT RUPTURE BASED ON ESTIMATED RUBBER CROSS SECTION AND TIME OF CURE

equalization. The real rupturing strength of the rubber itself is not so markedly reduced by compounding as would be expected.

ENERGY ABSORPTION AND HYSTERESIS UNDER RECURRING ALTERNATION OF STRESSES

Preliminary to the main portion of this investigation, one compound, A, cured 1 hr. at 300° F. was subjected to alternating stresses between 0 and

300, 600, and 900 lbs. per sq. in.; 100 and 400, 700, and 1000 lbs. per sq. in.; 200 and 500, 800, and 1100 lbs. per sq. in. These stresses therefore commence at 0, 100, and 200 lbs. per sq. in. and increase by 300, 600, and 900 lbs. per sq. in.

In Figs. 19, 20, and 21 are given the extensions at maximum (solid lines) and minimum (dotted lines) plotted against the number of the cycle. The following is apparent:

1—The minimum extensions not only increase as the minimum stress increases, but spread further apart.

2—The maximum extensions increase, although but slightly compared to the minimum extensions.

3—The lines thus plotted are not straight lines although approaching asymptotically to a straight line.

Figs. 22, 23, and 24 exhibit energy absorption (solid lines)

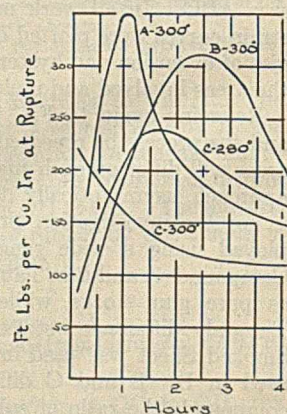


FIG. 18—RELATION BETWEEN ABSORBED ENERGY PER UNIT VOLUME AT RUPTURE AND TIME OF CURE

⁴ THIS JOURNAL, 13 (1921), 707.

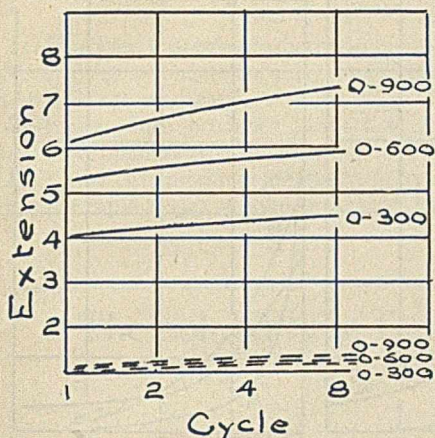


FIG. 19

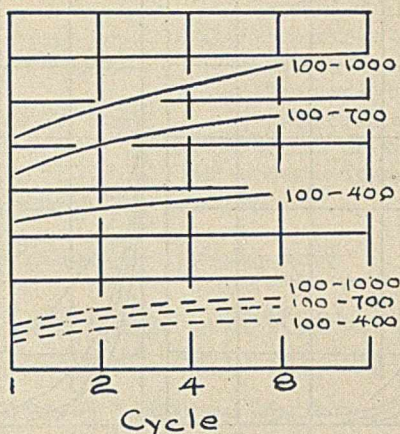


FIG. 20

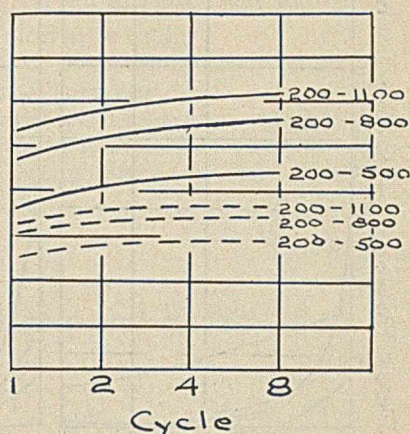


FIG. 21

RELATION BETWEEN CYCLE NUMBER AND MAXIMUM AND MINIMUM EXTENSIONS, COMPOUND A, CURED 1 HR. AT 300° F.

Fig. 19—Stresses alternating between 0 and 300, 600, and 900 lbs. per sq. in. Fig. 20—Alternating between 100 and 400, 700, and 1000 lbs. per sq. in. Fig. 21—Alternating between 200 and 500, 800, and 1100 lbs. per sq. in.

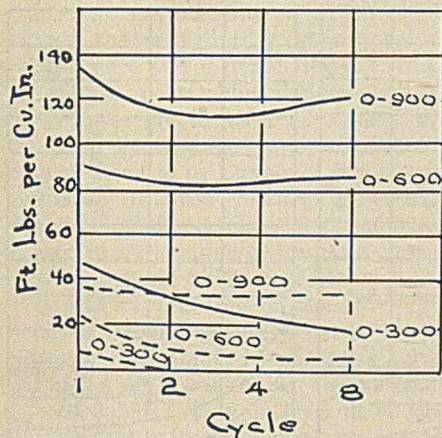


FIG. 22

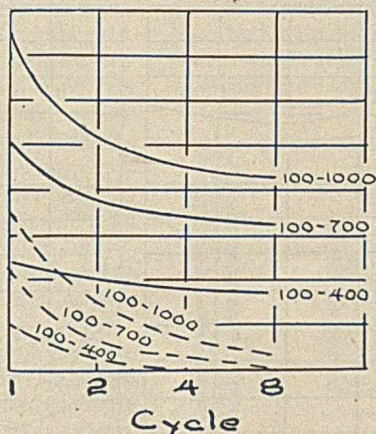


FIG. 23

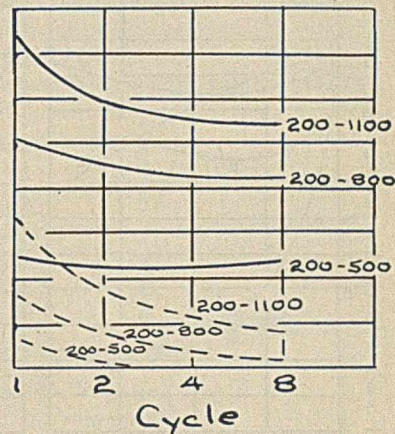


FIG. 24

RELATION BETWEEN CYCLE NUMBER AND MAXIMUM (SOLID LINES) AND HYSTERESIS (DOTTED LINES) ENERGY PER UNIT VOLUME, COMPOUND A, CURED 1 HR. AT 300° F.

Fig. 22—Stresses alternating between 0 and 300, 600, and 900 lbs. per sq. in. Fig. 23—Alternating between 100 and 400, 700, and 1000 lbs. per sq. in. Fig. 24—Alternating between 200 and 500, 800, and 1100 lbs. per sq. in.

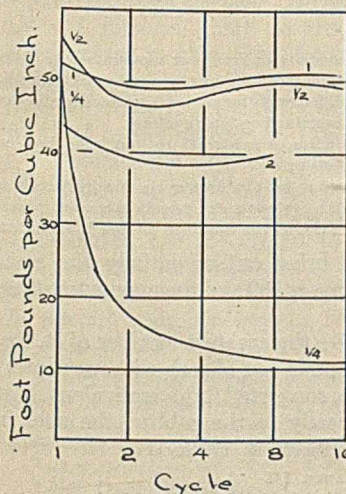


FIG. 25

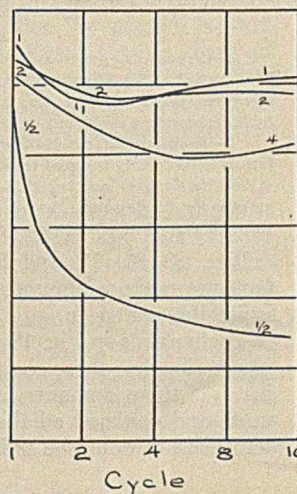


FIG. 26

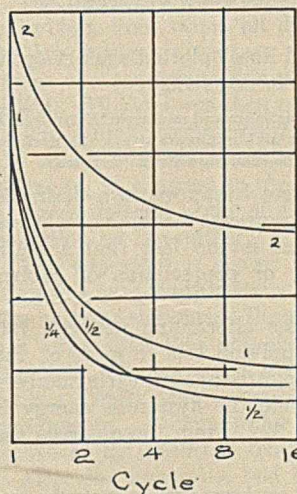


FIG. 27

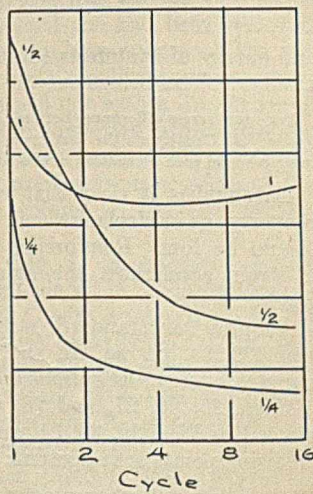
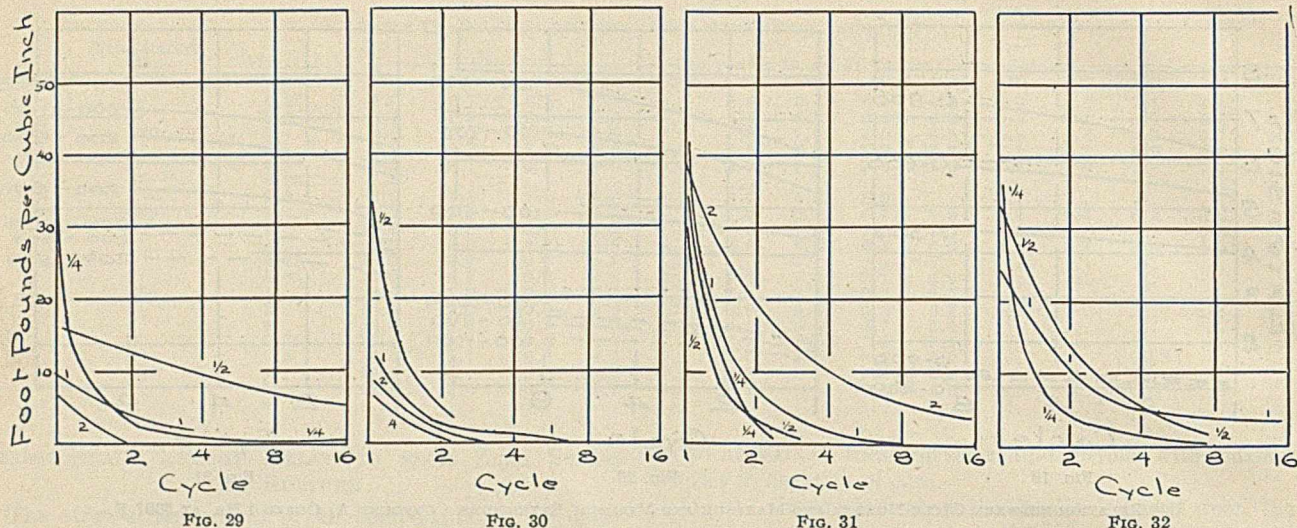


FIG. 28

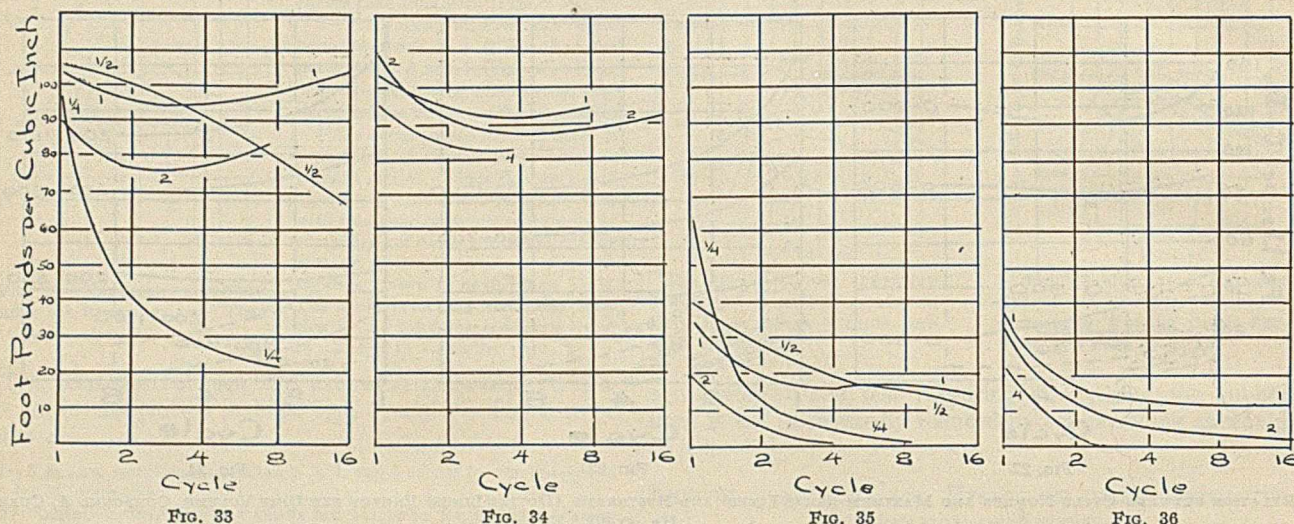
RELATION BETWEEN CYCLE NUMBER AND MAXIMUM ENERGY ABSORBED PER UNIT VOLUME, STRESSES ALTERNATING BETWEEN 100 AND 400 LBS. PER SQ. IN.

FIG. 25—Compound A, cured 0.25 to 2 hrs. at 300° F.
FIG. 26—Compound B, cured 0.5 to 4 hrs. at 300° F.

FIG. 27—Compound C, cured 0.25 to 2 hrs. at 280° F.
FIG. 28—Compound C, cured 0.25 to 1 hr. at 300° F.



RELATION BETWEEN CYCLE NUMBER AND HYSTERESIS ENERGY PER UNIT VOLUME, STRESSES ALTERNATING BETWEEN 100 AND 400 LBS. PER SQ. IN.
 Fig. 29—Compound A, cured 0.25 to 2 hrs. at 300° F.
 Fig. 30—Compound B, cured 0.5 to 4 hrs. at 300° F.
 Fig. 31—Compound C, cured 0.25 to 2 hrs. at 280° F.
 Fig. 32—Compound C, cured 0.25 to 1 hr. at 300° F.



RELATION BETWEEN CYCLE NUMBER AND MAXIMUM ENERGY ABSORBED PER UNIT VOLUME, STRESSES ALTERNATING BETWEEN 100 AND 700 LBS. PER SQ. IN.
 FIG. 33—Compound A, cured 0.25 to 2 hrs. at 300° F.
 FIG. 34—Compound B, cured 1 to 4 hrs. at 300° F.
 RELATION BETWEEN CYCLE NUMBER AND ENERGY OF HYSTERESIS PER UNIT VOLUME, STRESSES ALTERNATING BETWEEN 100 AND 700 LBS. PER SQ. IN.
 FIG. 35—Compound A, cured 0.25 to 2 hrs. at 300° F.
 FIG. 36—Compound B, cured 1 to 4 hrs. at 300° F.

and energy of hysteresis (dotted lines) plotted against cycle number. This brings out the following facts:

For equal stress differences between maximum and minimum the hysteresis loss is: (1) Greater on the first cycle for high minimum stress; (2) declines more rapidly with increasing cycles as the minimum stress increases.

This makes it clear that where hysteresis is a desirable property, as in airplane shock absorbers, the minimum stress should be low. Reinforcing this is the fact that a state of strain accelerates the aging or depreciation of rubber goods.

Adopting as standard, stresses alternating between 100 and 400 lbs. per sq. in. and applying this to most of the samples, energy absorptions are plotted against cycle numbers in Figs. 25, 26, 27, and 28, while the hysteresis energy is plotted in Figs. 29, 30, 31, and 32. From these curves the following points are apparent:

- 1—The energy absorbing capacity at maximum stress is greater for pure gum stocks A and B than for compounded stock C (Figs. 25 and 26 vs. 27 and 28).
- 2—The effect of increasing the duration of cure may be divided into two phases:

a—From low cure to an intermediate optimum or moderate cure there is an initially high hysteresis, decreasing rapidly as the number of the cycle advances, this stage becoming modified with longer cure to lower values of hysteresis on first cycle, but better sustained on later cycles.

b—From an intermediate optimum or moderate to long cure the hysteresis is uniformly lowered for all cycles.

Another way of putting this is that on the first cycle the hysteresis is greater for shorter cures, but in later cycles the hysteresis increases, passes through a maximum and then decreases as the duration of cure is extended.

Figs. 33, 34, 35, and 36 bring out essentially the same facts where the minimum stress is 100 and the maximum stress is 700 lbs. per sq. in.

The maxima in Fig. 18 give the greatest number of ft. lbs. per cu. in. that these compounds can absorb without rupturing. If these amounts are converted into equivalent heat units and confined adiabatically to the rubber, the rises in temperature would be as indicated in Table III.

COMPOUND	Maximum Ft. Lbs. per Cu. In.	Specific Volume Heat	Rise in Temperature F.
A	350	0.4	31
B	310	0.4	28
C	240	0.45	19

CONCLUSIONS

1—Fine Para possesses no distinct advantage over plantation rubber so far as tensile capacity, speed of cure, or hysteresis endurance are concerned.

2—Excess cure produces lower hysteresis on all cycles than more moderate cure.

3—Under cure produces greater hysteresis on the first cycle, but more rapid decay on following cycles than moderate cure.

4—The chief advantages of a pure gum stock lies not in a higher hysteresis on the first cycle but in:

a—Greater capacity to absorb energy prior to rupture.

b—Superior hysteresis endurance.

c—Greater rate of extension per rate of energy absorption, hence transfer of energy from airplane to shock absorbers and reverse is slower, thereby setting up lesser stresses in the airplane.

The Solubility of Gases in Rubber and Rubber Stock and Effect of Solubility on Penetrability^{1,2}

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The recent rapid development of rubberized balloon fabric has led to an extensive study of the penetration of gases through rubber and the various factors influencing this penetration. Edwards and Pickering³ have shown that for any one gas the rate of penetration through a given sample of rubber is directly proportional to the partial pressure difference and increases rapidly with the temperature. The relative penetrability values obtained by them for various gases are in good agreement with similar values determined by Graham⁴ and Dewar.⁵ Comparable results were also obtained by Daynes.⁶ Since there was no apparent relationship between relative penetrability and density of the gas, Graham postulated that the penetration mechanism consisted in the solution of the gas on one side of the rubber, with a subsequent diffusion of the dissolved gas through the rubber and vaporization on the other side. Later investigators are inclined to take the same view.

Though penetrability is thus made a function of the solubility of the gas in the rubber, the mathematical relationship has been indeterminate on account of the lack of accurate solubility data. By weighing sheets of rubber after exposure to the gas, Wroblewski⁷ obtained rough solubility data for nitrous oxide, carbon dioxide, hydrogen, and air. Values were also given for temperature coefficients but all his results were subject to very large experimental error. Hüfner⁸ states that between 0° and 25° C. a gray vulcanized rubber stopper in an atmosphere of carbon dioxide absorbs about its own volume of the gas. He finds no absorption for hydrogen and nitrogen, and no absorption for oxygen beyond that involved in oxidation of the rubber. From a study of equilibrium pressures for a known volume of gas in contact with the rubber, Reychler⁹ determined the solubility at 18° C. of carbon dioxide at 1.06 volumes and sulfur dioxide at 26 volumes per volume of rubber.

Recently Daynes,⁶ by measuring the "lag" or time consumed in saturating the rubber membrane in the Shakespear permeameter, has attempted to separate the permeability coefficient into its absorption or solubility coefficient and its diffusion coefficient. He worked with hydrogen, carbon dioxide, nitrous oxide, air, oxygen, and ammonia, but his results are open to the criticism that the "lag" period measured

must have a relatively large correction applied for instrument lag. His interpretation of results is also somewhat vitiated by curious errors in density values assumed (page 305).

Recently this Laboratory, in connection with an investigation undertaken for the Goodyear Tire & Rubber Co., has been making a study of the solubility of gases in rubber and rubber stock, using a direct experimental procedure capable of giving more accurate results than any hitherto published.

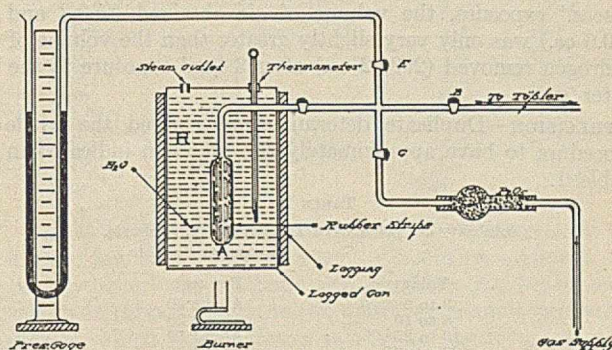


FIG. I—APPARATUS FOR DETERMINING SOLUBILITY OF GAS IN RUBBER

EXPERIMENTAL PROCEDURE

The procedure consisted essentially in leaving thin strips of rubber, from which all dissolved gas had been removed by evacuation, in contact with an atmosphere of the gas under the conditions desired until equilibrium was established. This gas was then pumped out with a Töpler pump and measured over mercury, due correction being made for the void gas in the container system used. This procedure, therefore, in contrast to those previously attempted, allows a direct determination of the volume of gas held in free condition by the rubber.

The apparatus is shown in Fig. I. A weighed amount of rubber cut into thin strips was placed in the glass bulb A. Connections were made through C with a tube by which the gas (dried over P_2O_5 or soda lime) could be introduced into the bulb. By means of stopcock B connection was made with a Töpler pump and by means of E with a mercury manometer. A large water reservoir, R, around the bulb served as the means of temperature control.

After the apparatus had been carefully tested for leaks, the rubber was placed under high vacuum for 48 hrs. to exhaust all dissolved gases. Preliminary experiments demonstrated that for the thickness of rubber used, and at room temperature, 24 hrs. were required for equilibrium to be

¹ Presented before the Division of Rubber Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

² Published as Contribution No. 38 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

³ *Chem. Met. Eng.*, **23** (1920), 17, 71.

⁴ *Phil. Trans.*, **156** (1866), 399.

⁵ *Proc. Roy. Inst., Gt. Britain*, **21** (1915), 558, 813.

⁶ *Proc. Roy. Soc. London*, **97A** (1920), 286.

⁷ *Wied. Ann. Phys.*, **8** (1879).

⁸ *Ibid.*, **34** (1888), 1.

⁹ *J. chim. phys.*, **8** (1910), 39, 617.

established in the case of all gases save ammonia and sulfur dioxide; at 100° C., only 2 hrs. were required. A corresponding time was used for pumping out the dissolved gas. The time required for equilibrium for ammonia and sulfur dioxide was about twice that for the other gases.

To determine a solubility value, the evacuated rubber was left in contact with the dry gas under the desired conditions until equilibrium was established, as indicated by the constancy of the pressure in the bulb. Stopcocks C and E were then closed and the gas (void gas and dissolved gas) in the bulb system ABCE was pumped out and measured. The difference between the total volume and void volume represented the dissolved gas. This quantity was calculated over to the basis of cc. gas (N. P. T.) per 100 cc. of raw rubber, or in the case of the compounded samples, cc. gas (N. P. T.) per 100 cc. of rubber actually present in the mix.

DETERMINATION OF VOID VOLUME—From gage readings, it was found that when a gas appreciably soluble in rubber was introduced into the bulb, the initial rate of solution was very rapid. Consequently, the void volume was determined by introducing hydrogen into the bulb system containing the evacuated rubber and at the end of 5 min. pumping it out and measuring the gas. Gage readings during that interval had shown that the volume of hydrogen taken up by the rubber was so nearly zero as to be well within the other experimental errors involved. Confirmation of this very low solubility for hydrogen is shown by the fact that when air was introduced into the bulb system and removed after 5 secs.' exposure, the volume of air obtained (260.3 and 260.6 cc.) was only very slightly greater than the volume of hydrogen removed (260.02 cc.) after 3 hrs.' exposure to the latter gas.

PRECISION—Duplicate determinations showed the whole procedure to have approximately the precision indicated in Table 1.

Values	Maximum Possible Deviation Per cent
3 to 5	About 40
5 to 10	About 20
10 to 25	About 10
Above 25	About 5

SAMPLES USED

I. <i>Pale Crepe</i> —From a lot some 3 or 4 yrs. old.	
II. <i>Smoked Sheet</i> —Obtained from Akron together with III and IV. It is understood that this same rubber was used in compounding III and IV.	
III. <i>Original Composition</i> (by wt.)	
Smoked sheet	100
ZnO	10
Thiocarbonyl	3
Combined sulfur	3.2% of wt. smoked sheet present
IV. <i>Original Composition</i> (by wt.)	
Smoked sheet	100
ZnO	10
S	20
Thiocarbonyl	0
Combined sulfur	2.56% of wt. smoked sheet present

Sample IV obviously contains an abnormal amount of free sulfur.

EXPERIMENTAL RESULTS

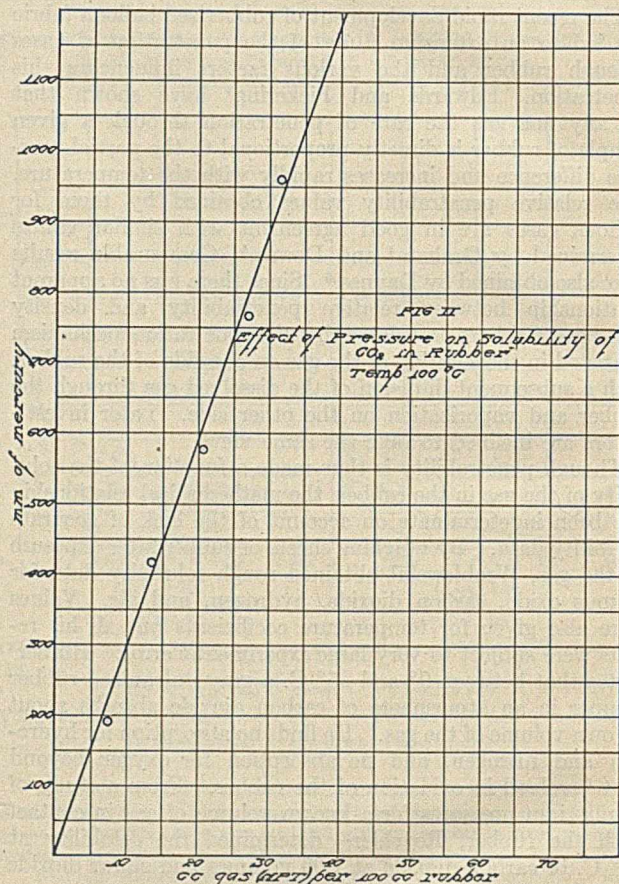
EFFECT OF SURFACE—Solubility Determinations made on a sample of rubber cut so that in Case A the surface exposed was about three times that in Case B, showed that there was no difference in the amount of gas held by the Rubber A and Rubber B. The effect of surface area is apparently negligible so far as final solubility is concerned, indicating that the gas is held in true solution and not by adsorption on the macroscopic surface of the rubber.

SOURCE OF GAS USED

CO ₂	Cylinder—97.5 per cent
CO	From Na formate + H ₂ SO ₄
CH ₄	From NaAc + NaOH (> 90 per cent)
O ₂	Cylinder (> 99 per cent)
H ₂	Cylinder (> 98 per cent)
N ₂	Cylinder (> 97 per cent)
SO ₂	Cylinder
C ₂ H ₄	From alcohol + P ₂ O ₅ —(> 90 per cent)
H ₂ S	From FeS and HCl
NH ₃	Cylinder (> 98 per cent)
He	Cylinder from Petrolia, Texas (est. 92 per cent He, 8 per cent N ₂)

SAMPLE OF CALCULATIONS

Sample IV. Vulc. coefficient = 2.56 per cent.
Equilibrium for 24 hrs. at room temperature
Wt. sample = 71.1 g. = 54.7 g. rubber = 59.4 cc. rubber
Bulb closed at 23.7° C. and 771.2 mm. Hg
Gas collected (at 23.7° and 771.2 mm.) = 125.9 cc.
Void volume (det. with hydrogen) = 67.2 cc.
Dissolved gas = 58.7 cc. (23.7° C. and 771.2 mm. Hg) = 54.8 cc. (N. P. T.) = 92.2 cc. per 100 cc. rubber



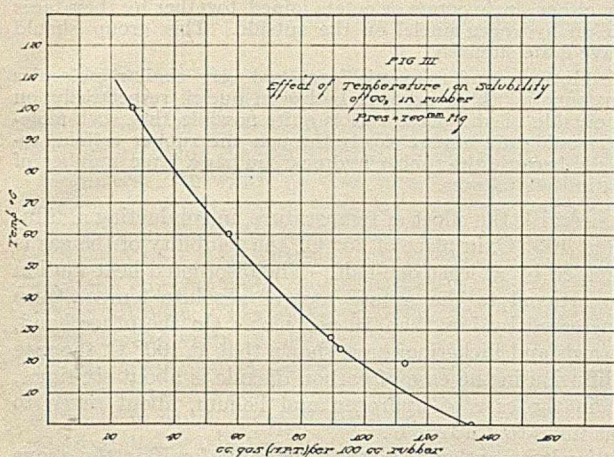
EFFECT OF GRADE OF RUBBER AND VULCANIZATION COEFFICIENT—The effect of the grade of rubber and vulcanization coefficient on the solubility of carbon dioxide at room temperature is shown in Table 2. Since these determinations were made at temperatures ranging from 16° to 24° C., the values were calculated to the common basis of 20° C. by referring to the slope of the curve shown later in Fig. III.

TABLE 2—EFFECT OF GRADE OF RUBBER AND VULCANIZATION COEFFICIENT ON SOLUBILITY OF CO₂ IN RUBBER

Pressure CO₂ = 760 mm. Hg.
Solubility reported in cc. gas (N. P. T.) per 100 cc. initial raw rubber

SAMPLE	SOLUBILITY	
	Observed	Calculated to 20° C.
I. Pale crepe (raw)	90 at 21° C.	92
II. Smoked sheet (raw)	108 at 16° C.	102
III. Smoked sheet (vulc. coeff. = 2.56)	92 at 24° C.	99
IV. Smoked sheet (vulc. coeff. = 3.2)	103.5 at 19° C.	101

There is a 10 per cent difference between unvulcanized pale crepe and smoked sheet. On the other hand, when smoked sheet is vulcanized to different coefficients up to



3.2 per cent, there is comparatively little difference between the volume of gas held by 100 cc. of the raw rubber and 100 cc. of the same rubber after vulcanization. The 10 parts of zinc oxide and 17 parts of free sulfur present also appear to exert no appreciable effect on the solubility when the results are calculated on the basis of the rubber present. Accordingly, free use has been made of either Samples III and IV in obtaining solubility data, though the sample used is always indicated.

EFFECT OF PRESSURE—A study was made of the effect of pressure on the solubility of carbon dioxide in rubber. These determinations were made at 100° C., on a sample of rubber from Lot IV. The results are shown in Fig. II.

It will be noted that the solubility is directly proportional to the absolute pressure within the limits investigated. This is additional proof that the gas is held in true solution rather than by adsorption; this evidence rules out the possibility of adsorption even on the surface of the colloidal units of rubber.

EFFECT OF TEMPERATURE—The effect of temperature on the solubility of carbon dioxide in rubber is shown in Fig. III. The rubber was taken from Lot IV, and the pressure was 760 mm. Hg.

The curve is the usual type of solubility curve. Using the solubility equation

$$\frac{d \log S}{dt} = \frac{\Delta H}{RT^2}$$

and plotting $\log S$ against $\frac{1}{T}$, the points fall fairly well on a straight line. From the slope of this line, ΔH (the molal heat of solution of carbon dioxide in rubber) is calculated to be about 3300 cal. It will be noted that the solubility at 140° C., or vulcanization temperature, will be very small. In the case of carbon dioxide, the solubility at 100° C. is about one-third that at 20° C. As seen from Table 3, in the case of the other gases the solubility at 100° C. is usually about one-half that at 20°, indicating a lower heat of solution than for carbon dioxide.

RELATIVE SOLUBILITY OF VARIOUS GASES—The relative solubility of the various gases in rubber is shown in Table 3. Rubber from Lots III and IV was used. The determinations were made at a gas pressure at 760 mm. Hg and at the temperatures indicated. The critical temperature for each gas is given in degrees Kelvin in Column 5.

As previously explained, the solubility of hydrogen is too low to be determined by the procedure used, and in the above

TABLE 3—SOLUBILITY OF VARIOUS GASES IN VULCANIZED RUBBER

GAS	Solubility cc. gas (N. P. T.) per 100 cc. rubber			Critical Temperature ° K.
	Sample III 20°-22°	Sample IV 20°-22°	100°	
He	<1.0	<1.0	5.0
H ₂	<1.0	<1.0	<1.0	33.0
N ₂	3.5	1.7	128.3
CO	6.2	3.6	134.4
O ₂	7.3	4.0	155.0
CH ₄	26.8	24.0	190.2
CO ₂	99	101	34.0	304.0
C ₂ H ₄	144	66	282.6
H ₂ S	273	373.4
NH ₃	930	406.0
SO ₂	1950	428

table, it has been indicated simply as less than 1. The same was found to be the case for helium. Comparing solubilities with critical temperatures, the order of the solubility in rubber of the various gases is the same as the order of their absolute critical temperatures, save in the case of the unsaturated ethylene, which indicates that the degree of solubility is roughly proportional to the ease of condensation of the gas.

In Table 4 are given comparative values of the solubility of the various gases in rubber and in water at 21° C. The values for water were taken from the Landolt-Börnstein "Tabellen," being largely the figures given by Winkler. In the last column are given the ratios of the solubility in rubber to that in water.

TABLE 4—SOLUBILITY OF GASES IN RUBBER AND IN WATER
Solubility given in cc. gas (N. P. T.) per 100 cc. solvent. Temp. = 21° C.

GAS	Rubber Sample III	R	
		H ₂ O	H ₂ O
He	<1.0 (Sample IV)	1.4	<0.7
H ₂	<1.0	1.8	<0.6
N ₂	3.5	1.5	2.3
CO	6.2	2.24	2.7
O ₂	7.3	3.0	2.4
CH ₄	26.8	3.2	8.4
CO ₂	99	82.9	1.2
C ₂ H ₄	144 (Sample IV)	11.6	12.5
H ₂ S	273 (Sample IV)	243	1.1
NH ₃	930	67,830	0.014
SO ₂	1950	3661.7	0.53

In the case of hydrogen and helium, the exact ratio is unknown, but is evidently small. As would be expected, the two hydrocarbons, methane and ethylene, are much more soluble in rubber than in water, whereas ammonia and sulfur dioxide, which form hydrates in aqueous solution, are much more soluble in water than in rubber. In the case of the other gases, the ratio is fairly constant.

RELATIONSHIP BETWEEN RELATIVE SOLUBILITY AND RELATIVE PENETRABILITY

If the process by which a gas penetrates through a rubber membrane is one of the solution of the gas on one side of the membrane, diffusion of dissolved gas through membrane, and evaporation on the other side, inasmuch as Edwards and Pickering³ have shown that for any one gas the rate of penetration is indirectly proportional to the thickness of the membrane, it can be assumed that this rate of penetration is determined by the second stage of the process, that is, diffusion of dissolved gas. The expression for the rate of penetration of a gas through rubber might thus be expected to take the form:

$$P = k D C$$

where k = proportionality constant depending upon the condition of the rubber, the temperature, etc.

D = rate of diffusion of an individual molecule,

C = concentration of gas in true solution (not including molecules which are combined chemically so as not to be able to move freely).

As a first approximation, it may be assumed that C is correctly measured by S , the solubility as determined in the previously mentioned experiments, and that D , the rate of diffusion through the rubber, is proportional to the dis-

ordered heat motion of the gas molecule, *i. e.*, inversely proportional to the square root of the molecular weight. Thus the equation for rate of penetration becomes:

$$P = K \frac{S}{\sqrt{\text{Mol. Wt.}}} \text{ or } K = \frac{P \times \sqrt{\text{Mol. Wt.}}}{S}$$

where P = relative penetrability, S = relative solubility, and K = proportionality factor depending upon the temperature, etc.

In the following discussion, values reported by Edwards³ have been used, as representing the most recent and probably the most accurate work. Carbon monoxide and methane were not investigated by Edwards and, accordingly, the values given by Dewar⁵ and Graham⁴ have been taken. This introduces a slight error, inasmuch as the values given by Edwards and Pickering were obtained at 25° C. and those given by Dewar and Graham at 15° C. The figures, however, are for relative penetrability compared to nitrogen and in each case were calculated on the basis of the value given for nitrogen by that particular investigator. Although all gases have not the same temperature coefficient, it is believed that no large error is introduced by assuming the same relative temperature coefficient between 15° and 25°.

In Table 5, eight gases are considered, for which both relative penetrability and relative solubility values ($N=1$) are now known. In Column 3 are given values for the term

$$K = \frac{P \times \sqrt{\text{Mol. Wt.}}}{S}$$

Table 5 shows that for four gases, oxygen, nitrogen, carbon monoxide, and carbon dioxide, whose solubilities vary 28-fold, there is a fair degree of constancy in the values calculated for K considering the fact that the experimental errors involved in the two determinations might be 10 to 30 per cent. The wide variation in the case of the other four gases—hydrogen, helium, methane, and ammonia—indicates, however, that some fundamental error must have been made in the underlying assumptions involved in the equation.

TABLE 5

GAS	Relative Penetrability	Authority	Relative Solubility (at 20°–22° C.)	K =		Relative Size of Molecule ($\times 10^4$)
				$\frac{P \times \sqrt{\text{Mol. Wt.}}}{S}$	$\frac{P \times \sqrt{\text{Mol. Wt.}}}{S}$	
Helium	4.04	E. & P.	0.3	—40		70
Hydrogen	6.25	E. & P.	0.3	29.5		119
Nitrogen	1.00	E. & P.	1.00	5.3		174
Carbon monoxide	1.31	Dewar	1.77	3.9		173
Oxygen	2.81	E. & P.	2.09	7.6		144
Methane	2.22	Graham	7.6	1.2		191
Carbon dioxide	18.1	E. & P.	28.3	4.2		191
Ammonia	50.0	E. & P.	266	0.78		165

Now, in deriving the expression for K , it was assumed that the rate of motion through the rubber is proportional only to the disordered heat motion, that is, inversely as the square root of molecular weight. This totally neglects any other factor, such as the relative size or the structure of the gas molecules, which it is quite reasonable to suppose should influence the rate of diffusion through a colloidal solid such as rubber.

In Column 4 are given relative values of molecular volumes as computed from the quantity b in van der Waal's equation. Pease¹⁰ has recently shown that these values are in close accord with the Lewis-Langmuir theory. The abnormally high diffusion rate of helium and hydrogen might well be explained on the basis of the relatively small size of gas molecule. Apparently, however, no such relationship holds in the case of the other gases.

If, however, we consider the structure of the molecules from the standpoint of the Langmuir theory, the eight gases readily group themselves into three different classes:

1—Helium and nitrogen, which do not form octets, are considerably smaller than the other gases and would be expected to diffuse more rapidly through a given medium.

2—Oxygen, nitrogen, carbon monoxide, and carbon dioxide form either single octets or octets joined together by their faces with no hydrogen nuclei on the outside. This group should behave quite similarly.

3—Methane and ammonia form two very similar molecules with four and three exposed hydrogen nuclei, respectively, on the outside of the octet. It is quite possible that such molecules would diffuse more slowly through the rubber colloid, especially because the rubber hydrocarbon has a large number of unsaturated linkages.

As regards the effect of temperature, in conducting a diffusion at 100° C. in place of 25° C., the solubility of the gas is decreased by at least one-half. The disordered heat motion (proportional to the square root of absolute temperature) is increased by less than 15 per cent. On the other hand, Edwards and Pickering³ have shown that at 100° C. the rate of diffusion in the case of carbon dioxide is about six times, and in the case of hydrogen and helium, about seven to eight times that at 25° C.

It is obvious, therefore, that the value for K in the above formula must increase ten- or twelve-fold for a 75° rise in temperature. This is, however, not surprising, for while it is somewhat greater than the change in the rate of diffusion of solutes through water, the order of magnitude is the same, and the coefficient of expansion of rubber is much greater than that for water, and its decrease in "viscosity" would undoubtedly prove correspondingly greater if it could be measured by ordinary methods. The viscosity of heavy oils varies thirty-fold in magnitude over a similar range in temperature.

On the whole, therefore, all the evidence seems to favor the customary assumption that the mechanism by which gas penetrates a rubber membrane is through diffusion of the gas, which is held in true solution. While both the solubility and molecular weight of the gas play their expected part in influencing the speed of diffusion, the size and structure of the gaseous molecule and the viscosity of the rubber itself are additional important factors in determining the precise rate of diffusion. The attempt has been made above to analyze these factors as far as it is possible with the limited amount of data now available, which are admittedly inadequate for positive conclusions.

SUMMARY

1—It has been found that when rubber absorbs a gas, this gas is, in most cases at least, held in true solution and not by adsorption.

2—In the case of carbon dioxide, which has about an average solubility, the amount of gas thus held in true solution by the rubber is, within the limits investigated, directly proportional to the pressure and is unaffected by degree of vulcanization or the presence of compounding ingredients.

3—The solubility decreases rapidly with increasing temperature.

4—Relative solubility values obtained for various gases show that there is a general relationship, such as might be expected on purely theoretical grounds, between the solubility and the density of a gas, and its relative rate of penetration through rubber. The indications are, however, that the actual size and structure of the gas molecule and the viscosity of the rubber likewise influence this rate of penetration, and in a direction which can be predicted.

ACKNOWLEDGMENT

The Laboratory wishes to express its appreciation for the helpful cooperation of the Goodyear Tire and Rubber Company and for their courtesy in permitting the publication of these results.

Cyanamide in Some Fertilizer Mixtures¹

By W. S. Landis

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At the meeting of the American Chemical Society in Chicago in 1920, Mr. R. H. Harger, of the United States Department of Agriculture, presented a paper entitled "The Changes Taking Place in Cyanamid when Used with Mixed Fertilizers,"² in which he described the behavior of certain experimental mixtures of fertilizer materials and Cyanamid made up in gram lots in the laboratory, and reported after a certain time interval a material decrease in the cyanamide nitrogen content and a corresponding increase in dicyanodiamide nitrogen. The author remarks that this results in a considerable waste of fertilizer nitrogen, and that methods should be evolved to prevent such waste. Fortunately, the facts as stated are not found applicable to standard brands of fertilizer in which cyanamide has been properly incorporated, some studies of which form the basis of this paper.

Observation of the rapid transformation which cyanamide undergoes in fertilizer mixtures, or even when applied alone to the soil, is not new. The decomposition and transformation have been the subject of world-wide investigation, and the principles developed are applied on an ever increasing commercial scale, there being found on the market numerous chemical products, such as ammonia, urea, dicyanodiamide and the guanidines, made from cyanamide, some of them in quantities quite comparable with those obtained from other sources. The general reactions involving these decompositions have been the subject of numerous publications and need not be repeated here.³

Returning to the Chicago paper, the author's discovery that the cyanamide nitrogen as such had completely disappeared from fertilizer mixtures in which cyanamide had been used in their formulation, was by no means a new one. In the "American Fertilizer Handbook" for 1914, the transformations taking place in cyanamide in fertilizer mixtures were referred to, this subject having been investigated years before Mr. Harger's experiments.

The surprising feature of Mr. Harger's paper, however, was his conclusion that the decomposition product of the cyanamide in the fertilizer mixture was "represented principally by, and in many cases quantitatively by the formation of dicyanodiamide."⁴ According to his experimental results, a mixture of cyanamide and moist acid phosphate containing 22 g. of cyanamide and 184 g. of acid phosphate, to which 16 g. of water were intentionally added, showed that in 8 days practically 90 per cent of the cyanamide nitrogen had been transformed into dicyanodiamide nitrogen.

Now dicyanodiamide is an article of commerce and has been so for many years. Exhaustive studies have been made on its production from cyanamide.⁵ A comprehensive review of the suggestions and methods of these investigators made in the laboratory of this company have confirmed most of

their findings. By the most efficient method of procedure, coupled with the most exacting laboratory control, we were able to transform about 85 per cent of the cyanamide nitrogen in aqueous solution into dicyanodiamide nitrogen. Since the solubility of cyanamide in water is a difficult and in many cases an inefficient process, the over-all transformation efficiency from cyanamide to dicyanodiamide has always been low. Every investigator in this field has noted the fact that in this transformation only a part of the cyanamide nitrogen goes to dicyanodiamide nitrogen and this fraction seems fairly constant, irrespective of the method of making the transformation, provided such method has good foundation in fact. In large-scale work where quantities of a ton or more are operated on and control is not quite so exact as in the laboratory, our experience has shown that less than five-sixths of the cyanamide nitrogen brought in solution can be transformed into dicyanodiamide nitrogen, and about one-sixth always goes to urea nitrogen. With less exacting control and more nearly paralleling factory conditions, this fraction going to urea nitrogen is materially greater than one-sixth and we consider it good factory practice if it does not exceed one-fourth. It is extremely interesting to find that Mr. Harger's accidental method, which involves no resolution of the cyanamide whatever, should be able to transform cyanamide into dicyanodiamide at a conversion efficiency of about 90 per cent.

EXPERIMENTAL MIXTURES OF ACID PHOSPHATE AND CYANAMIDE

However, more closely to parallel fertilizer conditions, and shortly after the reading of the Chicago paper, one of the large agricultural chemical companies mixed up a batch of commercial acid phosphate and cyanamide in one of its fertilizer factories. The mixture was of the proportion of 1900 lbs. of commercial acid phosphate and 100 lbs. of cyanamide, and the pile was carefully sampled by the agricultural company's chemist. Ten days after mixing (this elapsed time taken to represent periods similar to those reported at Chicago) this sample was tested in the laboratory with the following results: On the addition of picric acid as in the Harger procedure, precipitates were obtained without the addition of silver nitrate, indicating the presence of interfering materials. This precipitate was determined to be guanyl urea, equal to ammonia 0.21 per cent. Without extreme care in observation on the part of the analytical chemist in applying the Harger method this would have been reported as dicyanodiamide. After removal of the guanyl urea, silver nitrate was added and all the conditions of the Harger method followed out, and after adding the Harger correction factor dicyanodiamide equivalent to ammonia 0.03 per cent was obtained. A direct determination of urea showed urea equivalent to ammonia 0.66 per cent. Cyanamide equivalent to ammonia was determined as 0.06 and ammonia salts in terms of ammonia as 0.05 per cent. The above accounts for 1 per cent of ammonia out of a total of 1.2 per cent, the undetermined part being insoluble ammonia and forms which the writer could not determine analytically by accurate methods at his disposal.

This large-scale experiment, checked by two independent laboratories, seems to dispose effectually of the application of Harger's conclusions to even such an unusual kind of fertilizer mixture when prepared by actual manufacturers.

In order, however, to dispose of this matter finally, a con-

¹ Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

² Published in revised form under the title of "The Changes Taking Place in Cyanamid when Mixed with Fertilizer Materials," *THIS JOURNAL*, 12 (1920), 1111.

³ *Am. Fertilizer*, 54 (1921), 49; *Gaz. chim. ital.* (1918), II, No. 4, 358; *Trans. Am. Inst. Chem. Eng.*, 8 (1915) 267; Beilstein's "Handbuch der Organische Chemie."

⁴ In the paper as printed the conclusion as above given was modified and changed in form.

⁵ G. Grube and P. Nitsche, "The Polymerization of Cyanamide to Dicyanodiamide in Aqueous Solution," *Z. physik. Chem.*, 86, 65 (1913); G. Grube, "Technical Methods for the Production of Dicyanodiamide from Lime Nitrogen from the Standpoint of Chemical Kinetics," *Z. angew. Chem.*, 27, I, 368 (1914); D. R. P. 252,273; 279,133; 257,769.

siderable quantity of cyanamide was moistened and allowed to stand under such conditions as to insure about one-half of its nitrogen being converted into the dicyanodiamide form. The actual analysis of this cyanamide showed 10.8 per cent dicyanodiamide ammonia and approximately an equal quantity of cyanamide ammonia. A similar mixture with acid phosphate was made with this cyanamide which was positively known to contain dicyanodiamide, but strange to say the resulting mixture showed no test for the same upon analysis. In other words, the only conclusion is that dicyanodiamide is incapable of existence in such an acid mixture prepared according to the methods of the modern fertilizer mixing plant, all of which is quite in accord with the theory of its formation and decomposition.

MIXTURES OF CYANAMIDE WITH BASE GOODS

It has been known for a long time that amino acids react with cyanamide. In the few cases actually studied and reported in easily accessible literature,⁶ the reaction products noted are excellent plant foods. A very large amount of work along the line of cyanamide reactions with amino acids has been published in the form of theses by German students, and a comprehensive review of these is being made at the present time in order to throw more light upon this phase of the behavior of cyanamide in fertilizer mixtures.

The use of rough ammoniates in base mixtures is quite common practice in this country. The resulting base goods contain the larger part of their available nitrogen in the form of amino acids, and a study has been made of the constitution of fertilizer mixtures made up by various factories from these bases with cyanamide and other ingredients. The results of a few of these studies follow.

A mixture was prepared in the proportions of 820 lbs. of a well-known base goods and 180 lbs. of cyanamide. To insure the most complete decomposition of the cyanamide, the material was allowed to stand for 30 days after mixing and before sampling for analysis. The result of the analysis, reported on the basis of the cyanamide ammonia added being taken as 100 per cent, was as follows:

	Per cent
Cyanamide ammonia.....	2.5
Dicyanodiamide ammonia.....	3.1
Urea ammonia.....	45.7
Ammonium salts.....	4.3

No part of the remainder of the cyanamide ammonia, amounting to 44.4 per cent, together with the ammonia in the ammoniated base could be positively identified in a quantitative way by any known method at our disposal. It undoubtedly represents complex amino-cyanamide derivatives for which we have no adequate analytical methods.

Two samples of ammoniated base goods, formulated 8-3-3 and 8-2-2 from two different fertilizer plants and representing material placed on the market in the fall of 1920 in large tonnage, were examined very carefully by the various analytical methods at our disposal. These fertilizers were each formulated with 70 lbs. of cyanamide to the ton of finished fertilizer and each also contained about 1400 lbs. of ammoniated base per ton. The 8-3-3 contained 13.8 per cent moisture and the 8-2-2 contained 12.87 per cent moisture, both samples having ample water to insure reaction like that reported by Harger. The other elements were tobacco stems, rapeseed mix, ammonium sulfate, potash, and filler. The samples were investigated several months after mixing and undoubtedly the chemical status had reached equilibrium. In neither of these samples was any dicyanodiamide or guanyl urea found, nor did they contain cyanamide. Both contained urea to the extent of 30 per cent for the 8-3-3, and 15 per cent for the 8-2-2 brand, of the equivalent of the cyanamide nitrogen added, but

more than one-half of this cyanamide nitrogen could not be accounted for by any of the analytical methods at our disposal.

In view of the fact that we were looking for dicyanodiamide in these materials and were somewhat fearful that the various methods might fail to show its presence, we added 50 mg. of pure dicyanodiamide to water extracts of 8 g. of the 8-3-3 fertilizer mixture and proceeded with a determination by the Harger method. In two experiments carried out as nearly in duplicate as possible, only 39 mg. of dicyanodiamide in one case were recovered and 14.1 mg. in the other. In a third experiment where 35 mg. of dicyanodiamide were added to the water extract from 4 g. of the fertilizer, no precipitate whatever was obtained.

In view of this peculiar behavior of the 8-3-3 fertilizer, the 8-2-2 fertilizer, which was very similar in constitution, was not tested similarly at the time. Instead, a sample was obtained of a 7-7-5 brand, formulated with 820 lbs. of ammoniated base, 300 lbs. of 16 per cent acid phosphate, and 80 lbs. of cyanamide, together with 800 lbs. of tobacco stems, meal, ammonium sulfate, and muriate of potash. The moisture content of this fertilizer, which was marketed in large quantities last winter, was 9.94 per cent. No test for dicyanodiamide was obtained by any of the various methods, and dicyanodiamide was added to the sample, which was then analyzed by the Harger method. Four aqueous extracts were prepared on four samples of 4 g. each of the fertilizer, the use of the smaller samples of the fertilizer seemingly giving more accurate check results. To one of these samples 25 mg. dicyanodiamide were added, to the second 50 mg., to the third 75 mg., and one to the fourth 100 mg. In each case practically all the dicyanodiamide added was recovered by the Harger method. Of the total of 250 mg. of dicyanodiamide added in the four lots, a total of 253.2 mg. was obtained. If we assume this extra 3.2 mg. of dicyanodiamide recovered to represent the dicyanodiamide content of 16 g. of fertilizer treated, this product would have contained a total of 0.02 per cent dicyanodiamide expressed in terms of ammonia. This was the only fertilizer mixture containing ammoniated base in which the present investigators ever succeeded in recovering quantities of dicyanodiamide comparable to that added.

Feeling that possibly the tobacco stems and meals might have had some influence on the application of the Harger method to the determination of dicyanodiamide in these mixtures, we procured some samples of standard base goods from some of the large producers. One of the samples contained 2.56 per cent of ammonia, of which 75 per cent was water-soluble, and of which about 25 per cent was yielded as ammonia on distillation with magnesia. Several 10-g. portions of this ammoniated base were extracted with water and treated by the Harger method up to the point of addition of picric acid. Four portions were prepared, each corresponding to 4 g. of ammoniated base. To the first portion 20 mg. of dicyanodiamide were added, to the second portion 40 mg., to the third portion 60 mg., and to the fourth portion 80 mg. The picric acid addition and the ice bath treatment were then carried out. The portion containing 80 mg. of dicyanodiamide began to precipitate in 15 min., and the portion containing 60 mg. at the end of 25 min. No precipitates were obtained from the other portions, even at the end of an hour. All four samples were allowed to stand over night, those to which the 20 and 40 mg. additions of dicyanodiamide showing no precipitate on this long standing. From the portion to which the 80 mg. of dicyanodiamide had been added, only 54 mg. were recovered and from the portion containing 60 mg. of dicyanodiamide only 37 mg. were recovered. These experiments confirm our theories that the amino acids of the base mixture not

⁶ Richter, 3rd American Edition, 412; *Ber.*, 43 (1910), 2882; *Gaz. chim. ital.*, 45 (1915), 56.

only react with cyanamide, as is well known, but also have the property of reacting with dicyanodiamide to a certain extent, and that it would be impossible to have dicyanodiamide in a fertilizer mixture containing base goods and cyanamide when the latter is used in the recommended proportions.

In a parallel series of experiments to which cyanamide had been added, it was found that 4 g. of ammoniated base had the property of reacting immediately with approximately 15 mg. of cyanamide. Ordinarily this reaction between cyanamide and the base goods seems extremely rapid, but it was later found that the rapidity of this reaction was affected by the quantity of ammonium salts present in the aqueous extract of the base goods. The complex nature of this reaction on cyanamide prevented our obtaining any precise information which would enable us to plot the rate of this reaction with cyanamide. Certain complex guanidines, which could not be isolated and identified specifically, seemed to be formed in the presence of the ammonium salts.

CONCLUSION

From these few experimental results with samples of commercial fertilizer and special mixtures from various plants and various agricultural chemical companies, subjected to all the available analytical methods that offer any possibilities of yielding accurate results, the present writer has been entirely unable to parallel the conclusions enunciated in the Harger paper. Wherever dicyanodiamide has been found it has been in extremely small quantity, hardly exceeding the limit of precision of the method of analysis available. Every possible endeavor has been made to check the methods, prove them for their application to the case in question, or to confirm results by the use of several methods of analysis. The widest possible ranges of fertilizer mixtures have been studied. Straight mixtures of ammoniated base and cyanamide are at the present time undergoing extensive investigation with the idea of learning more of the various forms of cyanamide decomposition products therein and applying this information to the commercial fertilizer mixtures. While this work is far from complete, we have in no case encountered dicyanodiamide in even these simple mixtures. The recovery of direct dicyanodiamide additions has yielded extremely irregular results. For this irregularity we have no adequate explanation in many cases.

Methods are lacking for the constitutional analysis of these complex nitrogen compounds. Our own laboratory has been at work on these methods for years. We have reached only to the stage where we are absolutely certain of determinations of ammonium salts, cyanamide, guanyl urea, and urea.

In the case of dicyanodiamide ammonia, we are certain of the results in the absence of amino acids and other organic materials. In the majority of such cases we can check our results by transformation of the dicyanodiamide to guanyl urea and its determination as such. In the presence of amino acids we are able to prove accuracy of results in most cases, but we have records of a few examples where we cannot prove definitely whether the methods of analysis are applicable or not. In several cases we have encountered difficulties with some of the proposed methods because decomposition takes place incident to the reagents used or conditions imposed in the carrying out of the method. This has been a source of considerable difficulty which we believe has been overlooked by many of the investigators in this field who have not familiarized themselves with the character of cyanamide decompositions.

Our conclusion to-day is that in the ordinary commercial fertilizer formulated from the everyday fertilizer materials, and using cyanamide in the quantities recommended, there need be no fear of transformation to dicyanodiamide and con-

sequent loss of the plant food value of the nitrogen contained.

The complex fertilizer mixtures of to-day, and particularly those containing cyanamide, form a most attractive field for investigation of their constitution, and should be of great interest to the student of analytical chemistry desirous of investigating one of the most complicated, yet fascinating fields of his activity. The ability to determine the various forms of nitrogen in such a fertilizer mixture is very greatly desired and chemists have been coöperating and working on these methods in several laboratories for a considerable period of time; yet the field to-day is practically untouched.

Comments on Formation of Dicyanodiamide in Fertilizers¹

By J. E. Breckenridge

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In experiments made by R. N. Harger,² mixtures were made to correspond to 25, 50, 75, and 100 lbs. of cyanamide per ton of fertilizer with water added so that mixture contained 10 per cent moisture. Harger writes, "It will be noticed that while the formation of dicyanodiamide is less with smaller quantities of cyanamide used in the fertilizer, yet the change to dicyanodiamide is still very considerable with 50 pounds per ton."

In view of the fact that cyanamide had been used for some years in amounts approximating 50 lbs. to the ton, this statement disturbed the fertilizer industry, and there was some doubt as to whether or not in actual fertilizer manufacture there would be the results as indicated by the above experiments. No harmful results had been called to the writer's attention by the use of cyanamide as used in mixed fertilizers.

The author, therefore, prepared a laboratory mixture of 1900 parts acid phosphate (testing 12 per cent moisture and 16.50 per cent available phosphoric acid) and 100 parts of cyanamide (old stock). This mixture was tested at once for dicyanodiamide by the method outlined by Harger, with the following results:

	Dicyanodiamide Per cent
Fresh mixture.....	0.15
24 hours.....	0.26
9 days.....	None

Again a pile of fertilizer in the factory was sampled. This contained 40 lbs. of cyanamide to the ton, the other ingredients being the usual materials entering a fertilizer mixture, with 8 per cent phosphoric acid. The fertilizer was acid in reaction and was made up as in regular manufacture, in several hundred tons to a pile. This sample was tested for dicyanodiamide, and none was found.

The sample was sent to the Bureau of Plant Industry (Soil Fertility Investigations), Washington, D. C., and under date of September 28, 1920, the reply was "The examination of this sample of fertilizer in the Laboratory here shows it to be practically free from dicyanodiamide."

Since that proportion of cyanamide in the sample submitted was about what is used in fertilizer manufacture, the result confirmed our experience in the past; namely, that in general fertilizer manufacture no dicyanodiamide is present in fertilizers as shipped to the trade when 40 lbs. of cyanamide are used in complete goods containing 8 per cent available phosphoric acid, and that the conclusion reached by Harger is not confirmed in general fertilizer manufacture.

¹ Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

² THIS JOURNAL, 12 (1920), 1111.

Electrolytic Recovery of Magnesium from Salt Works Residue¹

By K. S. Boynton and Verne Langford with J. F. G. Hicks

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In view of the fact that the raw materials and power necessary for the production of magnesium at a comparatively low cost are to be found on the Pacific Coast, the problem of producing the metal from these raw materials was undertaken.

RAW MATERIALS

In the experimental work crude hydrated magnesium chloride, commonly called "bittern," was used as the source of magnesium. Large quantities of this bittern form the residues from the recovery of salt from sea water. The composition is as follows:

	Per cent
Insoluble.....	0.05
Ferric and aluminium chlorides.....	Trace
Calcium chloride.....	0.59
MgCl ₂ ·6H ₂ O.....	94.42
Sodium and potassium chlorides.....	4.32
MgSO ₄ ·7H ₂ O.....	0.59

Commercial ammonium chloride and sodium chloride were used as dehydrating agents. Dehydration of the magnesium chloride by heating it alone always resulted in the formation of basic salts, and the dehydrated mass was worthless for electrolytic purposes. The mixture finally selected contained:

	Parts
MgCl ₂ ·6H ₂ O.....	10.0
NaCl.....	1.
NH ₄ Cl.....	1.0

The following advantages are claimed for it:

- 1—Reduction of hydrolysis to a minimum.
- 2—Minimum amounts of sodium and ammonium chlorides.
- 3—A maximum current efficiency.
- 4—A maximum concentration of magnesium in the bath, for electrolysis.
- 5—Lowest viscosity of any bath tried.
- 6—Higher percentage yield.
- 7—Relatively low melting point.

DEHYDRATION OF CRUDE MAGNESIUM CHLORIDE

This mixture was dehydrated by heating gradually to 200° C. in a revolving steel cylinder, through which air was forced for the more rapid removal of steam and small quantities of hydrochloric acid gas. A few flint pebbles in the cylinder served to keep the mixture broken up. The anhydrous chlorides were heated in iron pots until ammonium chloride was entirely driven off, and the residue had melted. This fusion was electrolyzed.

ELECTROLYSIS

Two types of electrolytic cell were used: In one, both electrodes were carbon; in the other, the anode was carbon and the cathode iron. Two patterns of the carbon-iron cell, one the ordinary cylindrical pattern, and the other V-shaped, were found to be satisfactory. The carbon-carbon cell yielded the best results from a laboratory standpoint, but was considered impractical for work on a large scale.

Electrolyses were conducted in an atmosphere of illuminating gas. Obviously, any other cheap reducing or neutral atmosphere would answer the same purpose. It was possible to produce metal at a minimum voltage of 4, but the average for eleven runs was 6.2. As only a small generator was available for these experimental runs, the average amperage was only 100.

The average faraday efficiency for eleven runs with the iron cylindrical cell was 30 per cent, and the average time was 1.7 hrs. After readily reproducible conditions were obtained, it was a comparatively simple matter to predict the yield of a given run to within 25 per cent of the actual yield.

¹ Received August 18, 1921.

PURIFICATION OF THE MAGNESIUM

Metallic magnesium was deposited at the cathode surface in small molten globules or "shot," which slowly increased in size and were finally detached by the convection currents set up in the bath. These currents distributed the globules throughout the bath, the specific gravity of which was very nearly that of the globules. This accounts for the fact that the globules could be skimmed from the surface of the bath or scraped from the bottom of the cell during the same run.

At the end of each run the fusion was poured into a mold, cooled and crushed, and the metal was sieved out. The "buttons" of magnesium varied in size from minute spheres to globules weighing over half a gram.

To free the metal from occluded flux, carbon particles, oxides, etc., some dehydrated magnesium chloride was fused in a carbon crucible, fitted with an air-tight lid containing two holes to permit ingress and egress of illuminating gas. The magnesium shot were thrown into the fused mass and the lid clamped on tightly. The degree of purification of the metal is shown by the following table:

	Crude Magnesium Per cent	Refined Magnesium Per cent
Insoluble.....	Trace	None
Iron.....	0.74	0.42
Aluminium.....	Trace	Trace
Calcium.....	Trace	Trace
MgO.....	0.02	Trace
Magnesium.....	99.24	99.58

RECOVERY OF VOLATILIZED AMMONIUM CHLORIDE

Some experiments were made on the possibility of recovering the ammonium chloride by condensation. Small amounts of moisture very markedly lowered the efficiency of this condensation process, although better than 50 per cent recoveries were easily attained.

ESTIMATE OF COST OF PRODUCING MAGNESIUM ON SAN FRANCISCO BAY

From the analysis of crude "bittern" it will be seen that, theoretically, 8.88 tons (2000 lbs.) of this raw material are required to produce 1 ton of magnesium. Allowing 25 per cent wastage to maintain the purity of the electrolyte, 11.10 tons of "bittern," 1.64 tons of salt, and 1.11 tons of ammonium chloride will be required to produce a ton of metal.

DEHYDRATION—Since hydrated magnesium chloride contains 53.5 per cent of water, the weight of water in 11.10 tons of raw material would be 5.94 tons. One barrel of fuel oil will evaporate 1.3 tons of water in dehydrating alum. As the "bittern" loses its water at a lower temperature than alum, the above ratio seems to be a safe estimate. At this rate 4.57 bbls., or, to allow 10 per cent for removal of additional moisture of the mixture, 5.02 bbls. of fuel oil would be required for the dehydration of sufficient material to produce one ton of magnesium.

TIME AND POWER NECESSARY TO DEPOSIT ONE TON OF MAGNESIUM AT A FARADAY EFFICIENCY OF 30 PER CENT—1 faraday = 96,500 coulombs = 0.0264 lb. of magnesium. $\frac{2000}{0.0264} = 75,757.57$ faradays = 7,310,605,505 coulombs per ton of magnesium.

Therefore, to produce 1 ton of magnesium 24,368,685,010 coulombs would be needed.

$\frac{24,368,685,010}{3600} = 6,769,079$ ampere hours to produce a ton

$\frac{6759}{720 \text{ (hrs. in 1 mo.)}} = 9401.4$ ampere months

9401.4×6 (volts) = 56.41 kw.-mo.

Allowing 25 per cent (14.10) for interruptions, 70.51 kw.-mo. would be required for the production of 2000 lbs.

FREIGHT AND HANDLING OF RAW MATERIALS—The plant would be within a few miles of the source of the raw material, hence freight and handling would be a comparatively small item of expense. For each ton of metal produced, 18.85 tons of material would need to be freighted and handled.

LABOR—Six men, including a chemist, would handle the proposed plant.

OIL FOR HEATING CELL—The crude oil for outside heating of the cell would be required, at most, during one-fourth of the run. For this heating 5 tons would be required.

CARBON ANODES—About 200 lbs. of carbon anodes would be consumed per ton of metal.

ILLUMINATING GAS—For a cell of sufficient size to produce a ton of magnesium in 720 hrs., 50,000 cu. ft. of illuminating gas would be required to form a reducing atmosphere above the electrolyte.

COST OF PRODUCING 1 TON OF MAGNESIUM

Crude MgCl ₂ ·6H ₂ O	11.1 tons at \$30.00	\$ 333.00
Commercial NH ₄ Cl	11.1 tons at \$60.30	67.00
Commercial NaCl	1.64 tons at \$7.00	11.48
Oil for dehydration	5.02 bbls. at \$1.80	9.04
Illuminating gas	50,000 cu. ft. at \$0.50	25.00
Electric power	70.51 kw.-mo. at \$4.00	282.04
Oil for heating cell	5 tons at \$10.00	50.00
Anode carbon	200 lbs. at \$0.04	8.00
Freight and handling of raw materials	18.85 tons at \$5.00	94.25
Labor	6 men, including a chemist	1000.00
TOTAL			\$1879.81

$\frac{1879.81}{2000} = \$0.939$ per lb. to produce a ton of magnesium

Loss of Carbon Dioxide from Dough as an Index of Flour Strength^{1,2}

By C. H. Bailey and Mildred Weigley

DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION, UNIVERSITY FARM, ST. PAUL, MINN.

Flour strength studies conducted during the past quarter century have usually employed as the ultimate criterion of strength the comparative physical properties of yeast-leavened loaves of bread produced on baking. Humphries and Biffin³ suggest that "a strong wheat is one which yields flour capable of making large, well-piled loaves." Quality of the loaves is thus determined by their size or volume, and the texture and other related properties of the crumb. Baking tests, however, are not exact procedures which yield uniform results when the same materials are employed. Judgment comes into play to a considerable extent, and experts sometimes differ in their opinion of the relative merits of different flours which are being compared. Such tests do not of necessity indicate the reasons for variations that are observed, or the methods for effecting desired improvements. For these reasons efforts have been directed toward developing more exact methods for testing the properties of flour that are of significance in this connection. The work reported in this paper represents an attempt in this general direction.

PROPERTIES THAT CONSTITUTE STRENGTH

A consideration of the factors involved in the production of "large well-piled" loaves suggested to one of the authors⁴ that "the strength of flour is determined by the ratio between the rate of production of carbon dioxide in and the rate of loss of carbon dioxide from, the fermenting mass of dough." The absolute rate of carbon dioxide production in doughs made from different flours varies, to be sure, through fairly wide limits. When known, the rate can be varied in the desired direction, however, by adjustments in the formula, and particularly in the proportions of yeast, yeast accelerators, salt, fermentable sugars, and diastase preparations. The retention of gas is much more difficult to bring under control, since it is apparently determined in large measure by the percentage and physical properties of the gluten proteins in the flour. Hence, in testing flours, the ratio between production and loss of carbon dioxide apparently becomes of practical significance, and this was the point attacked in the present investigation.

¹ Presented before the Division of Biological Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

² Published with the approval of the Director as Paper No. 274, Journal Series, Minnesota Agricultural Experiment Station.

³ "The Improvement of English Wheat." *J. Agr. Sci.*, 2 (1907), 1.

⁴ C. H. Bailey, *THIS JOURNAL*, 5 (1916), 208.

CHARACTER OF FLOURS EMPLOYED IN INVESTIGATION

Two flours were employed, a "strong" flour milled from hard spring wheat, and a "weak" flour milled at Spokane, Washington, from typical soft wheat of that region. The composition, and the baking qualities of the two flours, determined by the method previously described by Bailey,⁴ are shown in Table I. The strong flour contained a materially higher percentage of crude protein, and on baking gave a loaf of larger volume and better texture than did the weak flour. The differences in these respects were considerable. As the flours were of about the same grade, as indicated by the ash content and color score, they were well suited to a study of properties responsible for variations in baking strength.

TABLE I—ANALYSES AND BAKING TESTS OF STRONG AND WEAK FLOURS

MARK	Moisture Percent	Crude Protein (N×5.7) Percent	Ash Percent	Volume of Loaf Cc.	Color Score	Texture	Expan-simeter Test Cc.
B878, weak flour.....	10.88	8.00	0.52	1200	97	85	520
Composite, strong flour	8.95	12.00	0.56	1580	98	100	910

That the two flours also varied widely in colloidal properties was established by the procedure developed by Gortner and Sharp,⁵ in which the change in viscosity of a mixture of water and on the addition of normal lactic acid solution is traced by a MacMichael viscosimeter. Table II gives the results of this test.⁶ Quite evidently there are decided differences in the properties of these two flours which are responsible for variations in the viscosity of such preparations. The

TABLE II—VISCOSITY IN MACMICHAEL DEGREES OF FLOUR AND WATER MIXTURES OF WEAK AND STRONG FLOURS

Normal Lactic Acid Added Cc.	Mixture contained equivalent of 25 g. dry matter + 100 cc. water	
	Weak Flour (B878) Degrees MacMichael	Strong Flour (Composite) Degrees MacMichael
0.0	32	68
0.5	32	73
1.0	38	104
1.5	43	135
2.0	50	161
2.5	53	183
3.0	56	196
4.0	60	212
5.0	61	221
6.0	62	222
8.0	62	222
10.0	61	219

⁵ "The Physicochemical Properties of Strong and Weak Flours. III—Viscosity as a Measure of Hydration Capacity and the Relation of the Hydrogen-Ion Concentration to Imbibition in the Different Acids." Presented before the Division of Physical and Inorganic Chemistry at the 62nd Meeting, A. C. S., New York, N. Y., September 6 to 10, 1921.

⁶ Determinations made by Paul F. Sharp.

flour which is regarded as "strong" on the basis of the baking tests gives a much more viscous preparation when mixed with water and lactic acid than does the weak flour.

METHOD OF DETERMINING LOSS OF CARBON DIOXIDE FROM DOUGH

The two flours were mixed into doughs with a mechanical dough mixer, using the following formula:

	Grams
Flour.....	350.0
Yeast.....	4.25
Salt.....	5.25
Sugar.....	8.75
Water.....	Sufficient

The water used in preparing the weak flour dough was equivalent to an average of 56 cc. per 100 g. of flour, while with the strong flour an average of 61.4 cc. per 100 g. of flour was used. These proportions of water resulted in doughs of as nearly the same consistency as could be produced with flours of such different properties.

Two series of determinations were made with these doughs. In the first, the dough was divided into aliquot parts, and the determination of the diffusion of carbon dioxide out of the dough was begun without any preliminary fermentation. Such doughs are referred to in the following discussion as "no previous fermentation" doughs. After removal from the mixer, the other series of doughs were allowed to ferment for several hours in a thermostat at 28° C. before the diffusion of carbon dioxide was determined. These doughs are designated as "normally fermented." The fermentation period varied somewhat, averaging 274 min. in the case of the strong flour and 248 min. in the case of the weak flour. During this period the doughs were "punched" or worked lightly three times. At the end of the period the doughs were regarded as ready for molding into loaves, and were accordingly kneaded vigorously on the bread board to remove as much as possible of the occluded gas.

In both series the doughs were weighed, and three aliquot portions were scaled off, each representing one-seventh of the total dough, or 50 g. of flour. All three portions were subjected to the same treatment with respect to kneading and molding. The first was dropped into a 1000-cc. measuring cylinder which contained 600 cc. of water and its volume was determined by the rise in the water level. The second portion was molded into a cylindrical form and placed in a dry 250-cc. measuring cylinder where its subsequent volume could be determined as fermentation proceeded. The third portion was molded to fit a shallow iron pan, about 7 cm. in diameter and 1.8 cm. deep. This quantity of dough filled the round pan about level full when firmed down. The pan was covered with a ground glass plate in an inverted dialyzer. The plate and the neck of the dialyzer were fitted with tubes as shown in Fig. 1. Both tubes were tightly sealed in place with wax and, when the glass plate was vaselined and seated, constituted the only means for the passage of gases into and out of the apparatus. The entire apparatus was placed in an air thermostat maintained at 34° C. (93.2° F.).

The inlet tube in the plate was connected to a source of moist, CO₂-free air at 34° C. (This air had been bubbled through 50 per cent sodium hydroxide solution, and then through water into a large cylinder where it attained the temperature of the thermostat before entering the dialyzer or fermentation chamber.) The outlet tube was connected to a Truog⁷ tower as modified by Bailey,⁸ where the carbon dioxide was absorbed in a known amount of barium hydroxide solution. The residual barium hydroxide was determined at

the end of the absorption period by titration with standard hydrochloric acid solution. The titration data were calculated over into terms of milligrams of carbon dioxide.

It was customary in these experiments to collect the gas given off during a period of exactly 30 min., then to switch

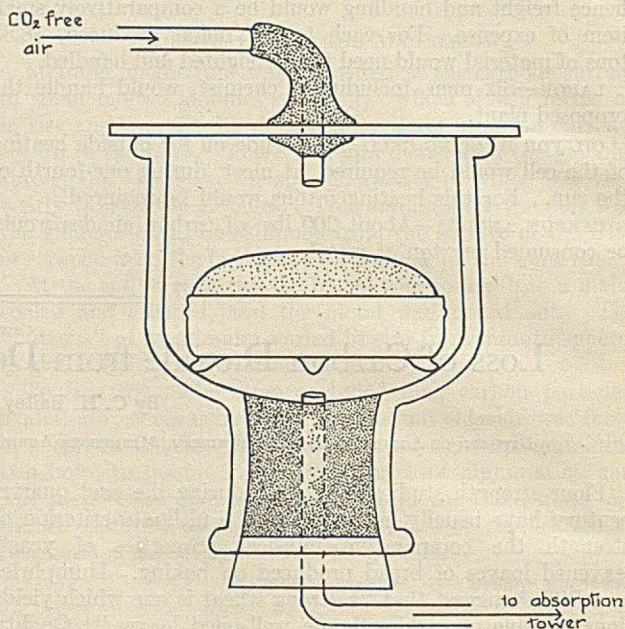


FIG. 1.—CHAMBER AND DOUGH ARRANGED FOR DETERMINATION OF LOSS OF CARBON DIOXIDE DURING FERMENTATION

the outlet tube to another Truog tower, where the gas was collected for another 30-min. period. During the second period it was possible to determine the residual barium hydroxide in the first tower, and recharge it for the third 30-min. period. In this way two towers served for the determination by 30-min. periods of the gas diffusing out of each dough until it definitely "fell" or partly collapsed. At the end of each period the volume of the dough in the graduated cylinder was noted, and these values, minus the initial volume of the same dough, represented the *increase* in volume due to retention or occlusion of the gases of fermentation. The maximum volume attained by each dough was recorded.

RELATION OF STRENGTH TO GAS RETENTION

Table III and Figs. 2 and 3 give the average data obtained with the strong and weak flours. From five to nine replicates are included in each set of averages in the table. Two series of comparisons are thus afforded: (a) The loss of carbon dioxide from the doughs per unit of time, and (b) the expansion of the dough per unit of time. The graphs establish the fact that the weak flour dough consistently lost more carbon dioxide per unit of time than did the strong flour dough. The largest relative difference is found at the end of 120 min. in the doughs not previously fermented when the strong flour dough had lost a total of only 56.6 mg. of carbon dioxide in expanding 140 cc., while the weak flour dough had lost a total of 113.0 mg. of carbon dioxide in expanding 120 cc. Less difference in the loss of carbon dioxide per unit of time was found when the strong and weak flour doughs fermented normally were compared. Such differences as existed were uniformly in the direction of smaller losses from the strong flour dough. The total losses of carbon dioxide up to the time of falling or collapse of the two doughs were apparently about the same in both cases, but owing to the difficulty in judging of the exact time when such a collapse or fall occurred, it was impossible to determine with precision the total loss of gas up to that time. The general shape of the curves, the distance between them, and the quantity of gas lost up to the

⁷ THIS JOURNAL, 7 (1915), 1045.

⁸ "Respiration of Shelled Corn," Minnesota Agricultural Experiment Station, Technical Bulletin 3.

point where the curves begin to "break" or change shape sharply appear of more significance than the quantity of gas lost up to the time of apparent collapse of the dough.

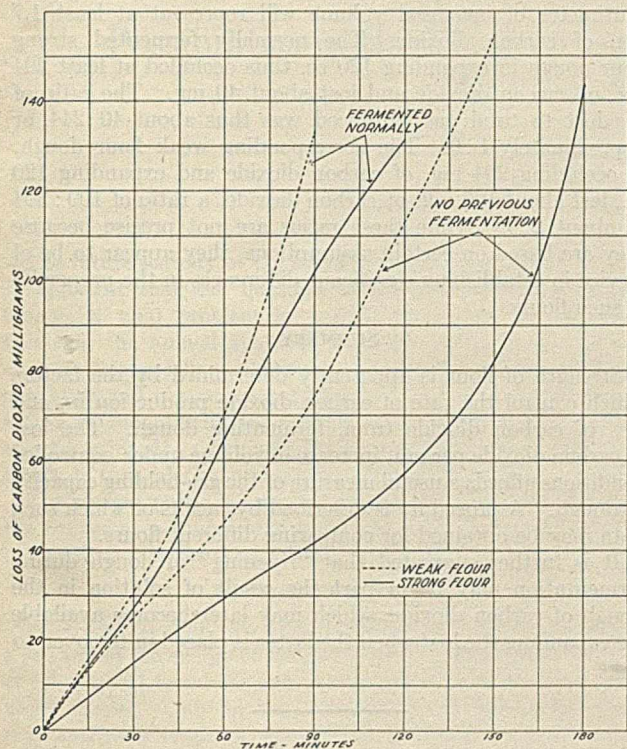


FIG. 2—LOSS OF CARBON DIOXIDE FROM DOUGH PER UNIT OF TIME

The rate of expansion of the strong flour dough was considerably greater than that of the weak flour dough. This is usual in such instances when an adequate quantity of sugar is included in the formula. In the case of each flour, the normally fermented doughs exhibited greater differences than the doughs not previously fermented. This was due to the fact that both of the weak flour doughs expanded to about the same maximum volume, while the strong flour normally fermented dough expanded considerably more than the strong flour dough not previously fermented.

TABLE III—AVERAGE LOSS OF CARBON DIOXIDE FROM, AND CHANGE IN VOLUME OF, DOUGHS MADE FROM STRONG AND WEAK FLOURS

Time Min.	STRONG FLOUR			Time Min.	WEAK FLOUR		
	Total Carbon Dioxide Loss of Dough Mg.	Total Volume of Dough Cc.	Increase in Volume of Dough Cc.		Total Carbon Dioxide Loss of Dough Mg.	Total Volume of Dough Cc.	Increase in Volume of Dough Cc.
0	...	63	0	0	...	63	0
30	15.1	78	15	30	25.4	74	9
60	29.6	113	50	60	46.3	101	38
90	41.9	165	102	90	74.0	144	81
120	56.6	208	140	120	113.0	183	120
150	81.8	226	163	150	154.7	192	129
180	143.9	226	163
No previous fermentation							
0	...	71	0	0	...	62	0
30	27.4	145	74	30	31.0	128	46
60	64.9	219	148	60	71.0	176	114
90	101.6	254	183	90	133.5	189	127
120	131.4	266	195
Fermented normally							

The data presented in Figs. 2 and 3 are combined in Fig. 4 and the losses of carbon dioxide are plotted against the change in volume of the corresponding dough. These data appear to be the most significant in this connection and establish considerable differences in the properties of the strong and weak flour doughs. It is evident that the weak flour dough lost decidedly more carbon dioxide per unit increase in volume from the start, and that when the dough began to collapse and break down it discharged carbon dioxide into the surrounding atmosphere at a much greater rate than did the

strong flour dough. Thus when the normally fermented strong and weak flour doughs had expanded 80 cc. they had lost 30 and 42 mg. of carbon dioxide, respectively, and when they had expanded 120 cc. they had lost 50 and 100 mg. Even greater differences between the two flours are observed when the doughs not previously fermented are compared.

CHANGES IN EXPANSION AND GAS RETENTION OF DOUGH AS RESULT OF FERMENTATION

Fig. 3 affords an interesting comparison of the strong and weak flour doughs as affected by previous fermentation. Both weak flour doughs expanded to the same extent, while corresponding strong flour doughs expanded 163 cc. when not previously fermented and 195 cc. when fermented normally. This suggests that fermentation effects more improvement in the properties of a strong flour dough than is brought about by a similar treatment of a weak flour dough.

The maximum volumes attained by the strong and weak flour doughs fermented normally differ in the usual direction. The curve representing expansion of the weak flour dough rises less rapidly and breaks earlier and more sharply than the corresponding curve for the strong flour dough. Instances have been occasionally observed in this laboratory where such a relation did not exist. For example, in comparing certain clear grade flours with the patent grade from the same mill, the clear grade dough would sometimes expand more rapidly and to a slightly greater maximum, although other aliquot portions of the same doughs when baked gave larger, better-textured loaves from the patent flour dough. For this reason some doubt has been cast upon the accuracy of a simple expansion test as an index of baking quality. Such data, considered in connection with the losses of carbon dioxide,

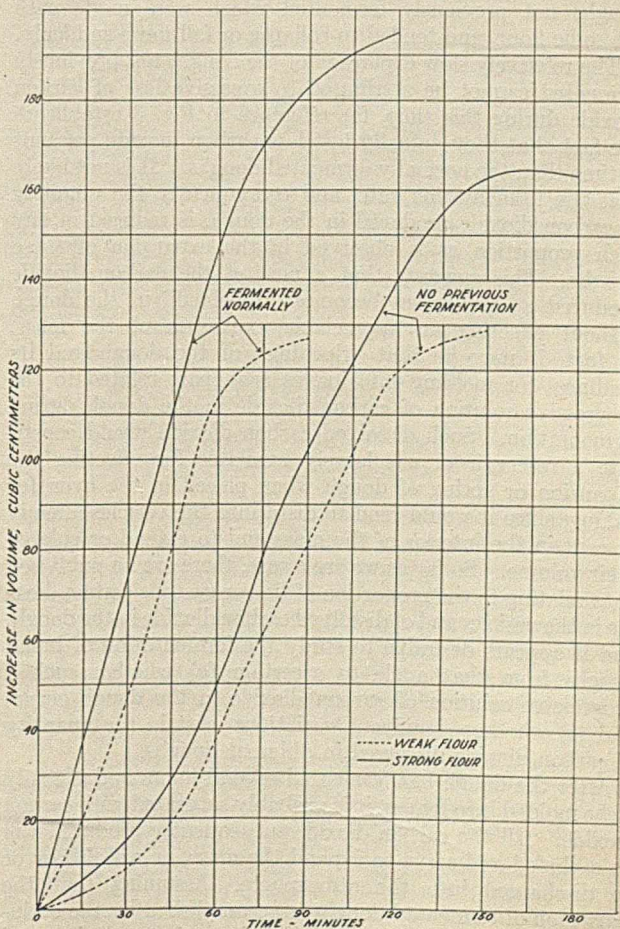


FIG. 3—RATE OF EXPANSION OF STRONG AND WEAK FLOUR DOUGHS

are of service in indicating the rate of gas production in the dough, which is one of the significant factors in determining baking strength.

The curves also indicate a decided difference in the rate of expansion of the doughs immediately after mixing (no previous fermentation) and similar doughs after normally fermenting for several hours. The former expanded slowly

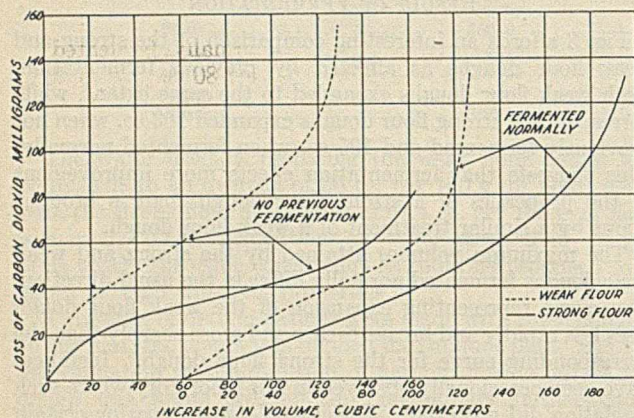


FIG. 4—RELATION OF EXPANSION OF STRONG AND WEAK FLOUR DOUGHS TO LOSS OF CARBON DIOXIDE

during the first hour, more rapidly during the second hour, and continued to expand somewhat during part or all of the third hour. Doughs normally fermented, on the other hand, expanded more rapidly during the initial period, and exhibited a diminishing rate during each successive period. They always reached their maximum volume sooner than the doughs not previously fermented which were made with the same flour, and tended to collapse or fall more suddenly.

The relatively slow expansion of the doughs not previously fermented cannot be attributed to excessive loss of carbon dioxide during this time, for reference to Fig. 3 establishes the fact that they actually lost less carbon dioxide per unit of time than the normally fermented doughs. It is not likely that the fermentation rate, and consequently the quantity of carbon dioxide produced in the dough, is reduced in any such proportion as is observed in the expansion of these doughs. This suggests that a part of the carbon dioxide produced at the outset becomes "dissolved" in the dough without effecting an appreciable expansion of the mass. In fact, it may be that "ripening" of the dough and its readiness for molding into loaves is in part related to the progressive solution of carbon dioxide in the dough during fermentation. Such dissolved carbon dioxide would constitute a reservoir of gas largely available for effecting the expansion or spring of dough when placed in the oven for baking, since it would tend to distil into the vesicles already present in the interior of the mass and to extend or enlarge their volume. So far as we are aware, there are no published data relating to the proportion of free or gaseous carbon dioxide in the vesicles and of dissolved carbon dioxide in the dough, and it appears desirable to study the fermentation of bread doughs from that angle to ascertain (a) whether such a progressive solution of carbon dioxide in the dough occurs and (b) whether significant variations exist in the quantity of carbon dioxide dissolved in different doughs.

After the dough has fermented several hours and is ready to be molded into loaves, it is probably saturated with carbon dioxide. All the carbon dioxide subsequently produced will be occluded and serve to expand the mass, or will diffuse or be discharged into the atmosphere. Assuming that the expansion of fermented doughs is accomplished by the occlusion of carbon dioxide resulting from fermentation and assuming further that such carbon dioxide is under atmos-

pheric pressure of about 730 mm. in the dough at a temperature of about 30° C., it follows that each milligram of carbon dioxide will expand the dough 0.59 cc. Thus each cubic centimeter of increased volume will represent at least 1.7 mg. of carbon dioxide. The normally fermented strong flour dough in expanding 120 cc. thus occluded at least 204 mg. of carbon dioxide and lost about 40 mg. The ratio of gas lost to total gas produced was thus about 40:244, or approximately 1:6. The corresponding weak flour dough, in occluding 204 mg. of carbon dioxide and expanding 120 cc., lost about 100 mg. of carbon dioxide, a ratio of 100:304 or about 2:6. While these ratios are not precise because they are based on certain assumptions, they appear to be of service in establishing significant differences in the properties of such flours.

SUMMARY

Strength of flour is apparently determined by the factors which control the rate of carbon dioxide production in, and loss of carbon dioxide from, fermenting dough. The loss of carbon dioxide per unit increase in volume under controlled conditions affords a useful measure of the gas-holding capacity of dough. A procedure is described by means of which such data may be obtained for comparing different flours.

It is further suggested that "ripening" of dough during fermentation may be in part the result of solution in the dough of carbon dioxide, which may later become available for expanding the loaf when the latter is placed in the oven to bake.

Report of American Committee on Electrolysis

The American Committee on Electrolysis, which is made up of representatives of the large national associations of public utility corporations and of the Bureau of Standards, has recently issued its second report. The report includes discussions of design, construction, operation and maintenance of underground structures affected by electrolysis, as well as discussions of electrolysis surveys and apparatus for electrolysis testing. It concludes with an analysis of present European practice relating to electrolysis mitigation, and an outline of researches which the committee consider necessary in this connection.

This report is for sale by the American Institute of Electrical Engineers, 33 West 39th St., New York City, at one dollar per copy.

The United States Civil Service Commission has announced examinations for chemical technologist at \$3600 to \$5000 a year, associate chemical technologist at \$2500 to \$3600 a year, and assistant chemical technologist at \$1800 to \$2500 a year to fill vacancies in the Chemical Warfare Service, Edgewood Arsenal, Md. Applicants must qualify in at least one of the following branches of chemistry: advanced inorganic, analytical, biological, explosives, metallurgical, organic, pharmaceutical, physical, and engineering. Applications must be filed before February 14.

Examinations have also been announced for assistant examiner, Patent Office, at \$1500 a year, to take place February 8, 9, and 10 and March 22, 23, and 24. Competitors will be rated on the following subjects: mathematics, physics, mechanical drawings, language, technics, and optional subject chosen from one of the following: mechanical engineering, civil engineering, electrical engineering, general chemistry, electrochemistry, and chemical engineering.

A short course in pulp and paper manufacture is to be given next year at the New York State College of Forestry at Syracuse University. The course will include elementary chemistry, elementary forestry, principles of pulp and paper manufacture, pulp and paper mill machinery, manufacture and testing of pulp and paper mill chemicals, manufacture of pulp and paper, practical paper testing, identification of woods and fibers, lectures, talks, and round-table discussion by prominent men in the industry, and inspection trips to a number of the larger mills and mill equipment manufacturers of New York State.

ADDRESSES AND CONTRIBUTED ARTICLES

Possibilities of the Plant Growth of the Moist Tropics to Furnish Materials for Liquid Fuel¹

(ABSTRACT)

By H. N. Whitford

YALE SCHOOL OF FORESTRY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT

The future scarcity of the country's liquid fuel supply is now so apparent that the question of its early replacement has become a vital problem in natural economics. A question involving the annual synthesis of some 4,900,000,000 gallons of a feasible gasoline substitute calls for the development of new ideas and new sources of energy. Our one great source of energy is undoubtedly that of the sun. How can this source best be utilized? Obviously in the growth of plant life from which, in turn, alcohol and other fuels may be made.

The present paper is intended to consider the possibilities of the tropics as a source of transformed solar energy capable of being utilized for the production of liquid fuel.

FOREST CROPS

WOOD CROPS—The raw material which is most abundant as a product of the energy of the sun is wood and the moist regions of all tropical countries still contain vast areas covered with virgin forests. Only in the moist tropics is growth so rapid that enormous crops of wood could be raised in short time, in order that quantities of wood sufficient to supply a large alcohol-producing plant could be raised on a small area. In temperate regions nature's cellulose-producing factory is working only part time; in the moist tropics, because of continuous heat and available moisture, it is running full time. Besides, the energy of the tropical sun is greater. Theoretically the moist tropics should have two or more times the capacity to produce a given quantity of cellulose in a given time than temperate regions. Practically such is the case. Measurements of certain species of soft hardwoods in the tropics indicate that they grow from three to five times as rapidly as such woods as cottonwood and white birch in our climates. One acre of ground in the tropics can be made to yield as much timber in a given time as five or more acres in temperate regions, and, other things being equal, the cost of assembling this raw material at the factory would be greatly reduced.

BAMBOO CROPS—Measurements made in the Philippines show that culms of certain species of bamboo will attain a height of from 66 to 82 feet in a single season; most of the growth takes place during three months.² Two to three years are required for the culms to harden.

Areas of wild small bamboo in the Philippines with an average height of 43 feet in one season are known to yield enough material to make 7 tons of pulp per acre, the cost of which for cutting and transporting by admittedly crude methods is \$1.25 per ton. A calculation of the acreage necessary to produce from this source 7,500,000,000 gallons of alcohol (the estimated equivalent of the present annual consumption of 4,900,000,000 gallons of crude oil) is included in Table I. These figures are crude and are given only to indicate the possibilities. Unfortunately we know little or nothing concerning the areas of bamboo in the tropics. In the eastern tropics it is found in pure stands or

mixed with hardwoods over vast areas, while in the western tropics it is of very limited occurrence.

TABLE I—YIELD FROM SMALL-SIZED BAMBOO FORESTS IN THE PHILIPPINES^{2,3}

Average yield per acre of dry material	14 long tons
Average yield per acre of pulp	7 short tons
Estimated average yield per acre of alcohol @ 40 gallons to ton of pulp	280 gal.
Acreage necessary to produce heat equivalent to 1920 production of gasoline in United States	27,000,000 (42,200 sq. mi.)
Amount of alcohol from this area	7,500,000,000 gal.
Acreage necessary on 3 years' rotation	81,000,000 (126,600 sq. mi.)
Average cost of raw material per gallon of alcohol	\$0.03 ^{1/3}

If we are to depend on bamboo for paper pulp or for alcohol, planted crops must be raised. A rough estimate of the cost of bringing them to maturity (5 years) is about \$26 per acre, but when once established and properly managed such plantings could be made to yield crops indefinitely.³ The yield per acre might perhaps be doubled and the acreage reduced one-half by selecting larger species. It is of interest that in the Philippines alone there are some 68,000 square miles of cut-over waste lands in grass and second growth forests that might be made available.

NIPA PALM—While alcohol can be obtained from the inflorescent stalk of many palms, the nipa seems to be best adapted for its commercial production, because, in the first place, it is grown in pure stands as part of the mangrove swamps of the tidewater regions throughout the Indo-Malay region. Secondly, it has no distinct above-ground stem, and its flower stalk is near the ground; consequently the alcohol can be collected easily and cheaply. The plant reaches maturity in 4 to 5 years. Without going into the different items in detail, Table II will show the yield per acre and costs of the raw material per gallon of 90 per cent alcohol.^{4,5,6}

TABLE II—YIELD AND COST OF ALCOHOL FROM NIPA PALM

750 plants per hectare that can produce sap
43 liters of sap per plant per season
32,250 liters of sap per hectare
6.5 per cent of sap = alcohol
2096 liters of alcohol per hectare = about 210 gallons of alcohol per acre
Cost of raw material per gallon of alcohol, 12 cents

One distillery (1911) was actually producing 93 per cent alcohol at a cost of about 20 cents a gallon on a 12-hour basis. If run 24 hours, it is estimated that this plant could produce alcohol at a cost of about 15 cents per gallon.⁶

The annual production of nipa alcohol in the Philippines is near to 3,000,000 gallons and only a small part of the entire area is under production, part of which is planted. The largest continuous area of nipa palm in the Philippines is about 22,000 acres. Unfortunately no data are available concerning the

¹ G. F. Richmond, "Philippine Fibers and Fibrous Substances. Their Suitability for Paper Making," *Philippine J. Sci.*, **1** (1906), 433; Part II, **1**, 1075; Part III, Sect. A, **2** (1907), 81; Sect. A, **5** (1910), 233.

² W. H. Brown and A. F. Fisher, "Philippine Mangrove Swamps," Bureau of Forestry, Manila, P. I., *Bulletin* **17** (1918).

³ W. H. Brown and E. D. Merrill, "Philippine Palms and Palm Products," Bureau of Forestry, Manila, P. I., *Bulletin* **18** (1919).

⁴ H. D. Gibbs, "The Alcohol Industry of the Philippine Islands. Part I," *Philippine J. Sci.*, Sect. A, **6** (1911), 99.

¹ Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

² W. H. Brown and A. F. Fisher, "Philippine Bamboos," Bureau of Forestry, Manila, P. I., *Bulletin* **15** (1918).

total acreage. Much more extensive areas are known to exist in Borneo, and the lumbering concern mentioned above is planning to utilize these for the production of alcohol. To equal the equivalent of 5,000,000 gallons of gasoline produced in the United States in 1920 would require an area of more than 50,000 square miles. If all the tidal swamps of the Indo-Malay tropics were planted to nipa the area available would probably fall far short of this. Nevertheless the possibilities of utilizing the present areas and enlarging them for the production of alcohol is worth considering.

WILD GRASSES—About 40 per cent (48,000 square miles) of the deforested area of the Philippines is covered by two wild grasses, *viz.*, cogon (*Imperata exaltata*), known in other parts of the Malay regions as langlang grass, and talahib (*Saccharum spontaneum*). Experiments indicate that these, especially cogon, compare very favorably with esparto grass in regard to yield of pulp, averaging about 45 per cent by the soda process. The cogon is a grass 5 or 6 feet in height and is found in the drier soils, while talahib, found in the damper soils, reaches a height of 9 to 10 feet. In some parts these grasses could be made to yield two crops per year. Unfortunately, no figures are available for their average acre yield.

In other parts of the tropics there are large areas covered with grasses that might be suitable for paper making and possibly alcohol, among which may be mentioned the cana brava (*Gynerium sagittatum*), a large bamboo-like grass found throughout the moist tropical climate of America. It is cultivated in many parts, especially Columbia and Venezuela, for construction purposes.

AGRICULTURAL CROPS

Unfortunately, reliable average statistics concerning the cultivation in tropical regions of strictly staple agricultural crops are not available. The figures given below are therefore subject to correction as additional information becomes available.

CASSAVA (*Manihot*)—Cassava is a woody plant 4 to 10 feet in height whose roots contain large quantities of starch. Crops can be grown in 6 months, but the best results are obtainable from 9 to 11 months. Figures on the yield per acre vary greatly, but reliable figures from Florida,⁷ British Guiana,⁸ and Brazil,⁹ indicate 10 tons per acre as an average. This would vary according to soil conditions. According to the Imperial Institute,⁹ the yield per ton is 30 to 35 gallons of 95 per cent alcohol. The cost of the raw material in Florida before the war, delivered at starch factories, was \$6.00 per ton, but in tropical regions it is probably much lower than this. Costs and yields are tabulated in Table III.

TABLE III—COST AND YIELDS OF CASSAVA

Yield per acre of roots	10 tons
Cost of raw material per ton	\$5
Per ton yield of alcohol	30 gal.
Per acre yield of alcohol	300 gal.
Cost of raw material per gallon of alcohol	16 $\frac{2}{3}$ cts.
Acreage necessary to raise the equivalent of the 1920 production of alcohol in U. S.	27,000,000 (about 40,000 sq. mi.)

It is the author's opinion that of all agricultural crops this is one of the most promising to investigate for the production of immense quantities of alcohol, since with improved methods of cultivation the yield per acre could undoubtedly be increased considerably.

CORN (MAIZE)—This crop is extensively raised in the tropics but exported to only a slight degree. Mexico stands next to the United States in acreage of corn, but follows Argentina in actual amount produced. The average production per acre in the United States is about 25 bushels, in Argentina (not tropical)

⁷ S. M. Tracy, "Cassava," U. S. Department of Agriculture, *Farmers' Bulletin* 167 (1903).

⁸ J. B. Harrison, "Food Plants of British Guiana," *J. Board of Agr. of British Guiana*, 10 (1917), 143.

⁹ "Cassava as a Source of Industrial Starch and Alcohol," *Bull. Imperial Institute*, No. 4, 17 (1919).

it is 27 and in Mexico (mostly highlands) it is 14 bushels; the methods of cultivation, however, in the last named are not conducive to high yields. In British Guiana, where 4 months are necessary to raise a crop, 18 to 25 bushels per acre are said to be the yield.⁷ Possibly two crops per year might be raised. With a production of 50 bushels, the same amount of corn would be raised in the tropics as in the United States, on an area one-half that in our own country. This high rate of production would seem somewhat problematic in view of various factors operating against it.

RICE—In the tropics the rice crop usually takes four to five months to mature. Where the rainfall is sufficient it can be grown without irrigation. It is probable that if the proper amount of soil moisture could be had, say by irrigation, two crops per year could be obtained.

COTTON—While cotton is of tropical origin, most of the world's production comes from the North Temperate region. Continuous rainfall and much cloudiness is detrimental to growth of cotton; hence very moist tropical regions are not suited to its production. In regions subject to drouth irrigation is necessary. While there are many extensive regions in the drier parts of the tropics that could be made to yield larger amounts than they are now doing, it is probable that the production per acre in the tropics cannot be increased over that of the best portions of our own cotton belt.

SUGAR CANE—This is essentially a perennial crop. In Cuba and the tropics five to ten crops are, in general, obtained from one planting, fully twelve months or more being necessary for the maturity of a crop. In Louisiana the best yields are obtained by planting annually or biennially since winter frosts damage the stubble; hence varieties must be chosen which mature in six to seven months. Black-strap molasses from refining sugar is the present source of most of our industrial alcohol.

SUMMARY

The above is an incomplete review of the possibilities of the tropics to produce crops of foodstuffs and wood capable of application to the manufacture of cellulose and alcohol. Little or nothing is known of the possibilities of many of the wild forest products for the manufacture of pulp suitable for paper making, or the amount of alcohol that they will yield by distillation or by fermentation processes. Until we find fast growing species suitable for these purposes it is nonsense to talk about producing them on a large scale. The few figures given serve merely to indicate the possibilities and are based on admittedly limited data.

The evidence, however, is conclusive that the tropical sun has the power to store up more energy in the form of cellulose in a given time than has the temperate sun, and if this is in a utilizable form it remains for the ingenuity of man to overcome the difficulties of profitably applying it.

American Metric Association

The American Metric Association held its annual meeting in Toronto, Canada, December 29, 1921.

The Canadian members present were unanimous in the opinion that the passage of an effective metric bill by the United States Congress would soon be followed by similar action in the Canadian Parliament. Prof. Henry G. Bayer of New York University discussed "The Evolution of Metric Weights and Measures." Edward Richards and other members of the Society of American Foresters spoke on the "Application of the Metric System to Forestry." Prof. E. C. Bingham reported that through the cooperation of the Association with the American Chemical Society and other organizations three hundred of the universities and colleges had agreed to order their supplies in metric units. Manufacturers and dealers have been found very willing to fill orders in this manner.

The Technical Paper and Its New Relation to Industry¹

By H. C. Parmelee²

NEW YORK, N. Y.

If we attempt to analyze the elements that have contributed to the evolution of modern civilization in all its variety and complexity, we are likely to come to the conclusion that the most powerful single force has been the rapid development in the means of communication between individuals, communities, cities, and nations. To such a degree of perfection have these means been developed, and so complete has been their conquest of conditions on our own earth, that intrepid pioneers are already attacking the problem of interworld communication.

Great industries have been founded in the course of these developments. Ships sail the seven seas to the uttermost parts of the earth; railroads cover the continents like networks of steel; aircraft cruise their routes regularly with incredible speed; the telephone and telegraph are known in the humblest village; radio communication is almost a commonplace; and finally the products of the printing press have long since lost the element of novelty and are accepted as an integral part of our daily life. These agencies have brought about the great transition from primitive society in which human intelligence was transmitted by word of mouth. They have at once simplified and complicated modern life; simplified it by bringing the peoples of the earth into closer contact, and complicated it by extending our relationships and increasing our duties and obligations. They have unified nations in war for a great cause, and they have given an impetus to peaceful industrial growth unparalleled in the history of the world.

But though all these agencies have contributed largely to the development of modern society, it is certain they have not been of equal value and importance. Ships, railroads, and aircraft may be developed ever so highly and yet be limited as means of communication if they transport only men from place to place. Important as are the telephone, telegraph, and radio in the quick transmission of intelligence to and from all parts of the world, they are still restricted to communication between fixed points and a small number of individuals. Obviously some other agency in combination with these has been responsible for that wide distribution of human knowledge and intelligence that characterizes modern society and which has been responsible for its development. Some other means has been evolved to reproduce for thousands and millions of individuals the product of the world's great intellects and lay it regularly before all who want it. It is in the discovery and perfection of printing and paper that we find the essential element in all this marvelous development. Modern civilization, said Lord Avebury in addressing an international gathering of paper manufacturers, depends upon the discovery of cheap paper and rapid printing for the wide distribution of information.

This we may accept without demanding exhaustive proof, for it requires no stretch of the imagination to visualize the influence of printing on the wide dissemination of knowledge. By this means industrial, political, and economic information has spread with amazing rapidity. By it the intelligence of one nation has become the property of the whole race, and the intellect of a great leader has been able to influence the trend of thought of the entire world. In short, we may accept the press as the means of communication par excellence and proceed to examine one of its comparatively small but important branches, namely, the industrial press, that has just begun to sense and exercise its power.

Industrial publishing has reached its highest development in

¹ Presented before the Chicago Section of the American Chemical Society, November 18, 1921.

² Editor of *Chemical and Metallurgical Engineering*.

the United States, where over 1200 periodicals are now devoted to industry in all its phases. The growth of this great publishing business has been coincident with the industrial expansion of the country itself. The first industrial paper of which we have record in this country was founded in 1846. In the next decade two more were established, but no great impetus was given to the business until after the Civil War when the country went through its marvelous period of growth and development. Industries of all kinds invited leadership, and industrial magazines sprang up to point the way. The result was that from one paper in 1846, three in 1856, and 25 in 1869, the number grew to 800 by the end of the century and to well over 1200 at the present time. Including Canada, it is estimated that there are in America between 1200 and 1400 industrial publications, the number varying with the method of classification.

An important group of the industrial press comprises what are known as technical papers because they deal with the technology of industry, with the application of science and engineering principles to the problems of production and management. It is in this group that you, as chemists, are most interested; and since both you and I have a still narrower interest in technical magazines devoted to the chemical industry we may confine further observations to papers of that class.

THE TECHNICAL PAPER OF THE EARLIER DAY

My topic, "The Technical Paper and Its New Relation to Industry," suggests a contrast with an earlier relation, and so we may go back for a moment and sketch that former relation briefly so as to emphasize the new order that must be expanded and developed if the technical paper is to live up to its opportunity for service and leadership.

Technical papers for the chemical and allied industries are of comparatively recent development in this country, but if we examine the early files of such papers we will find that they were devoted almost strictly to matters of technical interest. They recorded the results of scientific research and investigation and of progress in the arts. Processes and products were discussed in their scientific and technical aspects. The contributions were of a high order of merit, and the contributors were recognized scientists of learning and ability. On the whole the publication was maintained on a high plane of scholarship and was a credit to the profession. Its reliability and integrity were above reproach and its subscribers bore testimony to its value and influence in all technical matters. It was a tool of the profession rather than of the industry.

The *raison d'être* for such a magazine is not far to seek. It was a product of its time and it served its purpose well. Technical industries were in a state of rapid evolution, and the latest developments in technology were of primary importance. It was essential that the scientific foundation of industry be carefully laid in order that the superstructure might endure. In short, industry being more interested in, and most in need of, technical leadership and guidance, the function of the technical paper was plainly to serve along these lines.

THE NEW RESPONSIBILITIES OF THE TECHNICAL PRESS

But excellent as this service was, and adequate though it proved for its time, it will not suffice to-day. New elements have entered into our national industrial life and, by presenting new problems to industry, have at the same time laid new and additional responsibilities on the technical paper. It is no longer enough for it to treat of technology; it must consider the business and economic problems of industry as well. The tech-

nical paper can no longer fulfil its function if it merely discusses processes and products; it must also be the business exponent and mouthpiece of its industry, reflecting its needs and guarding its interests. It must become an integral part of its industry, serving all its needs. It must be of the industry as well as for it.

The perception of this new responsibility was quickened during and immediately after the war, when we faced industrial and economic problems that far transcended in importance the problems of technology. The Government itself was confronted with industrial problems of the greatest magnitude, and as a result of the war was involved in the most intimate relations with business and industry. There was the greatest need for some public agency to reflect the needs of industry to the Government and to interpret the intentions and acts of the Government to industry. In this condition industry found itself without a mouthpiece or exponent unless the technical press threw itself into the breach, which it promptly did.

Washington became a great center for technical and industrial news, requiring the closest daily contact on the part of the business press; and as a consequence of the early recognition of this fact, industry was served with pertinent government news through its technical papers.

The necessity for this arose mainly from the fact that the daily press in all its excellence was not equipped to meet the need. It was not and could not be intimately familiar with the details of industry, and consequently could not sense its needs. The whole country was face to face with a brand new crop of problems, and since industry had learned to follow its own technical papers in matters of science and technology it naturally turned to the same source for leadership in these new conditions. The technical paper promptly sensed and accepted the situation. It became a magazine of opinion on labor problems, on the tariff, on wages, on the cost of living, foreign trade, government policies, the patent system, revenue legislation and finance, and many other matters formerly regarded outside its editorial scope. It discussed industrial waste in all its forms; the necessity for better cost accounting, for greater safety in industry, for improved housing and sanitation, for more skilful management, for more research. It expressed its opinion on the regulation of business by the Federal Trade Commission and the Interstate Commerce Commission. It took up industrial relations between employer and employee and devoted much space to the numerous phases of that many-sided subject. It spoke with authority and competence on such matters as reorganization of government departments because some of its editors had been drafted from government service and knew whereof they spoke.

These things were invaluable because they reflected to the industry the opinions of men familiar with the industry itself and sympathetic with its needs. Speaking from a chemical point of view, it was not enough to discuss the technology of the industry; somebody had to present the economics as well. For example, coincident with the technical problem of fixing nitrogen was the question of government ownership and operation of nitrate plants and its effect on business. Of quite as much importance as how to make dyes was the question of establishing an industry in the face of foreign competition. The tariff was a paramount issue. We had the brains for dyemaking, but we needed the economic basis for an industry without which our technical brains would avail us nothing. The alcohol industry likewise was, and is, much more concerned with fanatical legislation than with methods of manufacture. All of these things were consistently presented in the technical press for the benefit of industry and the education of government officials.

In the matter of new developments there was the constant necessity of keeping the economic and industrial as well as the technical aspect clearly in mind. For this reason the technical

press has brought to industry vital statistics on consumption and production, on imports and exports. It has shown the close relation of plant location to industrial success. It has featured the importance of markets for new products and sources for raw materials. It has acquainted industry with pertinent activities of the Government, sometimes approving and sometimes condemning.

In its relation to the Government the technical paper has been constructive and helpful. Witness its service since the war in aiding in the disposal of surplus property; in suggesting new uses for materials held in large quantities by government departments; in discussing the function of the Government in research; in advocating reform in the Patent Office; in supporting the Chemical Warfare Service and creating public sentiment that resulted in establishing this branch of the service on a scale somewhat commensurate with its importance.

Probably the greatest stimulus to this new function of the technical press as an intermediary or connecting link between the Government and industry was the action of Mr. Hoover in inviting the editors of the business press of the country to assist him in solving many of the problems with which he was confronted in the Department of Commerce. This was at once the greatest recognition of the importance of the industrial press and a challenge to prove its usefulness by showing its intimate knowledge of industrial matters. What body of men in the country should be better able to reflect to the Government the needs of industry, and carry to industry the story of the Government's intention to aid and assist rather than hamper and restrict? So argued Mr. Hoover, and accordingly the memorable Hoover editorial conferences began in Washington last spring and have become a monthly event. They have resulted in laying before the Secretary of Commerce plans for elimination of waste, for standardization of sizes, types, and styles of industrial products, for correlating the bureaus and agencies in his department and making them function more directly for the benefit of industry. They have resulted in the first effort ever made in this country to publish monthly vital statistics on consumption, production, and stocks of critical commodities in the basic industries. Finally they have been helpful in the reorganization of the Department of Commerce by finding men from the industries to head the new commodity divisions that have been created. And all of these things, mark you, have been done by technical industrial papers that formerly devoted themselves wholly to matters of science and technology, because they have seen clearly the need of this new service to their respective industries. Much of the best work has been done quietly through committees, questionnaires, and researches, but it has been none the less effective. Mr. Hoover has generously recognized the value of this service in a message to the editors, in which he said in part:

The editors of the business press have shown a fine spirit of service. Your opportunity for leadership is unique and unchallenged. Upon you rests in large measure the responsibility of the control of industrial thought and opinion in the detail of the industrial, economic and technical problems which confront us.

LIMITATIONS OF THE DAILY PRESS

I have mentioned the inadequacy of the daily press in presenting to industry such matters as have just been discussed. They are essentially technical and hence not within the grasp or province of the daily newspaper. They will not be adequately presented for business and industry except through the medium of the industrial press. This is no reflection on the daily press but merely a recognition of its limitations and the consequent need for the industrial press. We may consider a few examples.

As an industrial disaster the explosion of the nitrate plant at Oppau, Germany, was of such magnitude as to interest the entire world. And because of its marvelous mechanism for

transmitting intelligence, the daily press gave us immediate reports of the occurrence. But the explosion had a far greater and deeper significance to chemical industry, and in all its attempts to give precise information that might be helpful the daily press failed utterly, as a result of its manifest limitations. Not only did it fail as a purveyor of precise, accurate, and reliable technical news of the event, but it exemplified the blind as leaders of the blind in its editorial comment. So great a newspaper as the *New York Times* drew the conclusion that German chemists had been experimenting with new and deadly gases, in violation of the terms of the treaty, and had wrought their own destruction through their discoveries. It called upon the Badische Company to show clean hands in the matter, and it looked frankly with suspicion on the whole affair. Mystery surrounded the explosion and consequently mysterious conclusions were drawn as to its cause and significance. The press dispatches having said that the disaster was due to "the decomposition and subsequent explosion of a large quantity of ammonia and sulfate of saltpeter," the *Times* suspected "experimenting of a secret nature," and thought it "not conceivable that the disaster at Oppau may have been due to covert experimenting by those chemists." All of which was of no help or consequence to the chemical industry, and it devolved upon the technical press through its enterprise and intelligence to inform the industry of the facts as nearly as they could be ascertained.

Another instance of the newspapers' inability to serve industry in technical matters is to be found in the attitude of the daily press toward the coal-tar industry. We may take as typical the editorial comment in the *Rocky Mountain News* of Denver, September 30, 1921, on "The West and the Coal-Tar Industry." The caption of the editorial immediately suggests a narrow sectional view of the proposed embargo on the importation of coal-tar products; and this is confirmed when we read later on that "if it can be shown that the fortified industry in time can reach out and make useful the coal deposits of Colorado, naturally Colorado would take more interest in the issue at Washington." No broad view of the coal-tar industry as a factor in national welfare. No conception of it in its relation to the other industries using dyes. No recognition of the fact that disarmament could proceed much more rapidly and taxes be reduced proportionately if the United States and all the nations each had a well-established coal-tar industry functioning in peace and guarding against war. Instead a small, sectional, wholly inadequate view of the matter. And yet the daily press regularly creates public opinion through pronouncements as incompetent as this.

Examples might be multiplied. Chemical warfare was first condemned in the daily press, and first supported by the technical paper. Reports of such conventions as President Wilson's first industrial conference and the recent unemployment conference were more reliable and pertinent in the industrial than in the daily press, for the reason that the latter was inclined to feature spectacular incidents and subordinate substantial accomplishments.

All of these things are in the nature of a service to industry and the public welfare now performed by the technical press. It is not spectacular, but far-reaching. It influences the intelligent leaders of industry to blaze the way to new reforms, initiate constructive policies, and establish sound principles and practices in industry.

This service to industry by the technical press is a leaven that eventually leavens the whole of society. Through the leadership of the technical magazine in its own industry, it spreads information and serves as a clearing house for new ideas that eventually are translated into economies for the benefit of society as a whole. The service to industry is direct, and to society indirect.

THE FUNCTIONS OF THE TECHNICAL PAPER

From this general portrayal of the activities of the modern technical paper we may proceed to summarize its functions in industry and study the mechanism through which they are performed.

1—The modern technical paper is still a magazine of information pertinent to the technology of the industry it serves. This is an important function that cannot be subordinated without jeopardizing industrial progress. Economies resulting in cheaper production must still be worked out through scientific research and the application of the results in the factory. But this is not service enough.

2—The modern technical paper also treats of the economics of its industry, informing its readers on the relation of finance, the tariff, and other legislation to business.

3—It is the newspaper of its industry, gathering weekly the items of personal and business intelligence on which its readers should be informed. Market movements and trade tendencies are reflected in reports gathered at first hand. Foreign as well as domestic news is obtained regularly by cable and wire.

4—The modern independent technical paper is a magazine of opinion—the mouthpiece of its industry. And herein lies one of the distinctive differences between it and the technical society magazine. The editorial independence of the industrial paper, its freedom from domination by any interest or allegiance to any group, makes it possible to adopt policies in the interest of the industry as a whole. Obviously this is denied to the society publication, which must serve primarily its own membership. Editorial opinion cannot be expressed with freedom on a wide variety of topics for the evident reason that the magazine must speak for the society. An independent industrial technical paper, on the other hand, labors under no such handicaps, being bound only to serve the best interests of its industry whether people agree with it or not. If subscribers do not like its policy they need not take the paper.

5—The modern technical paper sets a high standard of business ethics and practice in its industry. Both in its business and editorial departments it subscribes to a code of ethics that has been adopted by associations of business publishers and industrial editors. These standards are high and must be subscribed and adhered to by members of these associations.

The technical editor is pledged to consider first the interest of his subscriber. Truth and honesty must characterize his every activity. He is obligated to present the news of the industry free from personal bias and to determine the editorial contents of his paper independently of advertising considerations. The publisher also sets a high standard of business practice in the acceptance or rejection of advertising and in publicity regarding the character and extent of his circulation.

Periodical investigations are made to see that members are living up to these standards. This is one of the most powerful factors in making the technical paper a leader in its industry. With its own skirts clean it can consistently demand that its industry be free from unfair practices. Having adopted a high code of business ethics for itself it can, both by precept and example, urge similar action upon its industry. The adoption of a code of editorial ethics and business practice has been of the greatest benefit in establishing the independence of the technical paper.

The exercise of all these functions results in a service, first to industry and then to society, that makes the modern technical paper an essential element of industry. It was so regarded by the Government during the war; and it must be self-evident that in times of peace, publication of knowledge and intelligence is indispensable to the development of industrial literature. What, then, is the mechanism for exercising these functions? The answer is found in the editorial staff. And just as the technical paper's new relation to industry requires a broader service, so the modern editorial staff comprises a wider range of talent. In many respects it resembles a college faculty, being composed of men who are specialists in their respective branches of technology and industry. Papers covering the chemical and allied technical industries find it particularly necessary to have comparatively large staffs of qualified scientists, technologists, economists, and industrial experts. They are called upon to judge the competence of articles that form our technical literature. They are expected to reflect sound opinion on matters of public

policy in relation to their industries, and to take the lead in safe-guarding those industries from ill-advised legislation or private practice. They must display enterprise and initiative in discovering sources of news and information so that their industries may be kept abreast of developments. And it goes without saying that in addition to their ability they must be men of integrity with a keen sense of editorial ethics.

Nor can these things be accomplished without close personal contact with the industry itself. Travel by the editors is a *sine qua non* of successful industrial journalism. Conventions must be covered and reported in their essential features, for hundreds and thousands of men are unable to attend and must rely on the published record for their information. That this service is appreciated is attested by the correspondence following the publication of convention proceedings, asking for more detail or further information. Plants must be visited and processes described in order that textbook fundamentals may be amplified and brought up to date with practical details of current practice. In short, the modern technical paper cannot be edited from the desk, but it must show a familiarity with industry itself that is acquired only by personal contact. The consequence is that the industrial editor is enabled to see his industry as a whole and judge it impartially. This was strikingly exemplified at the last National Conference of Business Paper Editors in Chicago, when a résumé of conditions in ten basic industries was presented by as many editors of industrial magazines. These reviews were authoritative and could not have been pictured better, if as well, by industrial leaders themselves.

Such, then, is the new relation of the technical paper to industry, as seen by the technical editor. Such is the duty of the industrial and technical press, as well as its opportunity for service, as conceived by the publishers. It results in a service that is growing more and more expensive, but which yields results to industry that more than justify the publisher's outlay. No single industrial unit could afford to maintain for itself the service thus rendered to industry at large. It is a service that is destined to be expanded rather than contracted, just as industry itself becomes more complex and needs broader vision and leadership.

This evolution holds its lesson also for the individual. Just as the technical paper must supplement its technology with the economics and business of industry, so must the individual broaden his scope in order to find his greatest usefulness. Science will never develop its greatest usefulness to society as long as it is translated into technology only. It must find expression also in sociology, in economics, and in the management of industry. This will call for broader training and more diverse talents among scientists, some of whom will continue to enrich the records of research while others develop managerial ability or technical superiority or acquire skill in the practical application of economics and sociology. The ultimate aim—for the individual as well as for the industrial press—will be the perfection of our industrial processes, the elimination of waste, the stabilizing of labor and production, so that human happiness and standards of living may be increased. To such an end the modern technical paper is dedicated.

The Field for Chemists¹

By Wilder D. Bancroft

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Chemistry is the science which deals with all properties and all changes of matter that depend on the nature of the substances concerned. According to this definition,² which is broader than the usual one, chemistry is the fundamental and dominant science, which may account for its being the most fascinating one. Chemistry, as thus defined, may be interpreted to include all of what is known as physics except the law of gravitation, the laws of motion, and a few other abstract formulations. Everything else that gives life and interest to physics is chemistry by definition. Our friends, the physicists, look upon physics as the fundamental science because physics was a well-developed subject before there was any scientific chemistry worth mentioning. This method of reasoning is natural but not necessarily sound. As children we were told that great oaks from little acorns grow. This is true but not the whole truth. If we have only the acorn, it is, of course, the important thing; but, later, one sees that the acorn is merely an interesting subdivision or product of the oak.

Engineering is largely applied chemistry. If it were not for the specific properties of iron, copper, concrete, brick, and all the other materials of engineering, there would be no such subject as engineering, which, speaking broadly, is the art of making the structural properties of matter available to man.

In the biology of the present and the future, we are interested in the chemical changes in the living organisms due to heredity and environment. Growth is a chemical change and the internal and external structures are the result of a series of chemical changes. After the first stages of identification, enumeration, and classification have been passed, the interests of the biologists are largely chemical, and the closer the contact with chemistry

the better the results. This has been shown very clearly in the brilliant work of Loeb and his pupils; and Clowes has made it clear that Loeb's results as to the antagonistic action of sodium and calcium salts on protoplasm can be duplicated in a remarkable way with oil and water emulsions.

In curative medicine we are dealing largely with the action of drugs. In preventive medicine we are dealing largely with inoculations, diet, exercise, and fresh air. In the first case we are checking and eliminating an abnormal chemical process, sickness, by the action of one set of chemicals on the system. In the second case we are preventing the occurrence of a disturbing chemical process, sickness, by the action of another set of chemicals on the system. Owing to the difficulties involved and to the number of variables concerned, our knowledge of the chemistry of medicine is not yet what it should be; but it is clear that real progress will be made just in so far as we study physiology and medicine as subdivisions of chemistry.

Geology is the study of the chemistry of the earth, and agriculture is clearly a subdivision of chemistry. The fertility of the soil and the growing of crops are chemical problems in spite of the fact that they have been studied empirically for centuries.

Professor Stieglitz of the University of Chicago has said that chemistry makes possible the scientific control of such widely divergent industries as agriculture and steel manufacturing.

It governs the transformation of the salts, minerals, and humus of our fields and the components of the air into corn, wheat, cotton, and the innumerable other products of the soil; it governs no less the transformation of crude ores into steel and alloys which may be given practically any conceivable quality of hardness, elasticity, toughness, or strength. Exactly the same thing may be said of the hundreds of national activities that lie between the two extremes of agriculture and steel manufacture. Moreover, the domain of the science of the transfor-

¹ Prepared January 1921. Received November 7, 1921.

² *Science*, [2] 27 (1908), 979.

mation of matter includes even life itself as its loftiest phase. From our birth to our return to dust, the laws of chemistry are the controlling laws of life, health, disease, and death. The ever clearer recognition of this relation is the strongest force that is raising medicine from the uncertain realm of an art to the safer sphere of an exact science. To many scientific minds it has even become evident that those most wonderful facts of life, heredity and character, must find their final explanation in the chemical composition of the components of life-producing, germinal protoplasm; mere form and shape are no longer supreme, but are relegated to their proper place as the housing only of the living matter which functions chemically.

RESEARCH PROBLEMS IN PURE CHEMISTRY

The student who wishes to take up research work either in pure or applied chemistry can find innumerable problems in every field and of any degree of complexity and importance, from work that can be done by an undergraduate to work that no one sees how to do at present. No matter where we turn, we find that we have only touched the fringe of the subject. A few illustrations may be helpful. To those in the Chemical Warfare Service, the war brought out clearly the meagerness of our knowledge even in regard to the simplest organic compounds. It would be quite impossible to-day to write a satisfactory monograph showing the reversible equilibria between the compounds of carbon, hydrogen, and oxygen, even if we limited ourselves to compounds containing not over three atoms of carbon to the molecule. If we went as high as compounds containing six atoms of carbon, our monograph would consist chiefly of gaps.

The whole problem of chemical affinity as applied to organic compounds is in a very rudimentary state, and while we are accumulating data in regard to free energy, our progress is very slow. The Periodic Law is still very much of a mystery to us and we do not know why a consideration of the atomic numbers removes some of our troubles. We know a good many facts about catalysis in general and contact catalysis in particular; but we have no adequate theory on the subject, though the poisoning of catalytic agents is not the mystery it once was. While several books and innumerable articles have been written on the subject of indicators in quantitative analysis; nobody has collected the facts that the analyst really wants.

When it comes to color, we speak learnedly of chromophoric groups; but we do not know why anhydrous copper sulfate is colorless, why a solution of copper sulfate in glycerol is green, or why the absorption spectrum of a concentrated copper bromide solution is very closely the sum of the absorption spectra of a copper sulfate solution and liquid bromine.

The organic chemist finds an enormous amount of scientific work still to be done in connection with the synthesis of dyes. The whole field of chemotherapy is just opening up. The problem of plant synthesis has scarcely been touched. We can make in the laboratory many of the substances which the plant makes. Some of them, such as alizarin and indigo, we can make more cheaply than the plant can and of a higher degree of purity; but we cannot make any of them in the way the plant does. The plant does not use reverse coolers or sealed tubes; it does not boil with sulfuric acid or fuse with caustic potash; it has not metallic sodium and chlorine gas for reagents. The reagents on which the plant can draw are air, water, and a few mineral salts. With these and under the influence of heat, light, difference of electrical potential, and enzymes, the living protoplasm manufactures its product.

While the general theory of photochemistry is quite simple—that light tends to eliminate the substances which absorb it—our knowledge of the chemistry involved is so limited that we cannot actually treat photochemistry scientifically. We have made no progress in the direct utilization of the sun's rays and, while we think we know something about the conditions for chemiluminescence, we cannot produce cold light even though the firefly has shown us that it can be done.

TECHNICAL PROBLEMS

On the more strictly technical side, the problems are so numerous that it will only be possible to indicate a few. If our present civilization is to pull through, the scientific man must speed up production of crops and goods so that the masses of the people can live decently. While everybody will have to help in this, the bulk of the strain will come on the chemist and he must be prepared to meet it. We appreciate already the importance of nitrogen fixation and of getting potash from feldspar. The whole question of the better utilization of our petroleum resources is a vital one. Fortunately this has been realized by the oil producers and consumers, and Dr. Van H. Manning, formerly Director of the United States Bureau of Mines, has been appointed Director of Research of the American Petroleum Institute, which means that this work will be pushed as rapidly as possible. The American Institute of Baking is trying to improve the quality and keeping power of bread. The use of flotation processes has made it possible to work ore deposits which otherwise could not be handled profitably. The statement has been made that sixty million tons of ore are treated annually by these processes in the United States. While this is very gratifying, the development has been largely empirical so far, and we apparently have no realization as yet of the possible future applications of these processes.

When we consider ceramics, rubber and other plastics, paints, varnishes, leather, dyeing and printing, cellulose, cellulose nitrates and acetates, photography, etc., all subjects involving a large amount of colloid chemistry, we find that the industries concerned have a vast amount of empirical information as to what happens and know practically nothing about why it happens. The silicate industries are avowedly empirical and so is the dyeing industry. The rubber industry knows practically nothing about the theory of vulcanization, to take a single illustration. So far as can be learned the people in the cellulose nitrate industry do not even know how many cellulose nitrates there are or what their real properties are. The photographic industry has only empirical knowledge in regard to emulsions and has no adequate theory in regard to photographic developers. Nearly all of the tanneries in the country are run on an empirical basis. While many firms in these various industries have made a great deal of money, all our experience is that every increase in the scientific knowledge of a subject is followed sooner or later by an improvement in the technical processes, and it is certain that the industries in question will prove no exception in spite of the fact that each industry, which is run on an empirical basis, invariably believes that its case is exceptional. The recent work of Dr. Wilson on quebracho and gambier and on the analysis of tannin brings out clearly some of the important things which had been overlooked by the leather industry. All these industries will eventually be put on a sound scientific basis and this work will have to be done by chemists.

PRESENT POSITION OF THE CHEMIST

The general position of the chemist is better than it has ever been before. The war has brought to the public mind an appreciation of the importance of chemistry. Some of the universities have already put their professors of chemistry on a special basis and the others will have to follow suit if they hope to fill vacancies with good men. In most universities the pay of the younger members of the staffs has, very properly, increased more relatively than that of the full professors. There used to be very few research fellowships for men who had received their doctor's degree, but now we have the National Research Council Fellowships in Physics and Chemistry which are open only to applicants who have received the doctor's degree or its equivalent. Some of the universities have similar research fellowships. The du Pont Company is giving a number of unrestricted fellowships open to graduate students, and other companies are doing likewise though not to such an extent.

In the industries the Research Laboratory of the General Electric Company is the best known; but there are a number of other large ones, those of the Western Electric Company, the du Pont Company, the Eastman Kodak Company, the National Carbon Company, The Barrett Company, the National Aniline Company, the Goodrich Company, the Goodyear Company, the Brown Company, and the one of the General Electric Company at Nela Park being conspicuous instances. In addition very many companies are running smaller research labora-

tories. It looks also as though in the plants the ratio of chemists to engineers was going to increase considerably. Of course, the almost insane demand for chemists that prevailed at the end of the war has ceased and most companies are now discharging chemists as well as other technical men. When the present industrial depression is over, things will adjust themselves and we shall get on a normal basis. It looks now as though the next thirty years would be the period of the chemist just as the previous thirty years were the period of the engineer.

SOCIAL INDUSTRIAL RELATIONS

Charity

By H. W. Jordan

SYRACUSE, NEW YORK

We have just passed through the annual newspaper orgy of vicarious charity in behalf of each city's One Hundred Neediest Families. The lavish expenditure of printer's ink and other folk's money revealed little effort to prevent the return next Christmas of the same families, reinforced by new members and supplemented by other households attracted to the honey of newspaper readers' cash; each donation duly announced in the paper.

One hardship the war brought upon these Neediest Families was jobs. Although the managers of the professional charity organizations succeeded in holding their staffs intact, their clientele dwindled almost to the vanishing point. Plenty of work, lack of drink through prohibition, and diversion of public emotion to the soldiers and of public money to Liberty Bonds, nearly killed the vested interests of organized charity. We came near proving that "Poverty would cease if charity be stopped for a year."

Now that peace rages, the army of constitutionally needy are back in their city trenches. Their crushing cost of maintenance merits serious consideration. Syracuse and other cities have organized Community Chests to handle the collection of charity funds by an annual drive, followed by distribution of the money pro rata to each nice, certified charity.

COMMUNITY CHESTS HAVE A FAR GREATER MISSION THAN THAT OF HANDLING MONEY. They offer an opportunity of doing a splendid social industrial service by applying science through research upon charity, as science has been applied through research to industry. If chemists and engineers can secure appointments on the directing boards of Community Chests they will be able to undertake this sorely needed social study. But if Community Chest management be restricted to captains of finance, with little scientific thought and puny social imagination, who make the Chests mere money feed tanks, they will only aggravate pauperism.

CITY POVERTY IS A SOCIAL BY-PRODUCT OF MODERN INDUSTRY. Specialized employment, herding of people in rented quarters, feeding folks on factory cooked, paper packaged food, complete dependence upon wages or salary for a livelihood with no recourse to farms or villages for partial or temporary relief from unemployment, living conditions that promote tuberculosis, venereal disease and other crowd maladies; these and similar circumstances of city life that spring from modern industry, have forced 15 to 20 per cent of our people below the line of adequate, permanent self-support. Only in times of extremely abundant employment does the percentage fall to 10.

In a herd of livestock if 10 to 20 per cent yielded no milk or wool or eggs, and were unfit for meat, the owner would be

bankrupt. No farmer would permit his stock to sink to that low ebb, except through malignant disease or prolonged drought.

Yet industry which depends upon capable, contented labor to produce goods, and on normal thrifty people to consume them is confronted by a population of which one-fifth, on the average, has been surrounded by conditions beyond their individual control, which make them collectively a steadily increasing economic and social dead load; economic because if employed they are incompetent, and if idle they must be fed, clothed, and housed; social because every adult man and woman of them is a persistent voter.

This submerged fifth dominates city elections. They roll up huge metropolitan majorities in election of politicians who cater more and more to the selfish, emotional demands of the ignorant and unthinking. They elect men who vote huge sums in long term bonds for short-lived improvements; men who enact laws of momentary expediency designed to regulate and restrict engineering industry to the verge of bankruptcy.

When the chemical industry, the railroads, the telephone or electric power companies, or other enterprises of modern applied science seek legal enactments in harmony with economic and biological laws we are overruled by these legislators.

IN AN ARTICLE, "PHILANTHROPIC DOUBTS," IN LAST SEPTEMBER'S *Atlantic Monthly*, Mrs. Cornelia Cannon, wife of the distinguished biologist, Walter B. Cannon, discusses the more salient features of social charity. She sets forth the fact that charity does little more than wrap costly sterilized bandages around social cut fingers that would not have been cut if we had whittled away from us. She reaches the conclusion that charity is a practical failure because it is neither constructive, progressive nor preventive. It is merely static.

"Philanthropists belong to the class on which the injustices of our present basis of society have borne lightly," says Mrs. Cannon. "They serve unconsciously as a bulwark of the *status quo*, for whose defects they are ready and eager to apply palliatives. They are the great menders and patchers-up of society, not the surgeons who cut deep into the festering sore and scrape the bone. They express the tenderness and pity of man, not his reasoning intelligence. So long as we placate our intelligence and pacify our consciences by our philanthropies, we put off the day of attack on the sources of poverty."

She urges more effective citizenship of intellectual people, to the end that we root up the causes of poverty.

RURAL AND VILLAGE COMMUNITIES HAVE NO POVERTY OF THE SORT THAT BURDENS INDUSTRIAL CITIES. Modern industry has brought modern poverty. Highly specialized industry has stripped the individual of his resources of individuality, even to the extent that he no longer prepares his own food or shines his own shoes. His amusements have become passive and commercial. Eighteen thousand people sitting, watching eighteen men hired to play baseball, is the national game. Naturally, under these conditions, when life's burdens grow heavy, the individual with minor ambition lies down and lets the com-

munity lug his load. And the community competes for the job.

Psychological analysis of the drafted men showed about 15 per cent in Class D, Inferior Intelligence, and 10 per cent more in Class D—, Very Inferior Intelligence—25 per cent in all. These men and their sort, who were not worth shipping to France, are the people that charity fosters and rears. A statistician has figured that at the present rate of increase of the subnormal and the declining birthrate of the rest of us we will all be paupers, idiots, or insane in 267 years.

It is a vital necessity that the industries that arose from science applied to the mechanic arts by chemists and engineers shall undertake similar research to transform the parasitic 20 per cent into self-supporting people.

THE PROFITS OF NINETEENTH-CENTURY INDUSTRY came from exploitation of natural resources and from creation of huge, new industries by applied science—steel, automobiles, moving pictures, talking machines, dyes. All these enterprises were made successful by managers, staff, and workmen who had superior versatility and resourcefulness acquired on the farms and in the villages where they were raised. As these reservoirs of material and human resources are becoming exhausted, the profits of twentieth-century industry must come from correct social adjustment; from elimination of social waste, maintenance of cheap, abundant prime necessities of life—food, clothing, housing—and modernized primary and secondary education.

Unless these social factors be brought into and kept in harmony with economic and biological laws, industry and all thrifty people will be crushed by wages inflated by high cost of simple living, and by confiscatory taxation and legislation that is the legal expression of hostile public opinion of the majority, a majority made chiefly by the incompetent and charity classes, D and D—.

These jaws of the social industrial vise—high cost of living and confiscatory public opinion—are steadily closing in on the railroads, the telephones and upon all public utilities and industrial enterprises in which the savings and life insurance of thrifty people are invested. Unless these forces be diverted into constructive, economic, biological work we chemists and engineers, and indeed all intellectual people, will be smothered by the suffocating forces of mediocrity. It has already happened in Russia.

COMMUNITY CHESTS will be industrial coffins if they be used only to provide money for additional courses on the walls of the already too high reservoir of city poverty and social discontent. But if they supply administrative ability and adequate funds for social scientific research to disclose the causes of poverty and to set the subnormal fifth of our people at steady, productive work, they will be life-buoys for the thrifty and for industry. They offer an opportunity for chemists and engineers to undertake practical citizenship of the highest order.

PERKIN MEDAL AWARD

The sixteenth award of the Perkin Medal was made to Dr. William M. Burton, President of the Standard Oil Company of Indiana, at the meeting of the American Section of the Society of Chemical Industry, held in Rumford Hall, Chemists' Club, New York City, Friday evening, January 13, 1922.

The meeting was unique in that four past presidents of the Society, Drs. Chandler, Remsen, Nichols, and Bogert, were present on the platform. It had been expected that Dr. R. F. Ruttan of Toronto, the present head of the Society, with whom our American chemists became acquainted at the meeting in New York last September, would also be present at the meeting, but he was unable to attend.

In his introductory remarks, Mr. S. R. Church, Chairman of the Section, declared that "seldom if ever has the Perkin Medal Award attracted such widespread interest as has been aroused concerning the present event. In selecting the medalist from a great industry that is outside the narrow classification of chemical industries, the Medal Committee has once more demonstrated a catholic consideration of the problem, 'What constitutes a signal achievement in applied chemistry?'"

Dr. Ira Remsen dwelt on Dr. Burton as a student at Johns Hopkins. He emphasized the essentials of a successful career in chemistry or any other professional activity, as being fundamental knowledge, imagination, courage, patience, and skill. Dr. Remsen called attention to the point which was also stressed by Dr. Herty and Mr. Wiles, that in the case of Dr. Burton we have a chemist recognized as an executive. Dr. Remsen declared that more and more chemists are coming into executive positions, both in educational institutions and the industries, and urged that it is the duty of the chemist to enter into such activities.

Dr. Herty's sympathetic picture of the personality of Dr. Burton, Mr. Wiles' discussion of the future of the chemist in industry as seen by a patent attorney, and Dr. Burton's address of acceptance are printed herewith.

The medal was presented by Dr. Chas. F. Chandler, as Senior Past President of the Society, residing in this country. Dr.

Chandler recounted briefly Dr. Burton's industrial career. He became chemist with the Standard Oil Company at Cleveland, Ohio, in 1889, was transferred to the Standard Oil Company of Indiana in 1890, became assistant superintendent of the works in 1892, general superintendent in 1895, director in 1911, vice president in 1915, and president in 1918. Dr. Chandler dwelt particularly on the trip which he and Dr. Burton made to Germany in 1895, as representatives of the Standard Oil Company, to prevent adverse legislation on the part of the German government against American petroleum.

Dr. Burton received the Willard Gibbs Medal in 1918,¹ in recognition of his distinguished work in petroleum chemistry.



The Personal Side of Dr. Burton

By Chas. H. Herty

The charm of biography persists always. The results of a successful man's work are set forth in the public record, whether it be in the form of scientific publications, of official status, of some great engineering feat, of the size of his income tax, or what not. Back of the life accomplishment, however, is the personality of a human being who, following the bent of his own genius, has triumphed over the difficulties which beset us all.

What manner of man did it? That is the question which kindles a different kind of interest from that due to a knowledge of what the accomplishment is. For out of such studies of many types of men we gain here and there suggestions, self-applicable, which help us over our own rough spots and give us hope.

In the case of Dr. Burton, or "Billy," as he was lovingly called by us in student days at Johns Hopkins University, there is added another to the long list of successful men who were born

¹ THIS JOURNAL, 10 (1918), 483.

in the country and passed their early days entirely ignorant of cement sidewalks. What a pity we couldn't all have persuaded our parents to move out to the country before we were born. At any rate, it was Billy's good luck to enter the world under such favoring circumstances in the year 1865. In 1886 he graduated from Western Reserve University, receiving the A.B. degree. The next three years were spent at Johns Hopkins University, from which institution in 1889 he received the Ph.D. degree.

It is peculiarly fitting that the Perkin Medal should be awarded to him in this the first year of President Harding's administration, for right well does he represent the return to normalcy, all of his friends to whom I have written emphasizing the fact that from boyhood to the present time he has always been a normal individual. He has cultivated no particular hobby, considered by many to be an essential necessary to distinction, but has carried through life a love of experiment and an ardent zest for the lathe and mechanical tools. It is easy to understand, therefore, that in the environment in which he has worked he not only succeeded in cracking oil but carried the work on to a successful application on a large scale.

He plays no outdoor games, not even golf. This sounds abnormal, but to offset it he recently obtained keenest satisfaction in installing in his home under his personal direction a radiator system

at one-fifth the estimate furnished by a contractor, and who wouldn't rejoice at getting the best of a plumber? I insist he is normal.

To him the days of college life and associations are as full of meaning as ever and he wears still his college fraternity pin.

Steadily he has been advanced in that company with which he began work after completing his university training, until to-day he occupies the presidency.

Throughout this advancement he has remained the same sincere, sympathetic, level-headed man to whom his friends and associates come with their problems for his sound advice.

That he has worthily won this great honor from his associates in business all agree, that throughout it all he has preserved his unaffected selflessness all will rejoice; but there is another aspect of his success which deserves not only record here but wide heralding at this stage in the development of American chemical industries. The industry with which he is connected is one of our early and now thoroughly stabilized industries, and it is peculiarly worthy of note that the Standard Oil Company of Indiana has chosen for its chief executive a chemist. Not all chemists are qualified to be executives, but certainly our chemical industries will be placed on a much sounder basis when the chemist of proper qualifications is given opportunity to share in the determination of corporate policies. Billy Burton's record may yet prove the harbinger of a new day.

The Chemist in Industry

By Russell Wiles

The patent lawyer is in a peculiarly favorable position to obtain a bird's-eye view of industry as a whole and of the general tendencies of industrial development. No one is in such close touch with so many industries and certainly no one has had occasion to study the general progress of industry so carefully.

EPOCHS OF INDUSTRIAL PROGRESS

Industrial progress might be divided into epochs almost as distinct from each other as the paleolithic and the neolithic ages and, like those ages, overlapping each other. The first great stride toward modern industry was the steam engine. To it, for many years, inventors have given their best efforts, but so far as great progress in this field is concerned nothing has been done for years.

The steam engine having supplied power, there followed an immense development of power-driven machinery of all sorts, resulting in the production of old articles at lower prices and countless new articles which it would not have paid to make by old methods. While new machines are still being made, very little of a novel or fundamental character has been done for many years. The principles of machine design are well understood, and it is the commonly accepted belief that an auto-

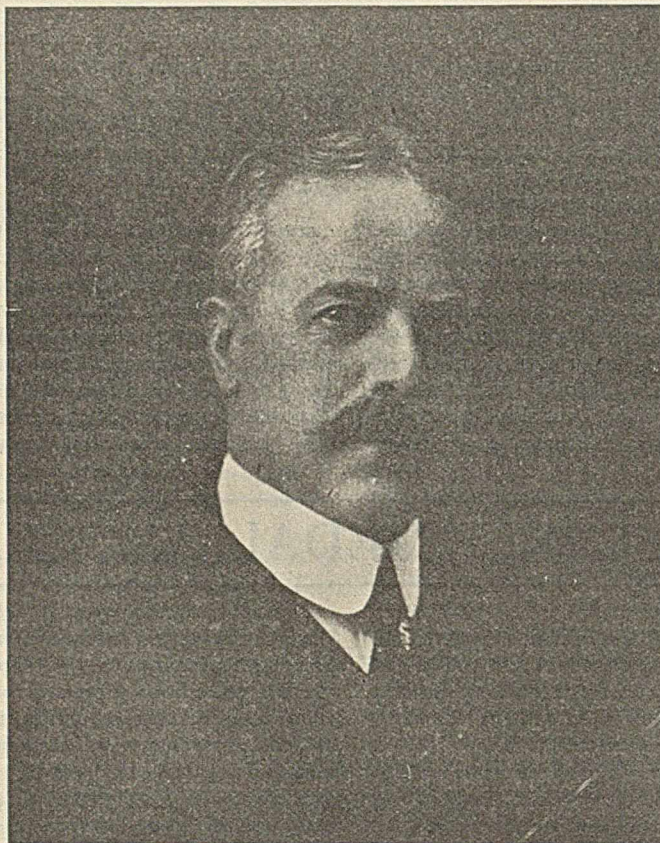
matic machine can be made, which will do anything desired, providing the demand for its product is sufficiently great to justify machine manufacture.

For the last half century the most conspicuous inventions have been those of the electrician. He has given us the telephone, the telegraph, the dynamo, the motor, the electric light, and countless minor conveniences, the aggregate effect of which has been to revolutionize society. The work of the electrician has not ceased, but the fundamental principles of electricity are quite thoroughly developed and, in the main, progress will probably follow lines which are to-day generally predictable.

Of recent years the development of the internal combustion engine has provided us with many hitherto unknown luxuries, conveniences, and necessities.

THE PLACE OF THE CHEMIST

It is only, however, in the last few years that the chemist has begun to take his proper place in industrial development. Great chemical discoveries have been made in the past. Much has been done in chemistry as a pure science, but it is within comparatively recent years that the chemist has emerged from his laboratory and that industry, as a whole, has felt the need of close coöperation with him. Where, ten years ago, big practical applications of chemistry were rare or confined to a few specialized industries, to-day nearly every progressive plant is regularly employing chemical assistance in one form or another, and



WILLIAM M. BURTON

there is scarcely an industry which has not been more or less affected by the progress of chemical science. Chemical inventions, at least as exemplified in my own practice, are at least ten times as numerous as they were a decade ago.

The work of Dr. Burton may well be regarded as an early example of the great things the chemist is to accomplish in the future, rather than as an achievement which is to be unique in history. The epoch-making inventions of the future will probably be those of the chemist and physicist. It is hard, indeed, in this day of physical chemistry and molecular physics to say where one science begins and the other leaves off. Perhaps it is in the border region common to both that we may look for the most startling discoveries.

The chemist is to-day not only giving us fresh supplies of old products, usually in better and purer form than we had before, and at lower prices, but he is giving us new compounds of every conceivable character with which to rebuild our general industrial structure. The time is not far distant when no engineering undertaking will be complete until the chemist has been consulted to ascertain if the structural materials are the best that can be obtained for the specific purpose. It will be as much the duty of the engineer of the future to build out of the right materials, whether synthetic or otherwise, as to build the right size and shape. The arts are to have available for their use not a few dozen basic materials of which everything must be built but thousands of materials, each having special points of advantage for certain particular uses, and chemical processes are sure to replace many complex mechanical ones. The chemist will revolutionize industry, not once but dozens of times. Indeed, it may well be questioned how long the name of your Society will remain distinctive. I expect to see the day when all industry will be more or less chemical industry.

That the oil industry, as particularly exemplified by the Standard Oil Company of Indiana, has been perhaps the first big established industry to be thoroughly overturned by the work of the chemist, is partly fortuitous—partly due to the remarkable ability of him whom we gather to honor to-night, and partly due to the remarkable organization which he has built up.

It was the discovery of the evil-smelling sulfur-bearing oil in Ohio which forced the chemist into the oil business. Dr. Burton was one of the very first thoroughly trained chemists in the oil industry. His solid groundwork in pure science had been acquired under Dr. Ira Remsen, who, perhaps more than any one else, is responsible for what the American chemist is to-day. Bringing a thoroughly scientific point of view and applying to his problems the methods of pure science, with his great natural ability and indefatigable industry, it was entirely unavoidable that Dr. Burton should profoundly affect the industry in one way if not in another. No man has ever had a more promising field—an enormous industry dealing with problems which ought to be handled in an essentially chemical manner and having no chemists at all. Dr. Burton would be the first to recognize his splendid opportunity, and it is characteristic of him that his opportunity never was neglected.

ORGANIZATION OF STAFF OF STANDARD OIL COMPANY OF INDIANA

But Dr. Burton alone never could have accomplished what has been done by the Standard Oil Company of Indiana. There has been much discussion in big corporations as to the best method of correlating the scientific force with the manufacturing force. All sorts of experiments have been attempted and all sorts of systems have been devised. The system worked out by the Standard Oil Company of Indiana, largely at the instigation of Dr. Burton, and of recent years under his guidance, is unique and amazingly successful. None but a scientifically trained man would have dreamed of such a system, and the operations of the Indiana Company are the best demonstration of the industrial value of scientific training.

The system is founded on the premise that a scientifically trained man is a good man for any job; the scientific staff does not cooperate with the manufacturing staff—it has become the manufacturing staff. The practice, so far as concerns chemists, has been to take on trained men for the laboratory force precisely as in many other plants. After brief association with the laboratory, during which the newcomer can become familiar with the peculiar problems of the works and particularly of some special department to whose problems he is assigned, he leaves the laboratory and goes into the works in some subordinate capacity. It then becomes his prime duty to test, on a practical scale, whatever improvements may fall within the sphere of his department. Having once become established in the works, it has been found that almost without exception the scientific men become excellent executives and their promotion is rapid.

The result is that the manufacturing department of the Company not only maintains an excellent research department, but that the whole manufacturing organization from top to bottom is largely dominated and controlled by men of scientific training. The Standard Oil Company of Indiana is unique in this regard and the tremendous success of its manufacturing department must be very largely attributed to the superb organization which Dr. Burton conceived and has built.

The system has been worked out to the fullest extent at the largest plant of the Company. Let it not be understood that the chemists are the only men of scientific training in the organization. There are more chemists here in executive positions than in any other industry of which I am aware, but along with them are a considerable number of engineers holding equally important positions, and whose cooperation on many problems is vitally necessary. We have become accustomed to finding engineers in executive positions; the Standard Oil Company of Indiana is unique in the number of chemists similarly employed. And it is unique, too, in the almost complete control of its manufacturing department by men of scientific college training. A brief survey of the personnel of the Company is extremely illuminating and is one complete answer to the problem of the relation of the scientific man to industry. Of the men I am about to enumerate, the majority hold a doctor's degree, and, those who do not, have had undergraduate training of an extremely thorough character in science or have the training of engineers.

The scientists in the Indiana Company include the president, another director, the general manager of western plants and his assistant, the superintendent, assistant superintendent, refinery superintendent, paraffin works superintendent, assistant superintendent of acid works, and head chemists, all of Whiting, the head of the department of service to licensees, in addition to the usual corps of research men in the laboratory. With such an organization no problem in applied chemistry seems difficult. There is scarcely a man on the manufacturing staff who is not personally capable of solving any ordinary chemical problem, of clearly understanding and passing judgment on any chemical processes submitted, or of putting any ordinary chemical process into practical operation.

Dr. Burton must be given the credit for evolving this system and developing this organization. He has proved by the acid test of practice that the scientifically trained chemist is not only a good theorist but nine times out of ten a first-class executive, and that as an executive he is supremely successful, because of the accuracy with which he can predict results and the speed and directness with which he attains them. This work of Dr. Burton ranks high in importance beside the creation of the process which bears his name.

* * *

In extending to William M. Burton this highest honor in your power, you honor one who has brought honor and credit to your profession, a scientist of scholarly ideals and high attain-

ments, an organizer of broad vision and confident faith in the future, an efficient and successful executive and, perhaps, greatest of all, a leader of men. Dr. Burton asks nothing of his men which he is not capable of doing himself. His greatest tribute, greater far than any award for scientific attainments, is the affectionate regard of those with whom he has worked for so many years and who know him best. Our greatest rewards are not degrees or diplomas, medals or decorations, but the esteem and affection of our associates. These Dr. Burton has long had in abundant measure.

But in honoring him you celebrate a great achievement of your own great profession. May this be only one of a host of like achievements which you have reason to recognize. May these awards, from year to year, mark equally great gifts to human knowledge and human comfort. The day of the chemist is here. You hold the future of industry.

Address of Acceptance

By William M. Burton

The work done under my direction which has perhaps attracted the most attention was carried on principally in the laboratory and refinery of the Standard Oil Company at Whiting, Indiana, and consisted in devising ways and means for the practical conversion of high-boiling fractions of petroleum into low-boiling fractions in such a way as to insure substantial yields of suitable products with a minimum loss and at a reasonable expense.

The problem became imperative with the advent of the internal combustion engine about fifteen years ago. The most commonly known example of such an engine is, of course, the automobile which, as constructed to-day, requires a fuel that evaporates at comparatively low temperatures, has a high heat value expressed in British thermal units, burns without leaving objectionable residues, does not possess an objectionable odor, is low priced, and can be produced in large quantities. Benzene, toluene, and alcohol are fairly well suited for the purpose, but their cost and their small volume of production render them largely unavailable.

The low-boiling fractions of petroleum naturally come into use for this purpose and up to about 1910 the supply of this fuel was sufficient to meet the demand. In fact, the automobile provided an outlet for the sale of these products which, to some extent, had been a drug on the market in the oil world. The older refiners in the country will remember when these so-called naphtha products were thrown away and allowed to run down the streams adjacent to the refineries, thereby causing a wilful waste and a fire menace to the surrounding neighborhood.

Prior to 1910 the average yield of naphtha or gasoline products from crude oil in the United States was about eleven per cent, this yield representing only the amount of such products (of the quality desired at that time) normally present in the crude petroleum, their separation being secured by ordinary methods of distillation at atmospheric pressure; and, further, this small yield was sufficient to furnish all that was needed for gasoline stoves and other industrial purposes prior to the advent of the internal combustion engine for transportation purposes.

When the automobile came into general use, however, it was perfectly clear that the normal yield of naphtha products suitable for fuel in self-propelled vehicles would not be nearly enough. At that time our refineries were selling about forty per cent of the products of crude oil for use as fuel and for gas-making purposes in lieu of coal. The remaining sixty per cent represented the normal yield of naphtha and gasoline, illuminating and lubricating oils.

The above-mentioned forty per cent fuel and gas oil comprised fractions boiling between 225° and 375° C. These oils

could, if necessary, be withdrawn from the market, and our problem was to convert them so far as possible into fractions boiling between 40° and 200° C., the product to be equal in quality to normal naphtha products and the yield and operating expense to be commercially practicable.

EARLY EXPERIMENTS

Our first experiments were directed toward making a suitable product by superheating the high-boiling vapors as such, but without pressure, somewhat along the practice observed in making Pintsch gas. We soon found, however, that this so-called "cracking" in the vapor phase required a temperature so high that the aliphatic hydrocarbons contained in the petroleum were largely converted into cyclic and aromatic bodies and fixed gases, unsuited for our purpose. The yield was poor and the quality most undesirable. Obviously our problem included the proposition of reducing the molecular weight without changing the general structure.

We next tried the use of various reagents and catalyzers, such as aluminium chloride and ferric oxide. Anhydrous aluminium chloride, indeed, produced some rather remarkable results. The yield and quality of naphtha products were fairly satisfactory but there was a substantial loss of oil in the operations, and the first cost of the anhydrous aluminium chloride, as well as the difficulty in recovering it from the residues, rendered this plan unattractive.

Nearly thirty years ago Sir Boverton Redwood and Professor Dewar in England patented a pressure distilling process for the purpose of increasing the yield of kerosene oil from the residues of Russian crude petroleum, but it never was applied industrially. It has been known, therefore, for some years that distilling petroleum under pressure served to break down the high-boiling fractions into low-boiling fractions but, as far as we could learn, no one had ever done it on the large scale and, in fact, such a proposition could not commend itself to a practical refiner because of the obvious dangers from explosions and fires.

But having tried everything else that suggested itself, we attacked the problem of distilling petroleum in considerable quantities (8000 to 12,000 gallons) under pressure of about five atmospheres. Our first still was of a welded design and was planned to handle 100 gallons of the high-boiling fractions. Obviously, the raw material first to be tried consisted of the so-called fuel oil, or reduced crude, meaning the residue of crude oil after the more valuable products had been removed. We soon found that we could not work profitably with this product; when distilled with or without pressure it produced quantities of coke that deposited on the bottom of the still and caused a red-hot bottom that would not stand any rise in pressure. The next proposition comprised the use of high-boiling distillates from the crude, *viz.*, oils boiling from 225° C. upwards. We distilled these distillates at a pressure of about five atmospheres and were thereby able to hold down the temperature to a moderate figure, the cracking being done in the so-called liquid phase. We found to our intense gratification that the low-boiling fractions produced belonged mostly to the paraffin series, which were easily deodorized and finished into products suitable for sale. Further, the yield of salable liquid was good and the production of fixed gases and coke was small.

LARGE-SCALE DEVELOPMENT

Experimentally, therefore, our work was successful. But the big problem remained to be solved. Could we build large equipment that would, in a practical way, secure the desired results and at the same time be durable and reasonably free from the fire hazard that always attends operations in an oil refinery? Some of our practical men said we could, but more of them said we couldn't. In this case, however, the majority was overruled and we immediately prepared plans and specifications for a

still eight feet in diameter and twenty feet long, built of one-half inch mild steel plate, which would charge 6000 gallons of raw material. It had a safety factor of 5, the working pressure to be 100 pounds and the bursting pressure 500 pounds.

The still was built and charged, with many misgivings on the part of the doubters, but with boldness and confidence exhibited by the rest of us. So soon as we had the still hot and pressure began to develop, we encountered our first difficulty. The still was built in a workmanlike manner and would have made a good steam boiler, but rivets and seams leaked badly under oil pressure where they would not under steam pressure. It was difficult to induce boilermakers to calk the leaks while the still was hot and under pressure, but we found men bold enough to do it, and the first run was sufficiently encouraging to induce us to proceed further. But the leaks persisted until Nature came to our aid and the minute portions of oil in the leaks gradually carbonized, they closed without our aid.

The experiments with the large still proved our results with the small one, *viz.*, the yield of suitable gasoline fractions was good; the loss was trifling; the cost was reasonable, and the fire hazard under close caution and supervision was not excessive. Further, we were astonished to find that the residue remaining in the still contained substantial quantities of asphaltine actually created (from a distillate containing none of it) by distillation under pressure.

We learned early in the work that operating at moderate pressure required a substantial dephlegmating system that would return to the still fractions boiling too high for our purpose, and allow the others to pass on.

A suitable safety valve that would operate properly with oil vapors at high temperature had to be devised. After making a number of runs with our 8 × 20 still, and in view of the fact that the demand for gasoline was increasing at a rapid rate, we asked for an appropriation of one million dollars to build sixty pressure stills eight feet in diameter and thirty feet long, each charging 8000 gallons of raw material. Considerable argument was required to convince any of our directors that such a revolutionary proposition could possibly be successful, but finally they voted in favor of it, and we went ahead.

It would require much more time than I have at my disposal this evening to give a full account of the minor difficulties that arose. We had solved the big points, but there were many smaller ones. For successful results we must operate with the oil at temperatures from 370° to 400° C. in the still. At 450° C. steel begins to lose its tensile strength and its capacity to withstand pressure. It is clear, therefore, that with this narrow margin great caution must be exercised to prevent overheating. The human element enters here, as it does in every feature of pressure-still operation, but we operated over eight years with hundreds of these stills in daily use, and manufactured millions of barrels of gasoline by this method before we had a fatal accident.

THE PRESSURE-STILL INDUSTRY TO-DAY

From the humble beginning of the 100-gallon still in our experimental laboratory, the Standard Oil Company of Indiana has in operation to-day over eight hundred pressure stills having a gross charging capacity of eight million gallons, and licensees under our patents are operating as many more, giving a daily production of two million gallons of gasoline out of about twelve and a half million gallons total daily output in the United States and Canada.

This amount of gasoline makes possible the use of two millions of motor vehicles more than could otherwise have been supplied from a given consumption of crude petroleum, and as a corollary of that proposition, and assuming 20 per cent of gasoline as a normal average yield from crude oil, the pressure-still process is conserving for future consumption an amount of crude oil nearly equal to one hundred million barrels per year.

The consumption of gasoline by internal combustion engines during the past decade has increased at a terrific rate. In 1910 the United States consumed approximately seven hundred million gallons, while for 1920 the Bureau of Mines statistics show a total gasoline production of four billion six hundred million gallons, of which eight hundred and fifty millions were made from natural gas, something over three billion gallons made by straight crude oil distillation, and seven hundred and fifty million gallons made by the cracking process. Further, statistics show that while the increase in crude oil production during the past decade has been one hundred and forty-two per cent, the increase in gasoline production has been over seven hundred per cent, and although some of this gasoline has been exported, the larger portion has been consumed by the ever-increasing number of automotive vehicles in this country.

The increase in production of crude oil has not been commensurate with the increased demand for its products, and the pressure-still process has filled at least part of the gap. Naturally, one is inclined to speculate on what the future will be regarding an adequate supply of these important commodities. One suggestion would be that some of the large amounts of oil now being used for fuel and gas-making purposes be replaced with coal, and substantial portions of the oil used for making gasoline, the coal consumption, in turn, to be replaced in part by the further development of hydroelectric power.

The American people are notoriously wasteful in the use of natural resources with which they are so richly endowed. It is hoped the work outlined above will be considered a slight contribution toward the curtailment of such waste.

It would be obviously unfair and unjust to close this paper without duly acknowledging the work done by my associates in successfully establishing the pressure-still process. Our patent attorneys, represented by Mr. Russell Wiles, contributed many useful and practical suggestions, and if it had not been for the invaluable assistance of Dr. R. E. Humphreys, Mr. E. M. Clark, Mr. T. S. Cooke, and many others connected with the Standard Oil Company of Indiana, satisfactory results would never have been secured.

A new color card showing dyes for cotton has been issued by the National Aniline & Chemical Co., Inc., which embodies several new and useful features. For the first time there has been produced a table of dyeings and tabulations explaining the fastness properties of each one of the dyes included, with the information given in easily understood language instead of being indexed and indicated by numerals. The tabulations explain such conditions as fastness to washing, light, acid, alkali, and hot pressing, as well as hydrosulfite discharge properties. General directions for the use of these dyes for cotton are also given.

Pfanstiehl rare sugars and amino acids, to the development of which the Special Chemicals Company of Highland Park, Ill., has given special attention, are now used by investigators around the world, from China and Japan, through every land in the new world, to Ireland, England, Denmark, France, and now to Germany. Because of their purity they have become a world standard and to America's credit it can now be said that another important contribution has been made to scientific accuracy and precision by means of materials of a new standard embodying the latest requirements of bacteriology.

A vocational course in papermaking has been started at Woronoco, Mass., under the auspices of the Strathmore Paper Company. The purpose of the course is to give a technical as well as a practical knowledge of the work in which the men are engaged. Under the present plans the company will pay for the various courses, charging small fees to students, and refunding the fees to all those who have passed a certain standard.

NOTES AND CORRESPONDENCE

A Foreign Opinion of the American Chemical Society

Editor of the Journal of Industrial and Engineering Chemistry:

Dr. Herty in his last editorial, and in his genial way, gave us a short sketch of the work accomplished by the American Chemical Society during these latter years.

May I call your attention to the published opinion of our distinguished fellow chemists in France and in Britain. From that excellent French publication, *Chimie et Industrie*, 6 (October 1921), 418, I make the following free translation of a report of the annual meeting of the Société de Chimie Industrielle:

Among the ideas presented by pen or word during this convention, there is one which seems of foremost importance for our country. It was expressed by Sir William Pope, to whom our Society has just awarded its Grand Medal of Honor, when he made the following statement in the presence of the Minister of Agriculture:

The American Chemical Society with its 17,000 members represents collectively all the interests of American Chemistry. On this account, it has become, in a way, the diplomatic corps of Chemistry in the United States, and every time the government has before itself questions where chemistry enters into play, senators and politicians immediately ask information and advice from the American Chemical Society.

If ever the Société de Chimie Industrielle of France saw itself honored as such an authority, what valuable services would our country obtain thereby!

Of course we all know that our politicians are not so ever ready to consult the American Chemical Society, but it is undeniable that since the growth and importance of our Society, its advice and opinion have frequently guided the Government and the better of our politicians.

L. H. BAEKELAND

YONKERS, N. Y.
December 3, 1921

The Chemical Industries of Holland

Editor of the Journal of Industrial and Engineering Chemistry:

As a chemist subscriber of *The Journal of Industrial and Engineering Chemistry*, I read the article on the "Chemical Industry and Trade of Holland" in your July number with much interest.

Generally speaking, your correspondent has very well represented the leading points, but I should greatly appreciate it if you would rectify or add a few points.

Under the heading of "Dyestuffs," it is said that the production thereof is insignificant and will probably remain so unless the Germans find it advisable to have plants in Holland. Your correspondent is probably not aware of the fact that, apart from a few smaller works which produced dyes even during the war, a company was founded about a year ago with the purpose of taking up the production of dyes with purely Dutch capital. This is the N. V. Nederlandsche Kleurstoffenfabriek (Dutch Dyestuffs Factory). The large banking houses, such as the well-known Twentsche Bank, Messrs. Mees & Co., large industrial concerns, such as the Bataafsche Petroleum Co., and other leading firms have all given money for establishing this national industry.

Further, your correspondent does not touch upon the large sugar factories which we have here in Holland. A large part of colonial sugar is refined here, and we have also some twenty beet-sugar factories. A fair amount of concentration has been effected of late in this industry, many beet-sugar factories having combined with the largest refining company under the name of "Centrale Suiker Maatschappij." It is very interesting to

see that this concentration has taken place although the tendency of the sugarmaking process is undoubtedly to make white sugar under the same roof with the beet sugar, so that each beet-sugar factory would make its own white sugar and not send its raw sugar to a refinery. The largest refinery here, probably having foreseen this, secured the necessary beet-sugar factories in the above-named company.

E. J. TOBI

CEINTURBAAN 213
AMSTERDAM, HOLLAND
August 24, 1921

Ceramic Research Colloquium

Held November 16 and 17, 1921, Ohio State University, Columbus, Ohio, under auspices of American Ceramic Society Committee on Research and Development, Central Ohio Local Section and Ohio State University Student Branch of the Society.

The Committee on Research devoted all day Wednesday and Thursday forenoon to the general question of policies and procedures most practical for stimulating ceramic research.

Research can be defined as systematic search for best ways and means of accomplishing some definite thing. A thoughtful study of and practice in best methods of accounting, marketing, etc., is research. Diligent thinking, experimenting and inventing of materials, mixtures, processes, and equipment for producing ceramic wares is ceramic research. It is only in these latter research problems that the Society is interested.

The American Ceramic Society was founded for and has continued to be engaged in the promotion of the ceramic arts and sciences through stimulation of research by individuals, corporations, governmental departments, universities, and associations of manufacturers. Holding of meetings for open discussions; planning by committees for unity in efforts; encouraging and assisting in coöperative efforts to ascertain facts relating to manufacturing; publication of literature, are examples of the means employed by the Society to promote ceramic arts and sciences through research.

The Society is divided into industrial divisions for the purpose of having more intimate contact with and knowledge of manufacturing problems. The divisional committees on research are requested to submit a list of research problems with a description of each item, suggestions as to where the problems might be undertaken and such suggestions and recommendations as they care to make. These lists will be studied and a grand program of activities planned, which program will again be submitted to the divisions for amendment or adoption. Some of the divisions already have such a list and have proceeded in interesting universities, governmental departments and associations.

One of the contacts sought by the Research Committee is that of the users of ceramic products. It is necessary, for instance, to understand the requirements of boiler refractories in order to know how to manufacture bricks for this purpose. The American Ceramic Society offers the best opportunity for the producers and users to meet in joint effort to solve the problems of the consumers.

A well-rounded sales promotion plan includes detail study of consumers' requirements. Sales promotion without this would not be successful. This is equally true in ceramic research. The interest of the consumer, which has for the most part been neglected in the past, will now receive adequate attention by the ceramists through the agency of the research committees of the Society and the divisions.

Actual contact will be had with the members of the Society

and with the public at large through the issuance of bulletins. No opportunity will be neglected to make the researches conducted under the auspices of the Society as thoroughly practical and far-reaching as is humanly possible. Fundamental science investigations are just as practical and necessary as are factory or routine investigations. Neither should or will be neglected. Industrial corporations and research institutions will be consulted for the purpose of finding not only the problems but also the means for solving them.

Standard methods and specifications have not in the past received the attention they deserve. The Society intends to promote the establishing of standards by securing the coöperation of all parties and agencies interested. The Society has joined as a member of the American Society for Testing Materials, and will have an official representation on all committees where the Society can give service. It is coöperating with all Divisions of the National Research Council that deal with problems of interest to ceramists. A working relation has already been established with the Fabricated Production Department of the Chamber of Commerce of the U. S. of America. The trade associations recognize the desire of the American Ceramic Society to coöperate with them in all matters of standards and researches pertaining to production. Contact is developing with the federal and state Geological Surveys, so that the Society can serve the Surveys in making their investigations the most practical.

This research colloquium was not devoted altogether to planning. Some research problems were discussed in detail.

At the public meetings of the colloquium, those attending obtained a much more clear and practical idea of the cause of plasticity in clays. The ultimate purpose for searching for the facts regarding plasticity is that this property may be developed in the white-burning kaolins. Ceramists have obtained several practical and applicable things from the studies which have already been made on this subject. The treatment of casting slips with salts to make possible the casting of intricate and heavy pieces is one of these, and increasing the bonding strength of clays is another.

More refined methods of testing were discussed. Dr. E. W. Washburn described a method developed at the University of Illinois for measuring porosity by determining the pressure caused by the air held in the pores of the test piece. The method he described is simple, accurate, and quick.

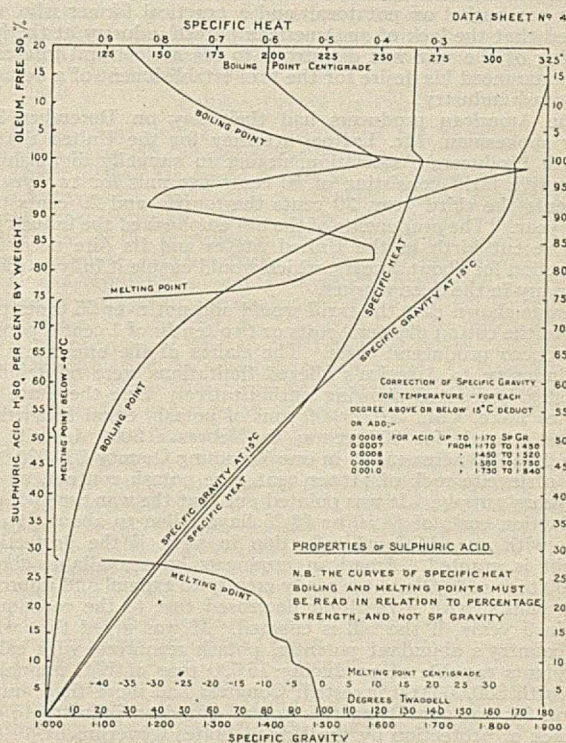
President Pence described the problems incident to casting of clay refractories. The method he described produces better ware but requires considerable floor space if the production is at all large. In a 50 per cent grog clay refractory 0.4 per cent of the weight of clay added as sodium carbonate would permit of the same degree of fluidity of the slip with one-half the amount of water.

The U. S. Bureau of Mines, with consent of the Joint Research Committee of the Four Heavy Clay Products Associations, described the work on kiln firing which the Associations are financing in coöperation with the Bureau. This work is progressing and when other groups of manufacturers learn of the results obtained it would seem that surely all ceramic manufacturers would be anxious to make a similar study of their kilns. A 10 to 15 per cent saving in fuel would soon pay all costs of the preliminary studies and all the equipment required to maintain the necessary control. We are learning that scientific control in manufacturing reduces costs and decreases dependence on experts. No research is worth while unless it carries through to the introduction of materials, processes or equipment, alike satisfactory to employees and employer in the control obtained.

It is believed that this meeting is only the first in the series of events which will bring a new era in ceramic manufacturing and keep this group of industries abreast with the ever-increasing requirements of the consumer.

Chemical Engineering Group of the Society of Chemical Industry

The Chemical Engineering Group of the Society of Chemical Industry is the first of what have been termed "Subject Groups" of the Society, corresponding in a general way to the Divisions and Sections of our American Chemical Society. It was organized in 1919 by a group of chemical engineers who felt the need of an organization in England, charged with the task of endeavoring to promote the interests of chemical engineering and its development along sound and scientific lines.



Among the activities of the Group is the publication of data sheets and charts, one of which is printed herewith in greatly reduced form. These sheets cover a large field of interest to the chemical engineer, and it is planned to publish a whole series, uniform in size, for filing in loose-leaf books. The sheets are sold at fifty cents per set. Membership in the Group includes the receipt of its publications. The headquarters of the Group are at 24, Buckingham Street, Strand, London, W. C. 2, England.

Calendar of Meetings

- American Institute of Mining and Metallurgical Engineers—
Spring Meeting, New York, N. Y., week of February 20, 1922.
- American Ceramic Society—24th Annual Meeting, St. Louis, Mo., February 27 to March 2, 1922.
- American Chemical Society—63rd Meeting, Birmingham, Ala., April 4 to 7, 1922.
- American Electrochemical Society—41st Meeting, Baltimore, Md., April 27 to 29, 1922.

A German process for making gasoline, called the Burgess process, has been developed by the originators of the Haber nitrogen fixation process. By means of this process, hydrogen is passed over carbon at 200 atmospheres pressure and at a temperature of 700° C. It is understood that this process has been examined in operation by the engineer of one of the large American oil companies who has reported that it is actually operating and producing motor fuel on a small scale.

WASHINGTON NOTES

HEARINGS ON POTASH

Opposition to protection of the American potash industry developing in the Senate Finance Committee hearings on December 29 was limited to five obstructionists: one a fertilizer man interested in German mines; one a representative of those interested; one alleged farmer's friend who claimed that one of the Central States used more potash than any other state in the Union; a professor who stressed a possible increased cost of 2 cents per bushel on potatoes; and a practical farmer who admitted that the lack of an American potash industry at the beginning of the war was disastrous to his agricultural interests and announced his desire for the firm establishment of a domestic potash industry.

The American producers had their day on December 30, their spokesman, Mr. LaRoe, attorney for the United States Potash Producers' Association, urging an annually diminishing protective tariff consisting of 50 cents per unit for two years, 40 cents the third year, 30 cents the fourth, and 20 cents the fifth year. The proponents of the bill emphasized the industry's very recent birth in the United States and its dire need for protection for about 5 years, which would enable it fully to meet Germany in the open market.

It was shown that the tariff would add not over 25 cents per acre to the cotton planters' costs or two-tenths of 1 cent a pound to tobacco producers' costs. The claims of the opponents of the industry to America's alleged limitations were refuted by statistics presented showing authoritatively that there are in Searles Lake, Cal., 20,000,000 tons of potash, equal to normal domestic needs for 100 years; in Nebraska 3000 deposits of from 1 to 600 acres each; in one Wyoming County 200,000,000 tons of leucite rock of 11 per cent pure potash content, or an 800 years' supply. It was pointed out that the war-time potash production costs of \$4.50 or \$4.25 have fallen to about \$1 per unit, with an additional reduction in sight if the protection sought is granted. American producers have available about 10,000 tons of K_2O and are ready greatly to expand and improve their plants, with a resultant decreased cost to the consumer, within 5 years, if the bill is enacted. It was urged that with the country's abundant potential potash resources, with existing plants capable of producing 75,000 tons of K_2O annually, and with \$30,000,000 invested, Congress had more than ample reason for not permitting this young American industry to die for lack of protection by the United States Government.

HOUSE PASSES BILL TO RELIEVE PATENT OFFICE SITUATION

A ray of hope appears on the horizon for the overburdened Patent Office in that the House has finally passed the Lampert bill to increase the salaries of the chief or principal patent examiners from \$2700 to \$3900 per year and those of the assistant examiners by amounts ranging from \$150 to \$900 per year. The bill provides an increase of force to the extent of one law examiner, 26 assistant examiners, and 22 clerks. While this bill is by no means adequate to relieve the present difficult position of the Patent Office, it is at least a step in the right direction, and it is hoped that the Senate will lose no time in acting upon the measure.

POSSIBILITY OF BURIED POTASH SALTS IN WESTERN TEXAS

In connection with borings for oil which are being made by the U. S. Geological Survey in the extreme western part of Texas, salts have been discovered that apparently possess at least the richness of the potash deposits of Alsace and Germany. Polyhalite, hydrated calcium potassium magnesium sulfate, has been found in a number of different levels in these borings, but as the wells are being drilled primarily for oils, information is not at present available as to whether the potash-bearing beds have a thickness of only a few inches or a much greater depth. The polyhalite examined contained 15.6 per cent of K_2O and it is believed that it can be used as a fertilizer in the pure state in which it is recovered, provided it is found in sufficient quantity.

BUREAU OF MINES LABORATORY CAR

In the coöperative work which is being conducted at the Columbus Station of the Bureau of Mines with the four heavy clay products associations, a laboratory car has recently been purchased. This is the first laboratory car that the Bureau has equipped and is similar to the Bureau's rescue cars. It is known as the "Car Holmes" in honor of the first director of the Bureau, and is a Pullman with living accommodations, labora-

tories, and office facilities for use at all hours. The investigation crew will visit various industrial plants with a threefold purpose: to cut down fuel consumption; shorten the time of burning; and improve the quality of the product. The first trip was made from Columbus to one of the hollow tile plants of the National Fireproofing Company at Haddonville, Ohio.

FURFURAL PRODUCTION AND UTILIZATION

In connection with the research work of the Bureau of Chemistry on the production and utilization of furfural, a small experimental plant has been installed at the Color Laboratory, Arlington Farms, Va., with a capacity of 30 lbs. per day. Corn-cobs digested with high pressure steam yield furfural equal to 6 or 7 per cent by weight of the cobs. The yield obtainable from other agricultural wastes will be investigated.

Over 300 lbs. of furfural have been manufactured in connection with production experiments at the Bureau of Chemistry during the past year. The greater part of this material has been supplied to several manufacturers for coöperative work on commercial utilization. The most promising field yet developed by this coöperation is that for the production of synthetic resins by the condensation of furfural with phenol. These resins have qualities suitable for electrical insulators and other molded articles which are being tested commercially.

LACK OF FUNDS DELAYS ESTABLISHMENT OF CHEMICAL DIVISION

The Bureau of Foreign and Domestic Commerce is finding it difficult to secure funds to organize a Chemical Division. Estimates have been submitted to Congress for the establishment not of one chemical division, as originally planned, but of three such divisions—one on heavy chemicals, one on dyes and drugs, and still another on paints and varnishes. If these divisions are organized a live contact will be maintained with the trade through the formation of an advisory committee in the industry itself, and whenever acute problems arise in foreign districts it will be the duty of a representative of the Bureau to travel to such points and assist in relieving the situation.

Under an informal agreement entered into between the Bureau of Mines and the Department of Geology, Indiana University, investigations of Indiana oil shales are now being conducted at the Indiana University under the direction of the Bureau of Mines.

The plans of the new building for coöperative laboratories of the Bureau of Mines and the University of Minnesota at Minneapolis have been completed and approved, the cost of construction being estimated as \$250,000, the funds for which are contributed by the State of Minnesota. The building will not be ready for occupancy in less than a year.

The demand for industrial alcohol has grown to such an extent that at the present time there are 58 formulas employed for its preparation. To meet the needs of both the manufacturer and the user, the Industrial Alcohol and Chemical Division of the Treasury Department, in coöperation with the Bureau of Standards, is at present engaged in the preparation of tables of specific gravities and weights per gallon of these various formulas. These tables will later appear as a government publication.

The Tariff Commission has in preparation for the Senate Committee on Finance a revision of the Summary of Tariff Information, 1920. This compilation will include statistics and other information for the first nine months of 1921.

The Tariff Commission is also compiling a digest of the hearings before the Senate Finance Committee.

The Bureau of Mines plans to engage an engineer who will be stationed at Reno, Nevada, to carry on nonmetallic investigations throughout the West.

A study is being made by the Bureau of Mines of the unsaturated hydrocarbons in industrial gases with a view to developing economic methods for the manufacture of alcohols therefrom. Ethyl and propyl alcohols are being sought particularly. Gas distilled from a mixture of oil and coal is at present being studied in coöperation with the Trent Process Corporation, of Washington, D. C.

PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

Although the question of naval disarmament, coupled with the Pacific question, seems to occupy a leading place at the Conference in Washington, one cannot neglect the matter of land disarmament, from the particular point of view which appeals to us chemists.

There has just been organized in Germany a Union for the defense of the interests of the German chemical industries. One of the first manifestations of the Union has been a complaint of the wasting away of chemical industry in Germany. It is evident that all the allied and neutral nations which were clients of Germany before the war have had to establish their own chemical industries. There has resulted at the present time a world over-production of chemicals, and Germany, who even in 1920 held second place in export of chemical products, finds her exports, and consequently her production, reduced in 1921 to 50 per cent of what it was in 1914. Further, the German chemical industry blames the import tariffs for this paralysis. Formerly, many German chemical products were exported to Switzerland, from which they were finally shipped to the various consumers. Exports to Switzerland in 1920 were 290 million marks, of which about half were chemicals, but Switzerland has just quadrupled her import duty, thus practically stopping the export of German products. Under these conditions, and in spite of the fact that the low value of the mark should at the moment aid the German chemical industry, the complaints of the directors of this industry, who go so far as to say that Germany cannot meet her obligations to the Allies on account of this economic situation, are explicable. These arguments might have some weight, did one not feel a back thrust at Mr. Francis Garvan and Dr. Herty, as well as at Mr. Victor Lefebure, gas officer in the British army. The last mentioned is at present conducting a campaign in England in which he is demanding severe control of German chemical factories, from the point of view of gas manufacture; it is this control which the Germans wish to avoid at any cost.

THE FUEL SITUATION

I have already mentioned several times a contest for a national fuel, with the object of finding a better formula for a motor fuel containing alcohol.

Mr. Marillier has just reported to the Académie des Sciences the solution of the problem. Absolute alcohol is miscible with gasoline, but 95 per cent commercial alcohol is not miscible. When 95 per cent alcohol is mixed with gasoline two layers are formed, and on account of the partition factor the water in the alcohol is almost entirely in the lower layer, while the upper layer contains gasoline with 10 per cent of anhydrous alcohol. This layer serves as a basis for the fuel, to which it is sufficient to add small quantities of benzene, methylene, and ether.

I have also frequently noted the prospecting for petroleum in various parts of France. At present, the boring at Vaux (Ain) is becoming industrially important. Three test borings were made in 1920 and the beginning of 1921. A fourth boring, ended in October, is yielding now steadily 90,000 cubic meters per day. The gas is to be used for lighting the town of Amberier. It contains 80 per cent of methane, 12 per cent of different hydrocarbons, higher homologs, the remainder consisting of nitrogen, carbon dioxide, and carbon monoxide. The calorific power is 9500 calories.

CARBONIZATION OF COAL

In the same field I have mentioned the recent discoveries of Mr. Charpy on the carbonization of coal.

This problem has found a special application in the case of the Sarre coals, which give a coke too friable for use in the large blast furnaces. Mr. Charpy has studied carefully the conditions of the oxidation of the coal, and the mixtures of fat and lean coals. He has arrived at the conclusion that to obtain a good metallurgical coke it is necessary, in addition to making a judicious mixture of the coal, to conduct the carbonization in two stages. In the first step, the coal must be raised instantly to a temperature of 450° to 500°; then, in the second step, the temperature must be raised extremely slowly to between 700° and 900°. These theoretical considerations have been tested out industrially in the basin of the Sarre, with good results.

1922 MEETING OF THE SOCIÉTÉ

The success of the meeting of the Société de Chimie Industrielle last October has led to plans for the 1922 meeting, which will be held in Marseilles, July 2 to 6. It will cover principally the chemistry of fats and the chemistry of vegetable products from the colonies. The meeting will take place at the same time as the interallied colonial exposition.

December 10, 1921

I have just met Professor Moureu as he was returning to his laboratory at the Collège de France. He gave me his impressions on his sojourn in the United States and recounted the unforgettable welcome he received. Naturally, Professor Moureu is very discreet in regard to the work of the Conference, but he told me enthusiastically of the reception which he received in various chemical fields, official, university, and industrial. He believes that the United States is making a great advance in chemical research and in the creation of a great industry, mineral as well as organic. This industry will be the most powerful in the world and, with the high idealism of the American people, it will be a guarantee of peace. For us Frenchmen it constitutes one of the best elements of our security.

January 6, 1922

PERSONALS

Mr. Ernest H. Hartwig resigned as assistant in chemistry at Purdue University in order to accept a position as instructor in the chemical engineering department at the University of Wisconsin, Madison, Wis.

Miss Henriette C. Liebe recently received her B.S. degree from the University of Wisconsin and has accepted a position with the Acme White Lead and Color Works of Detroit, Mich., where she is an executive research chemist in the research division.

Mr. Raymond L. Stehle recently resigned as assistant professor of physiological chemistry in the School of Medicine of the University of Pennsylvania to become associated with the faculty of medicine of McGill University, Montreal, as assistant professor of pharmacology.

Mr. Merrill C. Hart, who was chemist to the pharmacology department of the University of Minnesota, working on the synthesis of phenolic alcohols on funds granted by the U. S. Interdepartmental Board for Social Hygiene, is associated with the Upjohn Company at Kalamazoo, Mich., as research organic chemist.

Mr. W. H. Rodebush has been appointed associate professor in charge of the division of physical chemistry, University of Illinois, Urbana, Ill. Mr. Rodebush was formerly national research fellow at the University of California.

Mr. Harvey T. Kennedy, formerly a student in chemistry at Cornell University, Ithaca, N. Y., has become chemist in the Municipal Testing Laboratory, Rochester, N. Y.

Mr. James H. Ransom has changed his position as research chemist with the Michigan Smelting & Refining Co., Detroit, Mich., to head of the department of chemistry in James Millikin University, Decatur, Ill.

Mr. Gerhard K. Rollefson resigned as assistant in chemistry at the University of Wisconsin to accept a position as teaching fellow in chemistry at the University of California, Berkeley, Cal.

Mr. F. Arthur Patty, instructor in chemistry and pharmacy at the University of Washington, Seattle, Wash., accepted his present position last August with the Campbell System, Inc., Kansas City, Mo., as research chemist.

Mr. John C. Pennie, for many years a specialist in the practice of patent law, died at his home in New York City on December 23, 1921. Mr. Pennie was born in Albany, N. Y., in 1858. He graduated from Union College in 1877, and pursued postgraduate work in Germany at the Universities of Göttingen and Heidelberg. He entered the United States Patent Office as an examiner in 1880. He practiced patent law in Washington and New York and at the time of his death was a senior partner of the firm of Pennie, Davis, Marvin and Edmonds.

He was chosen by the United States Government as patent expert on the commission to negotiate peace, and spent six months in Paris advising with the representatives of other countries on the provisions of the Peace Treaty relating to patents. He was a member of most of the learned and scientific societies, of the Legion of Honor of France, and Commander of the Order of the Crown of Belgium.

Dr. William Frear died suddenly at his home at State College, Pa., January 6, 1922. Dr. Frear was born in Reading, Pa., March 24, 1860. He received the bachelor's degree from Bucknell University in 1881, and the doctor's degree from Illinois Wesleyan University in 1883. After two years as an assistant chemist in the U. S. Department of Agriculture, Dr. Frear became associated with the agricultural department of Pennsylvania State University, and had been director of the Experiment Station since 1887.

Following the lines of Dr. Smith's suggestions to members of the Society in regard to popular education as to chemistry, Dr. C. E. Kenneth Mees, director of the Research Laboratory of the Eastman Kodak Co., addressed the Rochester City Club on January 7 on the importance of scientific knowledge and its application to life.

Mr. Daniel H. Rupp, formerly chemist for the Clark-Parker Chemical Co., Los Angeles, Cal., and later with the U. S. Potash Co., at their Monolith cement plant, is at present connected with the City of Ironton, Ohio, as "chemist-in-charge" of water purification works.

Dr. Lansing S. Wells, until recently research chemist with The Barrett Company, Frankford, Philadelphia, Pa., has accepted an appointment as assistant professor of organic and physical chemistry, Montana State College, Bozeman, Mont.

Dr. R. L. High, for fifteen years chief chemist to the National Drug Company of Philadelphia, Pa., recently resigned his position in this capacity and opened the High Chemical Company at Savannah, Ga.

Mr. Donald Belcher is now employed by Perin and Marshall, consulting engineers, of New York City, as a chemical engineer on development work for a process which he worked on as a research chemist for Hayward and Schleicher, of Cambridge, Mass.

Mr. Louis J. Trostel, who for the past two years has been stationed at the Pittsburgh Station of the Bureau of Mines engaged on problems relating to industrial gases and dusts, resigned November 1 to take a position with the Bureau of Chemistry as assistant chemical engineer. He will there be associated with the work of the Bureau on chemical problems relating to explosions from starch and other carbonaceous dusts.

Dr. Raymond J. Miller, formerly with the department of physiological chemistry, Jefferson Medical College, Philadelphia, Pa., as research associate under Prof. Philip B. Hawk, is at present associate professor of pharmacology and physiological chemistry at Baylor University, College of Medicine, Dallas, Texas.

Dr. Minnie A. Graham, who has served as substitute for Prof. Charles J. Moore of the department of chemistry of Hunter College of the City of New York, has been appointed acting professor of chemistry at Wells College during the absence of Prof. Clara A. Bliss.

Mr. Arthur W. Davidson, who was library investigator at the library of the Chemists' Club from last February to August, has been appointed assistant professor of chemistry at the University of Kansas, Lawrence, Kans.

Mr. A. E. Marshall has resigned as works manager of The Davison Chemical Company and has returned to his former work as consulting chemical engineer, specializing in the design of plants for the manufacture of mineral acids and fertilizers, at Baltimore, Md.

Dr. Ernest Fox Nichols, who recently resigned the presidency of the Massachusetts Institute of Technology, is to return to Cleveland to resume the directorship of pure science in the Nela Research Laboratory of the General Electric Co.

BOOK REVIEWS

Organic Compounds of Mercury. By FRANK C. WHITMORE. (American Chemical Society Monograph Series.) xii + 397 pp. The Chemical Catalog Co., Inc., New York, 1921. Price, \$4.50.

The interest in the study of organic compounds of mercury has increased in recent years because of the need for some non-ionized mercury compound for use with organic arsenicals in the treatment of syphilis. This volume is principally confined to the consideration of true organic mercury compounds in which mercury is directly attached to carbon. The related subjects which are not discussed are made available for further study by the supplementary biographical lists included in the appendices. The author states in the preface that "the monograph will be arranged to serve both the general chemist who wishes to get a conception of what has been done in the field, as a whole, and the specialist who wishes to find out quickly what has been done in any particular field. It is hoped that the work will inspire further research in this interesting field. In general, enough detail is given to make evident the method, but not enough to serve as a laboratory guide in repeating any of the work."

One is impressed with the great variety of mercury compounds, the new methods of preparation, and the improvements in the older methods. Little more seems to be known about the part played by ethyl acetate in the formation of mercury alkyls than was known by Frankland sixty years ago. It is interesting to note that in making alkyl mercury compounds 0.1 per cent sodium amalgam gives the best results, while for the aryl compounds 2.7 per cent sodium amalgam gives the best yields.

The word "mercurate" has been introduced to conform with bromination, nitration, and sulfonation. In fact, it has been shown that mercuration of aromatic compounds follows the general rules of substitution except in the case of nitrobenzene. Mercuration of aromatic compounds with mercuric acetate has led to many new and interesting compounds. The properties of most of these compounds have been studied, but in a number of cases the constitution has not been definitely determined.

The fairest comment that can be made upon this book is that the author has accomplished that which he set out to do, and chemists are indebted to him for this admirable piece of work. Anyone familiar with these very interesting compounds will appreciate the service that he has performed. The book is well planned, well written, and well printed. It will make a valuable addition to any chemical library, and those interested in mercury compounds cannot afford to be without it. It is a real addition to our American chemical literature.

WALTER T. TAGGART

Animal Proteins. By HUGH GARNER BENNETT. xiv + 288 pp. D. Van Nostrand Co., New York, 1921. Price, \$3.75.

This is another volume of the series of Industrial Chemistry edited by Dr. Samuel Rideal. The title is clearly a misnomer, as the book can lay claim to being little more than a semipopular description of the manufacture of leather and glue. It does not describe, or even enumerate, the several proteins of which skin is composed. The only conceivable justification for the title is that the proteins of leather and glue are of animal origin. Of the six parts into which the book is divided, four are devoted to

tanning, one to glue manufacture, and one to by-products, with very brief mention of foods and fertilizers.

It was intended to include in each book of the series a general bibliography and also a selective bibliography to follow each section. In this book there is no general bibliography and the selective bibliography is so meager and inaccurate as to be of little value. The *Collegium* is given as the source of articles which it merely reprinted or abstracted, and apparently no attempt has been made to record titles accurately.

The book will appeal to the layman desiring a general description of leather and glue manufacture and to the practical tanner desiring to know something of processes other than his own. The author's attempt at chemical treatment, however, cannot be regarded as successful. The term *lyotrope* is used very freely throughout the book as though in itself it describes or explains numerous phenomena.

On page 26 we read: "In bating and puering the essential change is that before the process the swelling is due chiefly to adsorption of hydroxyl ions, whereas afterwards it is due chiefly to a composite lyotrope influence." Upon examination, this proves to be nothing more than a jumble of words, but it is typical of the attempts at theoretical treatment. In keeping with the meager bibliography, the author ignores, or is possibly unaware of, much of the literature on the phases of leather chemistry which he attempts to discuss.

As a rule, vegetable leathers are firmer and more solid than chrome leathers. The author explains this as being due to the greater deposition of solid matter on the surfaces of the fibers and in the spaces between them by vegetable than by chrome tanning. He apparently does not know that it has been demonstrated microscopically, in carefully controlled systems of both chrome and vegetable tanning, that there is no visible deposition of tanning material on or between the fibers, but that the tanning material diffuses completely throughout the protein substance, altering its chemical and physical properties. Vegetable tanning causes a much greater solidity by producing a greater increase in volume of the fibers than does chrome tanning. This is easily seen by examining sections of leather under the microscope.

While the book presents little that is new, its general descriptions of numerous methods of making leather will make it welcome as a book of reference in many tannery libraries.

J. A. WILSON

The Metallurgy of the Common Metals. By LEONARD S. AUSTIN (formerly professor of metallurgy, Michigan College of Mines). 5th edition, 615 pp., illustrated. John Wiley & Sons, Inc., New York, 1921. Price, \$7.00.

The "common metals" discussed are gold, silver, iron (and steel), copper, lead, and zinc.

The author has brought to bear his own practical experience of forty years in the fields of silver-lead and copper smelting. Experts have cooperated in preparing the chapters on cyaniding gold and silver ores and the metallurgy of zinc.

This edition brings the practice of 1913 up to date. Almost complete rewriting has been necessary.

The usual description of materials and processes has been vitalized in this excellent work by the insertion in the proper places of many data on cost of plant, materials, and operation. While such costs are constantly changing, they are still very useful.

The "Business of Metallurgy" is discussed in a very practical way in Chapters 48 to 50. The suggestions as to organization and management are an appropriate innovation. This side of metallurgy has been neglected heretofore in textbooks.

The list of errata, chiefly in figure reference numbers, is rather long and might cause confusion unless marked in at once.

This is the best metallurgical handbook with which the reviewer is familiar.

AS. O. HANDY

Industrial Hydrogen. By HUGH S. TAYLOR, D.Sc. (American Chemical Society Monograph Series.) 210 pp. The Chemical Catalog Co., Inc., New York, 1921. Price, \$3.50.

This volume is one of the American Chemical Society's series of scientific and technologic monographs. The author states that he has attempted to follow the twofold purposes of the monograph series as decided on by the Board of Editors, and his book not only outlines the fundamental principles and essential chemical facts of the industry of hydrogen production, but also attempts to trace the steps by which the present status of the industry has been reached, to detail what that present status is, and what lines of future development may be anticipated.

The book does not attempt to over-emphasize the engineering side of the subject, but puts more emphasis on the purely chemical side. On the other hand, the author has had in mind the possible application of his work to engineering projects, and has attempted to give the necessary data so that an engineering staff could readily base its calculations for actual plant details. No attempts have been made at giving cost data, or even estimating such, as the author has felt that this was going too far into details of actual commercial operation. It has been his aim, however, to supply sufficient data upon which cost calculations might be made.

The subjects treated in the different chapters are as follows: Hydrogen from Steam and Iron; Hydrogen from Water Gas and Steam; Hydrogen from Water Gas by Liquefaction; Hydrogen by Electrolysis; Hydrogen from Water; Hydrogen from Aqueous Alkalies; Hydrogen from Hydrocarbons; Miscellaneous and By-product Hydrogen Process; The Purification and Testing of Hydrogen. In each case the author has given a general résumé of the subject treated in the chapter without going into a great deal of detail, especially on the plant construction and operation side. He has, whenever possible, discussed fully the chemistry of the processes involved, and such discussion has been in simple and easily understood language. In no case has he gone into the detail that can be found in certain books, such as the British Admiralty "Hydrogen Manual," and the "Hydrogen Manual of the U. S. Air Service," but, on the other hand, the subject has been dealt with in a much more general and comprehensive way, giving not only what has been the practice in the past and is the practice in the present, but also suggestions as to future improvements. It is a book full of most excellent information for the general reader rather than a textbook for an operator of a hydrogen plant.

It is not to be expected that in a book covering so wide a field some errors would not creep in, especially when the author has had necessarily to deal with branches of the subject with which he has had no practical experience. These errors, however, are not serious. The book is an extremely useful one, and should be in every chemical laboratory.

R. B. MOORE

American Sulphuric Acid Practice. By PHILIP DEWOLF AND E. L. LARISON, with a special chapter by W. M. LECLEAR. vii + 270 pp. McGraw-Hill Book Co, Inc., 1921. Price, \$3.50.

This proves to be an interesting and suggestive book whether for the beginner or the specialist. Many of the illustrations are from photographs or working drawings and, generally speaking, the book has the advantage of a fresh point of view on the sulfuric acid industry, *i. e.*, the point of view of men who make sulfuric acid in the open surroundings of the metallurgical field and not in the secret star chamber of the chemical field.

The novice should, however, accept many of the statements made with reservations. The historical introduction contains numerous errors. From the technical point of view the book is open to the same criticism. Contrary to our authors' belief, contact process yields are, on the average, probably no better

than in good chamber practice and it is difficult to make them as good as are obtained in the best chamber practice. One would be compelled, according to our authors, to believe that oxygen carriers were not actual catalyzers, and that "fume" is not properly fume at all because it is not a true gas, and that high concentration fuming acid plants must be located in the driest climate possible. Something of the same carelessness appears in the authors' use of the English language: "Fuming acid has high melting points, the exact varying with the strength." In spite of the dual authorship, "I" and "we" are used interchangeably. Such blemishes, however, do not seriously interfere with the usefulness of the book.

More critical errors are not lacking: It is stated that "Even with the most careful handling somewhere about 2 to 3 per cent of sulfur will remain in the cinder from roasting pyrites." With good pyrites and careful handling this can be reduced considerably below 1 per cent. Again, it is doubtful if, to test acid bricks for a Glover tower, it is sufficient merely to immerse them in sulfuric acid and then to allow them to weather for a few weeks. Also, direct-connected immersed centrifugal pumps were used in 1905 for handling acid, instead of "put into use during the past three or four years."

On the whole, however, the book is a valuable contribution to the literature of the art.

WM. M. GROSVENOR

Soaps and Proteins—Their Colloid Chemistry in Theory and Practice. By MARTIN H. FISCHER, with the collaboration of GEORGE D. McLAUGHLIN AND MARION O. HOOKER. ix + 272 pp. John Wiley & Sons, Inc., New York; Chapman & Hall, Ltd., London, 1921. Price, \$4.00, net.

The chemical and physical relations existing between fatty acids and their salts and proteins and their salts led the author to investigate the former in order that through analogy he might better understand the proteins and their biological relations.

As indicated in the title, it is the evident intent of the author to treat everything on a colloid basis. The book deals with theoretical and experimental work on the colloid chemistry of soaps, with the author's version of the colloid chemistry of soap manufacture, and with the analogies in the colloid chemistry of soaps, protein derivatives, and tissues.

Any scientist has the unquestioned right to coin a new word at any time to meet a new situation, and colloid chemists have exercised this prerogative to the limit. One might even think they have strained it when they can use without blushing such words as lyophilic, gelation, solvation, syneresis, hydrophilic, dispersoid, lyophobic, and a host of others, and feel called upon to use such words as *solution* and *dissolving* in quotation marks and to refer to their use as "in the accepted parlance." It may be admitted that the molecular behavior that is responsible for many qualities of matter is not completely understood, but the word *solution* conveys a fairly definite idea to the everyday chemist, and to fight shy of the property of matter known as *solubility* will deprive one of means of explaining phenomena not otherwise explainable. The author seems to be profoundly neglectful of the law of mass action, and of Berthelot's Law and Gibbs' Phase Rule.

After discussing experiments and opinions of others on "salting out" soaps, the author concludes that:

Without recourse to too many or too violent assumptions, the following seems the simplest way out. The entire series of changes observed in the salting out of a soap by an alkali or a salt is readily understood if it is assumed that the added neutral salt or alkali hydroxide unites with the solvent to form a hydrate or solvate and that the consequent viscosity changes (including gelation) are dependent upon the changes in viscosity observed whenever one liquid is emulsified in a second.

Here again the author considers that he is dealing with an *emulsion* rather than a *solution*, and does not grasp a rational

explanation that is within his reach. For many years the reviewer has recognized that the "salting out" and the "settling" of soaps are simple examples of the phase rule. This seemed so self-evident that he has never thought of publishing it. To any solution of (sodium) soap in water or liquid solution of water in soap, let us add concentrated caustic soda solution, or salt or strong salt solution. At first a small amount of the added substance is dissolved in the soap and water. Soap is nearly insoluble in strong caustic soda or strong salt solution, and after addition of one or the other or both of these, an amount of salt or caustic alkali is present which can no longer remain dissolved in the soap-water phase as a homogeneous system, and a second phase begins to appear. We have now a phase of soap containing water and a little dissolved salt or alkali, and a phase of dilute solution of salt or caustic soda containing, at first, considerable dissolved soap. At this point there is a change in the viscosity. Further addition of salt or caustic alkali renders the soap still less soluble and precipitates most of the soap which was dissolved in the dilute salt or alkaline phase at the first appearance of the phase, and there are now two phases, the lighter consisting of most of the soap and containing some water and dissolved "lye," and the other consisting of "lye" or salt solution in which there is dissolved a small amount of soap. Soaps with low molecular weights are as a rule more soluble and a larger amount of salt or caustic alkali is needed to salt them out.

"Dehydration" is given as an explanation of many phenomena which to the reviewer would seem to be explained more clearly on the basis of solubility. The expression "complete dehydration" is used rather loosely to denote a condition wherein there is a separation of a concentrated soap, by no means free from dissolved water.

Throughout the book the author, after presenting his arguments, sets down in italics statements which might impress one as proved facts or fundamental general truths. Many of these conclusions are sound and have already been generally accepted, but some of them do not seem to follow from the facts or to be in strict accord with them.

This book will not be of service to the soap manufacturer or soap boiler. The chemist will, however, read it with a great deal of interest. It will be strange if he does not often dissent from many statements, but the man who is able to form his own opinions will be well repaid for reading the book, because of the independent thought it is sure to arouse.

MARTIN HILL ITTNER

Nos Usines Métallurgiques Dévastées. Introduction by LÉON GUILLET. 234 pp. La Revue de Métallurgie, 5, Cité Pigalle, Paris, 1921. Price, 25 fr.

Under this title the editors of *La Revue de Métallurgie* have gathered a number of monographs dealing with the wanton destruction of French metallurgical plants carried out by the German army during the war. Most of this destruction cannot possibly be excused on the grounds of military necessity and appears to have had only the firm purpose of systematically ruining the French metallurgical industry.

The monograph is illustrated with numerous photographs showing the conditions of the plants before the war and after the Armistice and will be a lasting witness of the barbarism with which the war was carried out by the Germans in France. Interesting maps are given showing the extent of the destruction and comparison of what the affected area would represent in proportion in such industrial countries as England and the United States. It would make interesting reading for those who believe in the regulation of methods of warfare by treaties and conventions.

J. ENRIQUE ZANETTI

Chemical Warfare. By AMOS A. FRIES AND CLARENCE J. WEST. x + 445 pp. McGraw-Hill Book Co., Inc., New York, 1921. Price, \$3.50.

This is an authoritative compilation and treatise prepared by two American officers exceptionally well qualified for the task. The result of the collaboration of these experts is, as might have been expected, a textbook which gives a full and generally dependable account of the history, development, and significance, of these new and terribly potent weapons, and should certainly find a place upon the shelves of everyone interested in the subject, as well as upon those of all army officers.

A Foreword by Major Gen. William L. Sibert, the distinguished engineer who was the first Director of C. W. S. and who remained its guiding intelligence until long after the signing of the Armistice, concludes with the following generous tribute to the chemical profession: "I feel that this book will show that the genius and patriotism displayed by the chemists and chemical engineers of the country were not surpassed in any other branch of war work and that to fail to utilize in peace times this talent would be a crime."

Many chapters of the book are made up in whole or in part of articles and addresses which have appeared elsewhere and are now gathered together in proper sequence. The official reports submitted to the Director by the various Divisions of the Service have been drawn upon freely, as well as the published contributions of those best qualified to speak on the subject.

In a compilation of this character it is not strange that some repetition and duplication occur and occasional minor discrepancies, but these are not serious and do not affect the value of the book.

Some of us would like to have seen rather more space given to the Chemical Service Section, not only because, as the authors point out, "This holds the distinction of being the first recognition of chemistry as a separate branch of the military service in any country or in any war," but also because it was the nucleus of what subsequently became the headquarters staff, or Administration Division, of C. W. S. To it, and not to the Administration Division, belongs whatever credit may be due for securing authority from the Secretary of War to furlough back to war industries and universities those chemists essential to a maintenance of our output of munitions and of trained men, and finally for obtaining the famous order of May 28, 1918, mobilizing the chemists of the country and placing upon the C. W. S. the responsibility for sending them where they could render to their country the maximum assistance.

In the judgment of the reviewer, the following additions would increase the value of the work, and it is to be hoped that they may be incorporated in subsequent editions: (1) A selected bibliography, for those who do not have available that published in "Special Libraries" (November 1919), and (2) an outline of the organization, personnel, plans, and policy of the Chemical Warfare Service.

MARSTON TAYLOR BOGERT

The Vitamine Manual. By WALTER H. EDDY. 121 pp. Williams & Wilkins Co., Baltimore, 1921. Price, \$2.50.

This small volume gives a concise survey of the investigations of vitamins made during the ten years they have been known. The essential facts are very clearly and readily presented, and the book will undoubtedly be greatly appreciated, both by those working in the field and those simply wishing accurate information on the subject.

There is first given an especially interesting account of how vitamins were discovered and this is followed by a short chapter on the attempts which have been made to determine the chemical nature of vitamins. It is to be regretted that the brevity of this chapter is due to the absence of positive information along

this line. Of the difficulties encountered in such studies, those resulting from the inadequacy of the physiological methods of vitamin testing are especially noteworthy. The author has, therefore, discussed in detail the available methods which have been developed for this purpose, including the recently proposed yeast test which, however, has, so far, not been shown to be specific for vitamins.

From a practical standpoint the information contained in the chapters on the sources of vitamins, the chemical and physiological properties of the vitamins, and how to utilize the vitamins in diets will be found of most general interest. The author's opinion on the recent crusade for the eating of yeast cakes will undoubtedly be appreciated by many.

The concluding chapter describes briefly the diseases that result from vitamin deficiencies, and finally there is given an excellent bibliography of some 560 references.

ATHERTON SEIDELL

Traité de Métallurgie Générale. By LÉON GUILLET. viii + 528 pp. J.-B. Ballière & Son, 19, Rue Hautefeuille, Paris, 1921. Price, paper covered, 40 fr.; limp binding, 50 fr.

This treatise is the first volume of an encyclopedia of mining and metallurgy to be published under the editorship of Léon Guillet. It forms part of a larger undertaking comprising encyclopedias of industrial electricity, of applied mechanics, of civil engineering and public works, and of industrial chemistry. The publication of 200 volumes is contemplated. The purpose is to discuss the most modern solutions of industrial problems based on scientific knowledge. Thirty-two volumes will be devoted to the study of metallurgy, each one written by a well-known expert.

This first book is divided into twenty-one chapters dealing, respectively, with metallurgical operations and their classifications; roasting and calcining; relation between roasting and calcining and the laws of physical chemistry; apparatus for roasting and calcining; smelting; relations between smelting and the laws of physical chemistry; smelting furnaces, distillation processes; relations between distillation and the laws of physical chemistry; distillation apparatus; electrometallurgy, electric furnaces; wet methods and amalgamation; apparatus for wet methods; electrolysis; wet methods and the laws of physical chemistry; apparatus for electrolysis; treatments of ores; casting of metallurgical products, ingots and their defects; slags; utilization of gases and dusts.

It will be seen that the subject is treated exhaustively and in logical sequence. For those who might be surprised that the fuels and the refractory materials are not included in this volume it should be stated that these subjects are to be dealt with separately in the next two volumes of the series.

Those who are familiar with Professor Guillet's writings know that they are characterized by a masterly grasp, breadth of view, clear and methodical exposition. The same qualities will be found in the present volume. The author, while a scientific man, never loses sight of the fact that metallurgy is essentially an applied science and that its value to the world at large depends upon its possible applications to industrial operations. Sound metallurgical operations, however, should rest upon well-known scientific phenomena, and metallurgical progress should be sought along scientific lines. With this in mind the author takes pains to link every metallurgical operation with the teachings of chemistry and of physical chemistry. Not only the student of metallurgy but the teacher as well and the practicing metallurgist should find in this important book much that is instructive, illuminating, and suggestive.

ALBERT SAUVEUR

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.

There has recently been a marked enlargement of development plans for the Argentine oil fields and it is claimed that the next few years will see a greater development than has been accomplished since the first well was drilled. (P. 18)

About three-fourths of Guatemala's imports of paints and varnishes consist of the ordinary prepared paints, which come chiefly from the United States. (P. 83)

After a long-continued suspension of imports of chemicals into Japan, the demand for foreign chemicals is increasing. About 3500 tons of sulfate of ammonia are said to have been ordered from the United States, while demand is brisk for formalin, rosin, and shellac. (P. 84)

A list of Brazilian oil seed, fruit, and nut trees and palms, showing the approximate proportion of the oil yield of each plant, has been prepared by the Director of the Museum of the Commercial Association of Para, and copies may be obtained from the Bureau of Foreign and Domestic Commerce. (P. 373)

Under the name of "Eulan" a new product of the German chemical industry has been placed on the European market. The base of the new product is reported to be Martius Yellow which, it is claimed, will render wool moth proof. (P. 450)

The production of the Comodoro Rivadavia oil fields for 1920 amounted to 1,540,492 bbls., an increase of 20.44 per cent as compared with the year 1919. (P. 843)

In connection with the use of fuel oil in Birmingham, England, a spirit of controversy has arisen concerning the calorific efficiencies of coal and oil. The results of the experiments conducted support the claim that a ton of fuel oil is equal to two tons of coal. (Pp. 843-4)

Rulings for marking imports for Canada are cited relative to the following subjects: Acids and chemicals, coal tar, dyestuffs, glue, mica, paints and oils, and tanning materials. (Pp. 854-7)

From statistics on hand the statement is made that Burma is capable of producing sufficient tin to make the Indian Empire self-supporting as regards this metal, provided the ores be smelted in India. (P. 893)

An act of the Indian Legislature provides that a customs duty shall be collected on all lac and refuse lac produced in India and exported to any port beyond the limits of British India or to Aden. (P. 922)

A French decree of November 4, 1921, increases the general rates of import duty on chloride of potassium and potassium sulfate. (P. 922)

By a recent decree, alcohol imported into Greece to be used for heating and lighting purposes can be denatured only upon approval of the Ministry of Finance. (P. 922)

The Chilean nitrate year 1920-21 was similar to the preceding 12 months in that it contained a period of optimism and one of depression, but with the important difference that the year 1919-20 began in inactivity and ended at a time when prosperity appeared to have returned, whereas in the following year the spirit of optimism with which the period began proved to be short lived and soon gave way to demoralization, resulting in the most serious crisis which the industry has ever known. (Pp. 927-9)

Under contemplated changes in Spanish tariff increased duties are proposed on a large number of American exports, including all kinds of petroleum. (P. 937)

Negotiations have recently been carried on between the owners of the Outokumpu copper mines in eastern Finland and some German copper mine owners for the lease of the Outokumpu mines or the sale of the raw ore from them. Experts say that if the mines are worked to their full capacity the production will amount to at least 6000 tons of copper a year, not counting the other products of which the sulfur alone is sufficient to satisfy the requirements of Finland's paper industry. (P. 947)

The Chuling Mining Works, which is working a lead mine in Chenping district, recently made its first shipment of lead. (P. 949)

The increase in the production of the French bauxite mines has followed closely the development of the aluminium industry. It is thought that the French production of aluminium is likely to increase from 25,000 to 30,000 metric tons as compared to 13,500 metric tons in 1913. The probable French consumption of bauxite might then be 200,000 metric tons per year. (P. 963)

The shipments of petroleum from the Tampico oil fields for the month of October 1921 reached a total of 16,052,589 bbls. of 42 gal. each, decreasing 1,154,537 bbls. from the September shipments. The decrease was due primarily to a restricted market for oil in the United States. (P. 969)

Much speculation is current respecting the prospect of discovering oil in the Province of Antofagasta, Chile. (Pp. 970-1)

Telegraphic dispatches indicate large American investments in Bolivian petroleum. (P. 971)

The salt industry of the Union of South Africa is described as being in a serious condition. (P. 973)

A royal Spanish order has been issued authorizing the unrestricted exportation of olive oil until further notice. (P. 983)

The island of Curaçao, West Indies, is gaining in importance because of the increasing development of the petroleum industry and of the proximity of the island to the new Venezuelan oil fields. (P. 988)

The Chilean government has sent a mining engineer to Iquique to investigate the report of the discovery of the new nitrate zone. (P. 989)

Almost contemporaneously with the issue of the mandate of administration for the islands of Nauru and Ocean, was the rediscovery of the great sulfur mountain of Vanua Lava in the Banks group of the New Hebrides. This mountain is one vast mass of sulfur, the quantity being 99 per cent sulfur and the balance ash. (P. 991)

The German Potash Syndicate has issued figures placing Germany's production of potash salts during the first six months of 1921 at 4,454,261 metric tons, or 497,373 tons of pure potash. (P. 994)

The outlook of the French chemical industry is decidedly brighter. The production of alcohol in France during the first 10 months of this year totaled 944,676 hectoliters, an increase of 210,264 hectoliters over that of the same period last year. (P. 1003)

The paralyzation in iron production in the North of Spain continues. (P. 1018)

The world's production of tungsten in 1920 was as follows: United Kingdom, 94 long tons; Southern Rhodesia, 15 tons; India, 2346; Federated Malay States, 234; New Zealand, 39; and the United States, 193 tons; a total of 2921 long tons. Each of these figures records a substantial decrease from the corresponding aggregate in 1919, which, in turn, was considerably lower than the production in 1918. (P. 1019)

The Estonian oil-shale exploitations are described, including the nature of the shale, production in 1920, utilization as fuel, distillation, and concessions to native and foreign interests. (Pp. 1028-9)

Statistics are given showing the production of two promising oil wells in the Tampico district, and the Panuco fields continue prolific. (P. 1030)

At the recent annual meeting of the Agricultural Society at Beziers, a committee was authorized to organize a competition with a view to discovering a practical and economical motor fuel with alcohol as the basis of its composition. (P. 1030)

Information relative to petroleum concessions in Honduras may be obtained from the Bureau of Foreign and Domestic Commerce or any of its district or coöperative offices. (P. 1030)

A process has recently been patented in Japan for the production of a fiber resembling artificial silk from China grass, or ramie. It is intended to patent the process in other countries. (P. 1030)

Trade lists are available in the Commercial Intelligence Division of the Department of Commerce relative to petroleum and mining companies operating in Egypt. (P. 1034)

General Australian tariff revisions or changes are noted with respect to aluminium, lactose, fertilizers, tanned hides, aromatic distilled waters, nonspirituous, tanning and dyeing extracts. (Pp. 1045-6)

CURRENT PUBLICATIONS

NEW BOOKS

- Alchemy: Its Science and Romance. J. E. MERCER. 245 pp. Illustrated. Price, \$3.50. The Macmillan Co., New York.
- Alcohol: Industrial and Power Alcohol. R. C. FARMER. Pitman's Technical Primers. 110 pp. Price, 85 cents. Sir Isaac Pitman & Sons, Ltd., London.
- Alkaloids: Some Microchemical Tests for Alkaloids. CHARLES H. STEPHENSON AND C. E. PARKER. 110 pp. Price, \$4.00. J. B. Lippincott Co., Philadelphia.
- American Pharmaceutical Association Year Book. Vol. 8. 1919. 748 pp. American Pharmaceutical Association, Chicago.
- American Society for Testing Materials: Proceedings. Vol. 21. 1921. 1197 pp. Price, paper, \$10.00; cloth, \$11.00; half-leather, \$12.50. American Society for Testing Materials, Philadelphia.
- Applied Calculus. F. F. P. BISACRE. 446 pp. Price, 10s. 6d. Blackie & Sons, Ltd., London.
- Asphalts and Allied Substances, Their Occurrence, Modes of Production, Uses in the Arts and Methods of Testing. HERBERT ABRAHAM. 2d Edition, revised. 612 pp. 208 illustrations. Price, \$6.00. D. Van Nostrand Co., New York.
- Bacteriology for Students in General and Household Science. ESTELLE D. BUCHANAN AND ROBERT EARLE BUCHANAN. Revised edition. 560 pp. Price, \$2.60. The Macmillan Co., New York.
- Biological Chemistry: Practical Biological Chemistry. GABRIEL BERTRAND AND PIERRE THOMAS. 348 pp. Illustrated. Price, \$3.75. Harcourt, Brace & Co., Inc., New York.
- Biophysics: An Introduction to Biophysics. DAVID BURNS. 435 pp. Illustrated. Price, \$5.50. The Macmillan Co., New York.
- Bleaching and Related Processes. J. MERRITT MATTHEWS. 676 pp. Price, \$8.00. Chemical Catalog Co., Inc., New York.
- Chemistry: Enzyklopädie der Technischen Chemie. FRITZ ULLMANN. Vol. 9. 1921. Urban & Schwarzenberg, Berlin.
- Chemistry: Vocational Chemistry for Students of Agriculture and Home Economics. JOHN L. WILLAMAN J. B. Lippincott Co., Philadelphia.
- Coal: The Analysis of Coal and Its By-products. S. R. ILLINGWORTH AND J. GRIFFITHS. 380 pp. Price, 21s. The Colliery Guardian Co., Ltd., London.
- Coal Manual for Salesmen, Buyers and Users. FRANK R. WADLEIGH. 184 pp. Price, \$2.50. National Coal Mining News, Charleston, W. Va.
- Colloids: Physics and Chemistry of Colloids and Their Bearing on Industrial Questions. Report of a General Discussion held jointly by the FARADAY SOCIETY and the PHYSICAL SOCIETY OF LONDON, October 25, 1920. 190 pp. Price, 2s. 6d. H. M. Stationery Office, London.
- Colloids: Kolloidchemie und Photographie. LÖFFLER-CRAMER. 2d Ed., revised. 112 pp. Price, 7s. 10d. net. Th. Steinkopff, Dresden, Germany.
- Contemporary Science. Edited with an introduction by BENJAMIN HARROW. 253 pp. Price, 95 cents net. Boni & Liveright, New York.
- Electricity: The Emission of Electricity from Hot Bodies. O. W. RICHARDSON. Monographs on Physics. 2d Edition. 320 pp. Price, 16s. Longmans, Green & Co., New York.
- Electricity: Rays of Positive Electricity and Their Application to Chemical Analysis. SIR J. J. THOMSON. 2d Edition. 237 pp. Price, 16s. Longmans, Green & Co., London.
- Engineering Steels. An Exposition of the Properties of Steel for Engineers and Users to Secure Economy in Working and Efficiency of Result. LESLIE AIRCHISON. 427 pp. Illustrated. Price, \$6.00. D. Van Nostrand Co., New York.
- Food Investigation Board. Special Report No. 5. Report on Heat Insulators. SIR ALFRED EWING AND SIR RICHARD GLAZEBROOK, Chairmen. Price, 3s. H. M. Stationery Office, London.
- Food: Vital Factors of Foods; Vitamins and Nutrition. CARLETON ELLIS AND ANNA L. MACLEOD. 500 pp. Illustrated. Price, \$5.00. D. Van Nostrand Co., New York.
- Glue: The Manufacture and Use of Plywood and Glue. B. C. BOULTON. 90 pp. Price, \$2.50. Isaac Pitman & Sons, New York.
- Industrial Fatigue and Efficiency. H. M. VERNON. 264 pp. Illustrated. Price, \$5.00. E. P. Dutton Co., New York.
- Industrial Mathematics Practically Applied. PAUL V. FARNSWORTH. 285 pp. Illustrated. Price, \$2.50. D. Van Nostrand Co., New York.
- Mechanical Handling of Goods; Modern Methods and Equipment for the Mechanical Handling of Goods in and about Factories, Workshops, Warehouses, Stores, Power Houses, etc.; with Data and Numerical Examples from Practice; for Engineers, Works Managers, Commercial Men, Students, and Others. C. H. WOODFIELD. 116 pp. Illustrated. Price, 85 cents. Isaac Pitman & Sons, New York.
- Metallurgy: Handbook of Metallurgy. CARL SCHNABEL. Translated by HENRY LOUIS. Vol. II. 2d Edition. 867 pp. Illustrated. Price, \$7.50. The Macmillan Co., New York.

- Mineralogische Tabellen. P. GROTH AND K. MIELEITNER. 176 pp. R. Oldenbourg, München, Germany.
- Mineralogy: Manual of Determinative Mineralogy. J. VOLNEY LEWIS. 3d revised and enlarged edition. 298 pp. Illustrated. John Wiley & Sons, Inc., New York.
- Oil Shales. H. B. CRONSHAW. Imperial Institute Monographs on Mineral Resources with Special Reference to the British Empire. 80 pp. Price, 5s. net. John Murray, London.
- Organic Chemistry: Theories of Organic Chemistry. FERDINAND HENRICH. Translated and enlarged from the revised German edition of 1918 by TREAT B. JOHNSON AND DOROTHY A. HAHN. John Wiley & Sons, Inc., New York.
- Organische Chemie. R. PUMMERER. Vol. III. Wissenschaftliche Forschungsberichte, Naturwissenschaftliche Reihe. 182 pp. Price, 10s. 9d. Th. Steinkopff, Dresden.
- Patents and Chemical Research. H. E. POTTS. 198 pp. Price, 8s. 6d. The University Press of Liverpool, England.
- Photographic Methods and Calculations. ARTHUR HOLMES. 515 pp. Price, \$6.00. D. Van Nostrand Co., New York.
- Petroleum: The Economics of Petroleum. JOSEPH E. POGUE. 375 pp. Illustrated. Price, \$6.00. John Wiley & Sons, Inc., New York.
- Physical Chemistry: Die Physikalische Chemie in der Inneren Medizin. H. SCHADE. 569 pp. Price, 21s. net. Th. Steinkopff, Dresden, Germany.
- Temperature Measurement: The Measurement of Steady and Fluctuating Temperatures. R. ROYDS. 173 pp. 82 illustrations. Price, \$4.00. D. Van Nostrand Co., New York.

RECENT JOURNAL ARTICLES

- Aluminum-Copper Alloys. ROBERT J. ANDERSON. *Brass World*, Vol. 17 (1921), No. 11, pp. 335-38; No. 12, pp. 364-68.
- Cellulose: La Fabricazione Industriale della Cellulosa al Cloro. Suo Sviluppo Presente ed Avvenire. UMBERTO POMILIO. *Giornale di Chimica Industriale ed Applicata*, Vol. 3 (1921), No. 10, pp. 443-50.
- Clay: A Study of Some Bond Clay Mixtures. D. H. FULLER. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 11, pp. 902-15.
- Cost Accounting: Some Phases of Chemical Cost Accounting. C. B. E. ROSÉN. *Chemical Age*, Vol. 29 (1921), No. 12, pp. 501-04.
- Dyes: Contribution à l'Étude des Colorants de Cuve: Interpretation d'Expériences Exécutées avec des Colorants de la Dibenzoyldiamino-anthraquinone. M. BATTEGAY AND J. CLAUDIN. *Chimie et Industrie*, Vol. 6 (1921), No. 5, pp. 592-95.
- Dyes: On the Fastness of Colors. J. MERRITT MATTHEWS. *Color Trade Journal*, Vol. 9 (1921), No. 6, pp. 213-20.
- Electrochemistry: Notes et Essais sur la Réduction de la Dépense d'Énergie dans les Opérations Electrochimiques. FERNAND BOITARD. *L'Industrie Chimique*, Vol. 8 (1921), No. 94, pp. 437-41.
- Leather: Physiological and Histological Studies on Flayed Skins. ALFRED SEYMOUR-JONES. *Chemical and Metallurgical Engineering*, Vol. 25 (1921), No. 23, pp. 1051-54.
- Leather: Water-Soluble Matter in Vegetable Tanned Hide Bellies. W. J. CHATER AND D. WOODROFFE. *Journal of the Society of Leather Trades' Chemists*, Vol. 5 (1921), No. 11, pp. 359-63.
- Leather: The Warble Fly Problem. ALFRED SEYMOUR-JONES. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 1, pp. 15-26.
- Metallurgy: Some Problems in Nonferrous Metallurgy. J. H. RANSOM. *The Metal Industry*, Vol. 19 (1921), No. 12, pp. 469-72.
- Photography: The Size-Frequency Distribution of Particles of Silver Halide in Photographic Emulsions and Its Relation to Sensitometric Characteristics. II.—The Methods of Determining Size-Frequency Distribution. E. P. WIGHTMAN AND S. E. SHEPPARD. *Journal of Physical Chemistry*, Vol. 25 (1921), No. 7, pp. 561-94.
- Porcelaines Electrotechniques. O. BOUDOARD. *Chimie et Industrie*, Vol. 6 (1921), No. 5, pp. 583-91.
- Potash: Greensand as a Source of Fertilizer Potash. R. NORRIS SHREVE. *The American Fertilizer*, Vol. 55 (1921), No. 14, pp. 35-36.
- Rosin Varnish: The Manufacture of Rosin Varnishes. P. O. SCRIBE. *Paint, Oil and Chemical Review*, Vol. 72 (1922), No. 1, pp. 10, 14, 15.
- Silk in Its Relation to Dyestuffs. EMILE CAGLIOSTRO. *Color Trade Journal*, Vol. 10 (1922), No. 1, pp. 1-5.
- Sulfuric Acid: The Concentration of Sulfuric Acid. JOHN WILFRID PARKES AND EDWIN GILLARD COLEMAN. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 22, pp. 2571-65t.
- Tannin: The Official Method of Tannin Analysis—Some Observations and Suggestions. H. C. REED AND T. BLACKADDER. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 1, pp. 9-15.
- Zinc Dust, Its Uses in the Manufacture and Application of Dyestuffs. J. MERRITT MATTHEWS. *Color Trade Journal*, Vol. 10 (1922), No. 1, pp. 14-16.

GOVERNMENT PUBLICATIONS

Notice—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.

Bureau of Mines

- Destructive Distillation of Mixtures of Oil and Coal. J. D. DAVIS, P. B. PLACE AND G. S. SCOTT. *Reports of Investigations* 2301. 13 pp. Issued December 1921.
- Dust Reduction by Wet Stopers. D. HARRINGTON. *Reports of Investigations* 2291. 5 pp. Issued November 1921.
- Eleventh Annual Report by the Director of the Bureau of Mines, Fiscal Year Ended June 30, 1921. 133 pp. Paper, 10 cents. December 1921.
- Gas Masks for Gases Met in Fighting Fires. A. C. FIELDNER, S. H. KATZ AND S. P. KINNEY. *Technical Paper* 248. 61 pp. Paper, 25 cents.
- Lignite Carbonization—Carbonized Residue Briquets. W. W. ODELL. *Reports of Investigations* 2298. 3 pp. Issued December 1921.
- Miners' Safety and Health Almanac for 1922. Published in cooperation with the U. S. Public Health Service for the use of miners. Compiled by R. C. WILLIAMS. 53 pp. Paper, 5 cents. Published December 1921.
- Monthly Statement of Coal-Mine Fatalities in the United States, September 1921. W. W. ADAMS. 12 pp. Paper, 5 cents.
- Monthly Statement of Coal-Mine Fatalities in the United States, October 1921. W. W. ADAMS. 9 pp. Paper, 5 cents.
- Precautions to Be Observed in Entering Abandoned Exploratory Shafts and Pits. B. O. PICKARD. *Reports of Investigations* 2295. 3 pp. Issued November 1921.
- Present Status of Coal Carbonization at Low Temperatures. J. D. DAVIS. *Reports of Investigations* 2292. 11 pp. Issued November 1921.
- Procedure for Testing Explosives for Permissibility for Use in Gaseous and Dusty Coal Mines, with Test Requirements, Tolerance Limits, and Schedule of Fees. *Schedule* 17. 12 pp. Paper, 5 cents.
- Properties of Typical Crude Oils from the Producing Fields of Northern and Central Texas, Northern Louisiana and Arkansas. E. W. DEAN, M. B. COOKE AND C. R. BOPP. *Reports of Investigations* 2293. 1 p. Issued November 1921.
- Recent Articles on Petroleum and Allied Substances. Compiled by E. H. BURROUGHS. *Reports of Investigations* 305. 23 pp. Issued December 1921.
- Storing Carbide with Explosives. C. E. MUNROE. *Reports of Investigations* 2280 (Revised). 3 pp. 1921.
- Treatment of Tungsten Ores of Boulder County, Colorado. J. P. BONARDI AND J. C. WILLIAMS. Prepared in cooperation with Colorado School of Mines. *Bulletin* 187. *Mineral Technology* 26. 70 pp. Paper, 25 cents.
- Treatment of Carbon Monoxide Poisoning. R. R. SAYERS AND H. R. O'BRIEN. *Reports of Investigations* 2304. 4 pp. Published December 1921.

Bureau of Standards

- Annual Report of Director, 1921. *Miscellaneous Publication* 47. Issued December 1921.
- Color Sensitive Photographic Plates and Methods of Sensitizing by Bathing. F. M. WALTERS, JR., AND RAYMOND DAVIS. *Scientific Paper* 422. Paper, 15 cents.
- Cutting Liquids. E. C. BINGHAM. *Technologic Paper* 204. Paper, 15 cents. Issued January 1922.
- Influence of Phosphorus upon the Microstructure and Hardness of Low Carbon Open Hearth Steels. E. C. GROESBECK. *Technologic Paper* 203. Paper, 10 cents. Published December 1921.
- Recommended Specification for Interior Varnish. *Circular* 117. Paper, 5 cents.
- Recommended Specification for Water-Resisting Spar Varnish. *Circular* 103 (2nd Edition). Paper, 5 cents.
- Specific Volume of Liquid Ammonia. C. S. CRAIG AND D. R. HARPER, 3RD. *Scientific Paper* 420. Paper, 5 cents. Issued October 1921.

Congressional Committee

- Potash. Hearing before the Committee on Finance, United States Senate, 67th Congress, Second Session on H. R. 7456. An act to provide revenue, to regulate commerce with foreign countries, to encourage the industries of the United States and for other purposes. *Tariff Schedule* 15—Free List. Part 53. 211 pp. December 29, 1921. Part 54. 406 pp. December 30, 1921.
- Phosphate, Oil, Oil Shale, Gas, and Sodium. Joint Resolution extending the time for the performance of certain acts under the Act of Congress approved February 25, 1920, entitled "An Act to promote the mining of coal, phosphate, oil, oil shale, gas and sodium on the public domain," and for other purposes. H. J. Res. 253. January 9, 1922.

Department of Agriculture

- Distillation of Stumpwood and Logging Waste of Western Yellow Pine. M. G. DONK, C. H. SHATTUCK AND W. D. MARSHALL. *Department Bulletin* 1003. 69 pp. Paper, 15 cents. Issued December 5, 1921.
- Drying Crude Drugs. G. A. RUSSELL. *Farmers' Bulletin* 1231. 16 pp. Issued November 1921.
- Getting Our Potash. W. H. ROSS. Separate 851 from Yearbook of the Department, 1920. 14 pp. Paper, 5 cents.
- Improved Method of Making Sugar-Beet Sirup. C. O. TOWNSEND AND SIDNEY F. SHERWOOD. *Farmers' Bulletin* 1241. 16 pp. Issued November 1921.
- Influence of Relative Humidity and Moisture Content of Wheat on Milling Yields and Moisture Content of Flour. J. H. SHOLLENBERG. *Department Bulletin* 1013. 12 pp. Paper, 5 cents. Issued December 22, 1921.
- Principles of the Liming of Soils. E. C. SHOREY. *Farmers' Bulletin* 924 (Reprint). Paper, 5 cents.
- Report of the Chemist. C. L. ALSBERG. 48 pp. December 1921. (Covering the work of the Bureau of Chemistry for the fiscal year ended June 30, 1921.)
- Volume Variation of Bottled Foods. H. RUNKEL AND J. C. MUNCH. *Department Bulletin* 1009. 20 pp. Issued December 16, 1921.

Geological Survey

- Gold, Silver, Copper, Lead, and Zinc in South Dakota and Wyoming in 1920. Mines Report. C. W. HENDERSON. Separate from Mineral Resources of the United States, 1920, Part I. 6 pp.
- Lignite in the Western Part of the Fort Berthold Indian Reservation South of Missouri River, North Dakota. C. M. BAUER AND F. A. HERALD. Separate from Contributions to Economic Geology, 1921, Part II. 62 pp. Published December 3, 1921.
- Lime in 1920. C. F. LOUGHLIN AND A. T. COONS. Separate from Mineral Resources of the United States, 1920, Part II. 12 pp.
- Manganese and Manganiferous Ores in 1920. H. A. C. JENISON. Separate from Mineral Resources of the United States, 1920, Part I. 13 pp. Published December 27, 1921.
- Microscopic Determination of the Nonopaque Minerals. E. S. LARSEN. *Bulletin* 679. 294 pp. Paper, 30 cents.
- Mineral Resources of the United States, 1918. Part II—Nonmetals. R. W. STONE, Geologist in Charge. 1557 pp. Cloth. 1921.
- Natural-Gas Gasoline in 1919. E. G. SIEVERS. Separate from Mineral Resources of the United States, 1919, Part II. 16 pp. Published December 7, 1921.
- Ore Deposits of Cedar Mountain Mineral County, Nevada. ADOLPH KNOPF. *Bulletin* 725-H. Separate from Contributions to Economic Geology, 1921, Part I. 22 pp. Published November 19, 1921.
- Ore Deposits of the Salmon River District, Portland Canal Region, Alaska. L. G. WESTGATE. *Bulletin* 722-C. Separate from Mineral Resources of Alaska, 1920-C. 24 pp.
- Pyrite at the Haile Mine, Kershaw, South Carolina, with a Note on Pyritization at the Brewer Mine near Jefferson. F. C. SCHRADER. *Bulletin* 725-F. Separate from Contributions to Economic Geology, 1921, Part I. 15 pp. Published October 21, 1921.
- Round Mountain District, Nevada. H. G. FERGUSON. *Bulletin* 725-I. Separate from Contributions to Economic Geology, 1921, Part I. 24 pp. Published November 21, 1921.
- Sand and Gravel in 1920. L. M. BEACH. Separate from Mineral Resources of the United States, 1920, Part II. 10 pp.
- Secondary Metals in 1920. J. P. DUNLOP. Separate from Mineral Resources of the United States, 1920, Part I. 15 pp. Published November 11, 1921.
- Silica in 1920. L. M. BEACH. Separate from Mineral Resources of the United States, 1920, Part II. 2 pp. Published October 11, 1921.
- Silver, Copper, Lead, and Zinc in the Central States in 1920. Mines Report. J. P. DUNLOP AND F. BEGEMAN. Separate from Mineral Resources of the United States, 1920, Part I. 38 pp. Published November 11, 1921.
- Superpower System for the Region between Boston and Washington. W. S. MURRAY AND OTHERS. *Professional Paper* 123. 261 pp. 1921.
- Taylor Creek Tin Deposits, New Mexico. J. M. HILL. *Bulletin* 725-G. Separate from Contributions to Economic Geology, 1921, Part I. 13 pp. Published November 18, 1921.

Public Health Service

- Studies on the Treatment and Disposal of Industrial Wastes. *Bulletin* 118. Paper, 10 cents. 1921.

Tariff Commission

- Tariff Information Surveys. Revised Edition, 1921. C-27. Articles in Paragraphs 162 and 163 of Tariff Act of 1913 and related articles in other paragraphs. Zinc Industry. 82 pp. Paper, 5 cents.
- Production Costs in Lithopone Industry. First Six Months of 1921. *Tariff Information Series* 24. 12 pp. Paper, 5 cents.

MARKET REPORT—JANUARY, 1922

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

	Jan. 1	Jan. 15
Acid, Boric, cryst., bbls.....lb.	.12 ³ / ₄	.12 ³ / ₄
Hydrochloric, com'l, 20°.....lb.	.01 ¹ / ₄	.01 ¹ / ₄
Hydriodic.....oz.	.19	.19
Nitric, 42°.....lb.	.06 ¹ / ₄	.06 ¹ / ₄
Phosphoric, 50% tech.....lb.	.12	.10
Sulfuric, C. P.....lb.	.07	.07
Chamber, 66°.....ton	17.00	17.00
Oleum 20%.....ton	22.00	22.00
Alum, ammonia, lump.....lb.	̄.03 ¹ / ₂	.03 ¹ / ₂
Aluminium Sulfate (iron-free).....lb.	.03	.03
Ammonium Carbonate, pwd.....lb.	*.07	*.07
Ammonium Chloride, gran.....lb.	.07 ¹ / ₂	.07 ¹ / ₂
Ammonia Water, drums, 26°.....lb.	.07 ¹ / ₂	.07 ¹ / ₂
Arsenic, white.....lb.	.07	.07 ¹ / ₄
Barium Chloride.....ton	50.00	50.00
Nitrate.....lb.	*.07	*.06 ¹ / ₂
Barytes, white.....ton	28.00	28.00
Bleaching Powd., 35%, works, 100 lbs.	2.25	2.25
Borax, cryst., bbls.....lb.	.05 ¹ / ₄	.05 ¹ / ₄
Bromine, pure.....lb.	.20	.20
Calcium Chloride, fused, f. o. b.		
N. Y.....ton	24.75	24.75
Chalk, precipitated, light.....lb.	.03 ¹ / ₂	.03 ¹ / ₂
China Clay, imported.....ton	18.00	18.00
Copper Sulfate.....100 lbs.	5.55	5.55
Feldspar.....ton	8.00	8.00
Fuller's Earth.....100 lbs.	1.00	1.00
Iodine, resublimed.....lb.	3.80	3.80
Lead Acetate, white crystals.....lb.	.11	.11
Nitrate.....lb.	.15	.15
Red American.....100 lbs.	.08	.08
White American.....100 lbs.	.07 ¹ / ₄	.07 ¹ / ₄
Lime Acetate.....100 lbs.	1.75	1.75
Lithium Carbonate.....lb.	1.50	1.50
Magnesium Carbonate, tech.....lb.	.06	.06
Magnesite.....ton	72.00	72.00
Mercury flask.....75 lbs.	*52.00	*52.00
Phosphorus, yellow.....lb.	*.28	*.25
Plaster of Paris.....100 lbs.	1.50	1.50
Potassium Bichromate.....lb.	.10 ¹ / ₄	.10
Bromide, imported.....lb.	*.14	*.13
Carbonate, calc., 80-85%.....lb.	.04 ¹ / ₂	.04 ¹ / ₂
Chlorate, cryst.....lb.	*.06	*.06
Hydroxide, 88-92%.....lb.	*.06	*.06
Iodide, bulk.....lb.	2.90	2.90
Nitrate.....lb.	.08	.08
Permanganate, U. S. P.....lb.	*.15	*.14
Salt Cake, bulk.....ton	17.00	17.00
Silver Nitrate.....oz.	.44 ¹ / ₂	.43 ¹ / ₂
Soapstone, in bags.....ton	12.00	12.00
Soda Ash, 58%, bags.....100 lbs.	*1.85	*1.75
Caustic, 76%.....100 lbs.	*3.70	*3.70
Sodium Acetate.....lb.	.04	.04
Bicarbonate.....100 lbs.	2.30	2.30
Bichromate.....lb.	.07 ¹ / ₂	.07 ¹ / ₂
Chlorate.....lb.	.07 ¹ / ₂	.07
Cyanide.....lb.	.26	.26
Fluoride, technical.....lb.	.10	.10
Hyposulfite, bbls.....100 lbs.	3.50	3.50
Nitrate, 95%.....100 lbs.	2.32 ¹ / ₂	2.37 ¹ / ₂
Silicate, 40°.....lb.	.01	.01
Sulfide, 60% fused.....lb.	*.04 ¹ / ₄	*.04 ¹ / ₄
Bisulfite, powdered.....lb.	.04 ¹ / ₂	.04 ¹ / ₂
Strontium Nitrate.....lb.	*.11	*.11
Sulfur, flowers.....100 lbs.	3.00	3.00
Crude.....long ton	20.00	20.00
Talc, American, white.....ton	18.00	18.00
Tin Bichloride, .50% sol'n.....lb.	.10 ¹ / ₄	.10 ¹ / ₄
Oxide.....lb.	.38	.38
Zinc Chloride, U. S. P.....lb.	.35	.35
Oxide, bbls.....lb.	.08	.08

ORGANIC CHEMICALS

Acetanilide.....lb.	*.29	*.29
Acid, Acetic, 28 p. c.....100 lbs.	2.50	2.50
Glacial.....lb.	.09	.09
Acetylsalicylic.....lb.	.75	.75
Benzoic, U. S. P., ex-toluene.....lb.	.60	.55
Carbolic, cryst., U. S. P., drs.....lb.	.11	.11
50- to 110-lb. tins.....lb.	.21	.21
Citric, crystals, bbls.....lb.	*.44	*.43

	Jan. 1	Jan. 15
Acid (Concluded)		
Oxalic, cryst., bbls.....lb.	.14 ¹ / ₂	.14 ¹ / ₂
Pyrogallic, resublimed.....lb.	1.75	1.75
Salicylic, bulk, U. S. P.....lb.	.24	.24
Tartaric, crystals, U. S. P.....lb.	*.26	*.25
Trichloroacetic, U. S. P.....lb.	4.40	4.40
Acetone, drums.....lb.	.12 ¹ / ₂	.12 ¹ / ₂
Alcohol, denatured, complete.....gal.	.46	.43
Ethyl, 190 proof.....gal.	4.85	4.85
Amyl Acetate.....gal.	2.15	2.15
Camphor, Jap, refined.....lb.	.92	.90
Carbon Bisulfide.....lb.	.06 ¹ / ₂	.06 ¹ / ₂
Tetrachloride.....lb.	.10 ¹ / ₂	.10 ¹ / ₂
Chloroform, U. S. P.....lb.	*.38	*.38
Creosote, U. S. P.....lb.	.40	.40
Cresol, U. S. P.....lb.	.17	.17
Dextrin, corn.....100 lbs.	2.50	2.50
Imported Potato.....lb.	.08 ¹ / ₂	.08 ¹ / ₂
Ether, U. S. P., conc., 100 lbs.....lb.	.14	.14
Formaldehyde.....lb.	*.10 ¹ / ₂	*.10
Glycerol, dynamite, drums.....lb.	.14	.15
Methanol, pure, bbls.....gal.	.75	.75
Pyridine.....gal.	1.75	1.75
Starch, corn.....100 lbs.	1.93	1.93
Potato, Jap.....lb.	.06	.06
Rice.....lb.	.18	.18
Sago.....lb.	.04	.04

OILS, WAXES, ETC.

Beeswax, pure, white.....lb.	.33	.33
Black Mineral Oil, 29 gravity.....gal.	.22	.22
Castor Oil, No. 3.....lb.	.10 ¹ / ₂	.10 ¹ / ₂
Ceresin, yellow.....lb.	.07 ¹ / ₂	.07 ¹ / ₂
Corn Oil, crude, tanks, mills.....lb.	.06 ¹ / ₄	.06 ¹ / ₄
Cottonseed Oil, crude, f. o. b. mill.....lb.	.06 ¹ / ₂	.06 ¹ / ₂
Linseed Oil, raw (car lots).....gal.	.69	.72
Menhaden Oil, crude (southern).....gal.	.35	.38
Neat's-foot Oil, 20°.....gal.	1.25	1.32
Paraffin, 128-130 m. p., ref.....lb.	.06	.06
Paraffin Oil, high viscosity.....gal.	.45	.45
Rosin, "F" Grade, 280 lbs.....bbl.	5.50	5.30
Rosin Oil, first run.....gal.	.36	.36
Shellac, T. N.....lb.	.65	.65
Spermaceti, cake.....lb.	.30	.30
Sperm Oil, bleached winter, 38°.....gal.	1.73	1.73
Stearic Acid, double-pressed.....lb.	.10	.10
Tallow Oil, acidless.....gal.	.77	.77
Tar Oil, distilled.....gal.	.60	.60
Turpentine, spirits of.....gal.	.91	.89

METALS

Aluminium, No. 1, ingots.....lb.	.17	.17
Antimony, ordinary.....100 lbs.	4.55	4.45
Bismuth.....lb.	1.55	1.65
Copper, electrolytic.....lb.	.13 ¹ / ₄	.13 ¹ / ₄
Lake.....lb.	.13 ¹ / ₄	.13 ¹ / ₄
Lead, N. Y.....lb.	.04 ¹ / ₄	.04 ¹ / ₄
Nickel, electrolytic.....lb.	.41	.41
Platinum, refined, soft.....oz.	93.00	93.00
Quicksilver, flask.....75 lbs. ea.	52.00	52.00
Silver, foreign.....oz.	.66 ¹ / ₄	.66 ¹ / ₄
Tin.....lb.	.33	.32 ¹ / ₂
Tungsten Wolframite.....per unit	2.50	2.50
Zinc, N. Y.....100 lbs.	5.15	5.10

FERTILIZER MATERIALS

Ammonium Sulfate, export.....100 lbs.	2.60	2.60
Blood, dried, f. o. b. N. Y.....unit	3.50	3.50
Bone, 3 and 50, ground, raw.....ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia.....	2.25	2.25
Fish Scrap, domestic, dried, f. o. b. works.....unit	3.25 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:		
Florida Pebble, 68%.....ton	5.00	5.00
Tennessee, 78-80%.....ton	8.00	8.00
Potassium Muriate, 80%.....unit	.75	.75
Pyrites, furnace size, imported.....unit	.14	.14
Tankage, high-grade, f. o. b. Chicago.....unit	3.00 & .10	3.00 & .10

*Resale or Imported (not an American maker's price).



COAL-TAR CHEMICALS

	Jan. 1	Jan. 15		Jan. 1	Jan. 15
Crudes			Acid Colors (Concluded)		
Anthracene, 80-85%.....lb.	.75	.75	Fuchsin.....lb.	2.00	2.00
Benzene, pure.....gal.	.29	.29	Orange III.....lb.	.50	.50
Cresol, U. S. P.....lb.	.17	.17	Red.....lb.	1.00	1.00
Cresylic Acid, 97-99%.....gal.	.80	.80	Alkali Blue, domestic.....lb.	4.50	4.50
Naphthalene, flake.....lb.	.07 1/2	.07 1/2	Azo Carmine.....lb.	4.00	4.00
Phenol, drums.....lb.	.11	.11	Azo Yellow.....lb.	1.50	1.50
Toluene, pure.....gal.	.30	.30	Erythrosin.....lb.	7.50	7.50
Xylene, 2 deg. dist. range.....gal.	.45	.45	Indigotin, conc.....lb.	2.50	2.50
			Paste.....lb.	1.50	1.50
Intermediates			Naphthol Green.....lb.	1.60	1.60
Acids:			Ponceau.....lb.	.80	.80
Anthranilic.....lb.	1.10	1.10	Scarlet 2R.....lb.	.70	.70
Benzoic tech.....lb.	.50	.50			
Broenner's.....lb.	1.55	1.55	Direct Colors		
Cleve's.....lb.	1.50	1.50	Black.....lb.	.70	.70
Gamma.....lb.	2.25	2.25	Blue 2B.....lb.	.60	.60
H.....lb.	.90	.90	Brown R.....lb.	.85	.85
Metanilic.....lb.	1.60	1.60	Fast Red.....lb.	2.35	2.35
Monosulfonic F.....lb.	2.30	2.30	Yellow.....lb.	1.50	1.50
Naphthionic, crude.....lb.	.65	.65	Violet, conc.....lb.	1.10	1.10
Nevile & Winther's.....lb.	1.30	1.30	Chrysophenine, domestic.....lb.	1.10	1.10
Phthalic.....lb.	.38	.38	Congo Red, 4B Type.....lb.	.90	.90
Picric.....lb.	.30	.30	Primuline, domestic.....lb.	3.00	3.00
Sulfanilic.....lb.	.27	.27			
Tobias'.....lb.	2.00	2.00	Oil Colors		
Aminoazobenzene.....lb.	1.15	1.15	Black.....lb.	.70	.70
Aniline Oil.....lb.	.17	.17	Blue.....lb.	1.25	1.25
Aniline Salt.....lb.	.25	.25	Orange.....lb.	.95	.95
Antraquinone.....lb.	1.50	1.50	Red III.....lb.	1.65	1.65
Bayer's Salt.....lb.	1.00	1.00	Scarlet.....lb.	1.00	1.00
Benzaldehyde, tech.....lb.	.45	.45	Yellow.....lb.	1.25	1.25
U. S. P.....lb.	1.25	1.25	Nigrosine Oil, soluble.....lb.	.90	.90
Benzidine (base).....lb.	.90	.90			
Benzidine Sulfate.....lb.	.70	.70	Sulfur Colors		
Diaminophenol.....lb.	5.50	5.50	Black.....lb.	.20	.20
Dianisidine.....lb.	4.75	4.75	Blue, domestic.....lb.	.70	.70
p-Dichlorobenzene.....lb.	.15	.15	Brown.....lb.	.35	.35
Diethylaniline.....lb.	1.00	.90	Green.....lb.	1.00	1.00
Dimethylaniline.....lb.	.40	.40	Yellow.....lb.	.75	.75
Dinitrobenzene.....lb.	.21	.21			
Dinitrotoluene.....lb.	.25	.25	Chrome Colors		
Diphenylamine.....lb.	.60	.60	Alizarin Blue, bright.....lb.	5.00	5.00
G Salt.....lb.	.70	.70	Alizarin Red, 20% paste.....lb.	.60	.60
Hydroquinol.....lb.	1.35	1.35	Alizarin Yellow G.....lb.	.85	.85
Metol (Rhodol).....lb.	3.00	3.50	Chrome Black, domestic.....lb.	.65	.65
Monochlorobenzene.....lb.	.10	.10	Chrome Blue.....lb.	.75	.75
Monoethylaniline.....lb.	1.00	1.00	Chrome Green, domestic.....lb.	1.50	1.50
a-Naphthylamine.....lb.	.30	.30	Chrome Red.....lb.	1.75	1.75
b-Naphthylamine (Sublimed).....lb.	1.50	1.50	Gallocyanin.....lb.	2.30	2.30
b-Naphthol, dist.....lb.	.30	.30			
m-Nitroaniline.....lb.	.85	.85	Basic Colors		
p-Nitroaniline.....lb.	.77	.77	Auramine, O, domestic.....lb.	1.80	1.80
Nitrobenzene, crude.....lb.	.10	.10	Auramine, OO.....lb.	3.00	3.00
Rectified (Oil Mirbane).....lb.	.11 1/2	.11 1/2	Bismarck Brown R.....lb.	.70	.70
p-Nitrophenol.....lb.	.75	.75	Bismarck Brown G.....lb.	1.00	1.00
p-Nitrosodimethylaniline.....lb.	—	—	Chrysoidine R.....lb.	.75	.75
o-Nitrotoluene.....lb.	.15	.15	Chrysoidine Y.....lb.	.75	.75
p-Nitrotoluene.....lb.	.70	.70	Green Crystals, Brilliant.....lb.	2.25	2.25
m-Phenylenediamine.....lb.	1.10	1.10	Indigo, 20% paste.....lb.	.45	.45
p-Phenylenediamine.....lb.	1.60	1.60	Fuchsin Crystals, domestic.....lb.	3.00	3.00
Phthalic Anhydride.....lb.	.38	.38	Magenta Acid, domestic.....lb.	2.00	2.00
Primuline (Base).....lb.	3.00	3.00	Malachite Green, crystals.....lb.	1.60	1.60
R Salt.....lb.	.60	.60	Methylene Blue, tech.....lb.	1.50	1.50
Resorcinol, tech.....lb.	1.50	1.50	Methyl Violet 3 B.....lb.	1.75	1.75
U. S. P.....lb.	2.00	2.00	Nigrosine, spts. sol.....lb.	.70	.70
Schaeffer Salt.....lb.	.70	.70	Water sol., blue.....lb.	.60	.60
Sodium Naphthionate.....lb.	.70	.70	Jet.....lb.	.90	.90
Thiocarbanilide.....lb.	.40	.40	Phosphine G., domestic.....lb.	2.50	2.50
Tolidine (Base).....lb.	1.20	1.20	Rhodamine B, extra conc.....lb.	8.50	8.50
Toluidine, mixed.....lb.	.30	.30	Victoria Blue, base, domestic.....lb.	3.50	3.50
o-Toluidine.....lb.	.20	.20	Victoria Green.....lb.	1.50	1.50
p-Toluidine.....lb.	1.25	1.25	Victoria Red.....lb.	7.00	7.00
m-Toluylenediamine.....lb.	1.10	1.10	Victoria Yellow.....lb.	7.00	7.00
Xylidine, crude.....lb.	.45	.45			
COAL-TAR COLORS					
Acid Colors					
Black.....lb.	.80	.80			
Blue.....lb.	1.50	1.50			

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White sugars of the highest grade are produced from syrups clarified with FILTER-CEL because all suspended solids are removed. Chemical defectants, such as lime and sulphur, can be eliminated, and a complete recovery secured from the cake.

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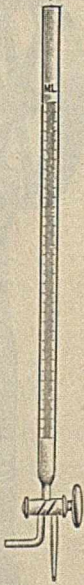
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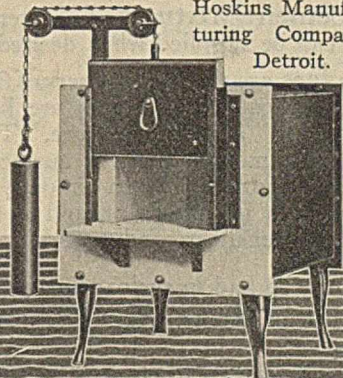
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Source, Uses, Where, HOW and WHY

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Various trade names are given to it but the Manufacturing methods are more or less identical

Electric Furnaces of the resistance type convert

Pure Silica Sand (SiO_2) and, Petroleum Coke (C), with small additions of salt and sawdust (between 1820°C . and 2250°C .) into Silicon Carbide Above 2250°C . Silicon Carbide dissociates or breaks down into graphite (C) and silicon (Si).

The Abrasive Material is formed in and confined to the central portion of the furnace product. This material is also used in mixtures where extreme refractoriness is demanded.

A Refractory Material commonly termed Firesand is the partially converted charge next to the crystalline silicon carbide mass. It is usually given a trade name as Crystolon Firesand, etc.

Crystolon Firesand consists of small amounts of silica sand, carbon, partially converted material and 70-75% silicon carbide (SiC).

Mixtures of Firesand and a refractory clay such as Kaolin serve as "rammed-up" linings in furnaces. Silicate of soda is sometimes used sparingly in mixing.

Norton Company does not supply mixtures containing clay. Most foundrymen prefer to prepare their own.

Crystolon Cement Mixtures of greater refractoriness can be supplied when desired.

Brass Founders are the largest users of firesand. Electric and gas pit furnaces are lined by "ramming up" a damp mixture. The core or shape is removed and the surface is repaired and trowelled to a smooth lining. Refractoriness is important and a firesand lining will meet most conditions.

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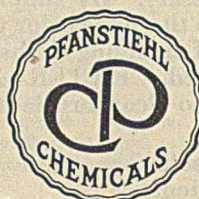
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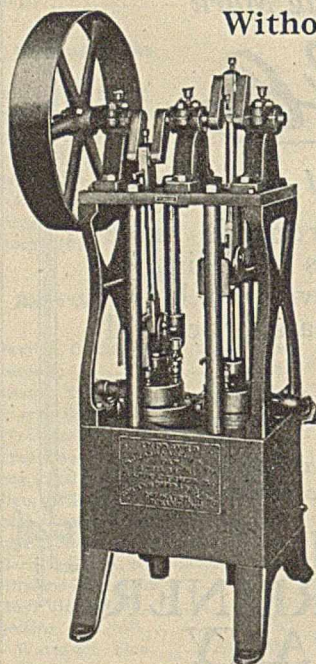
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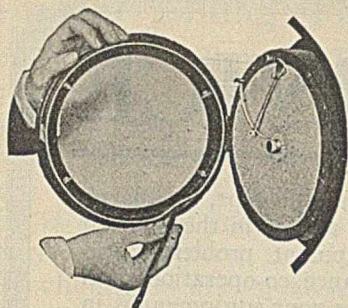
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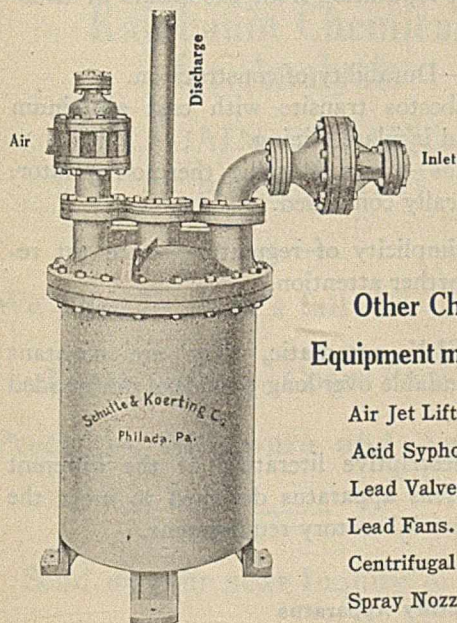
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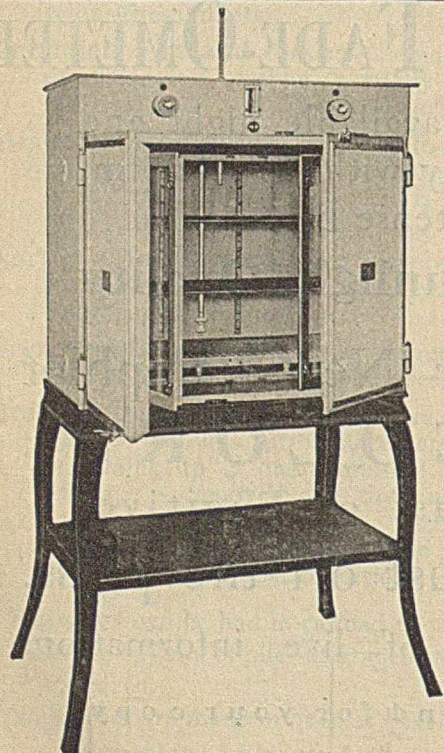
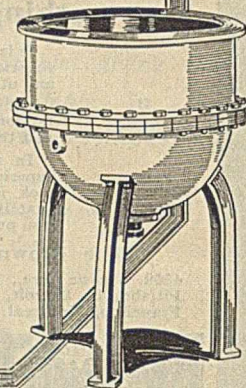
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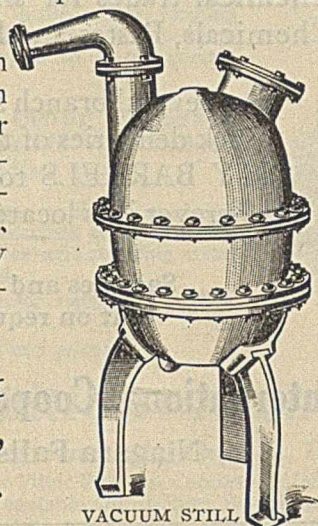
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822,424	June 5, 1906
836,558	Nov. 20, 1906
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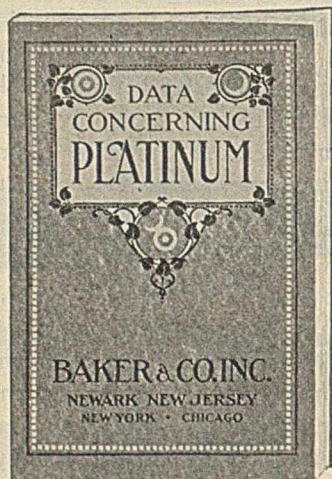
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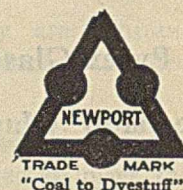
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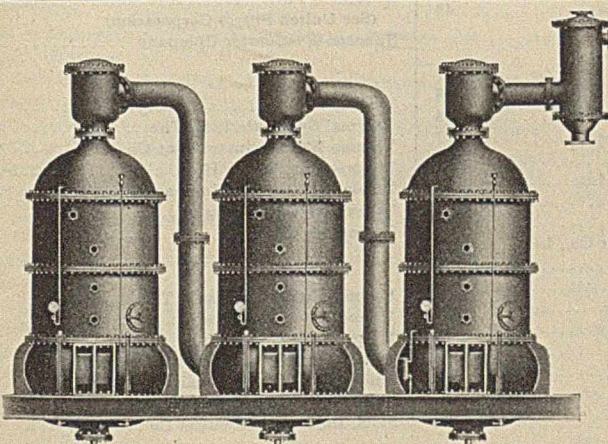
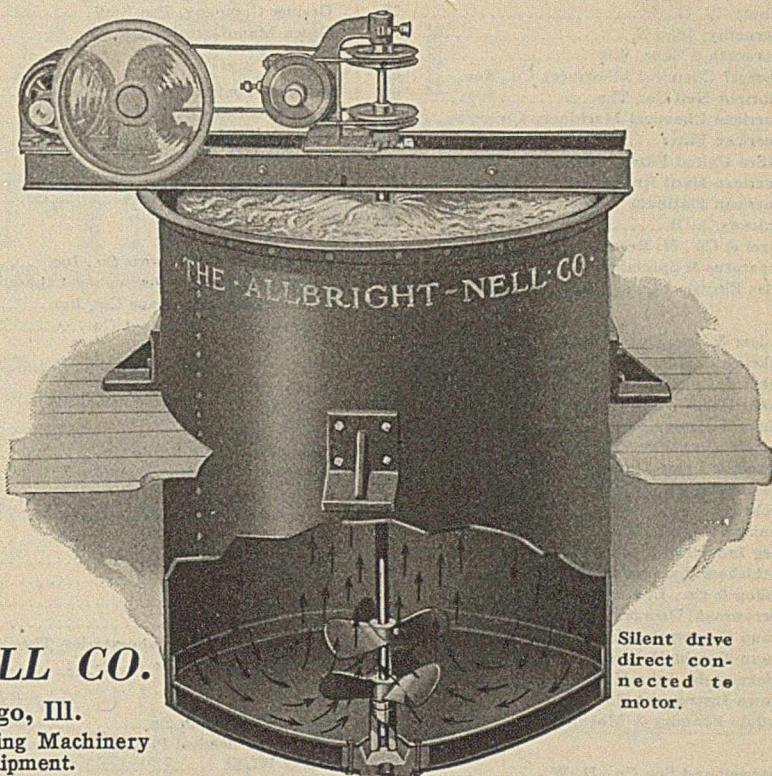
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