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A Frank Document

SOME months ago a restricted number of copies of the monograph on "The Chemical Industry," prepared by a group in Germany at the request of the League of Nations, were confidentially handed about, but not until the document with the answering statements prepared in Great Britain, France, Italy, and Poland was made generally available has it been possible for much to be said upon the subject. The complete document can now be had through the World Peace Foundation, 40 Mount Vernon Street, Boston, and we venture the opinion that the majority of readers will find it an amazingly frank statement.

The Preparatory Committee for the International Economic Conference held in Geneva in May of this year decided that it was desirable to submit to the Conference a series of memoranda setting forth the present position in certain major industries, including the chemical industry. The Fachgruppe Chemie des Reichsverbandes der Deutschen Industrie was selected by the committee as the organization most competent to prepare this memorandum, which is divided into twelve major headings, outlined by the Preparatory Committee of the League. These headings include a preliminary survey of the essential conditions governing the development of the industry in recent years, capacity for output, actual output, employment, hours of work, wages, raw materials, customs and tariffs, exports and imports, consumption, prices, and industrial organization. Although much of the discussion is necessarily based upon statistical data, the monograph states that such material is extraordinarily incomplete and in numerous places one is surprised to note that outside of the United States of America official figures necessary to support the arguments are unobtainable. Notwithstanding this, free use is made of statistics with the warning that allowances must be made in many cases.

In discussing conditions essential to the development of the industry, special reference is made to markets, technical developments, the supply of raw materials, and such factors as tariffs and customs, which are described as non-economic factors. The familiar fact that since 1914 the world has acquired capacity to produce far in excess of capacity to consume certain lines of chemical commodities is stressed and special attention given to the change in the relative position of the chief consuming and producing countries. It is estimated that there has been an increase of 35 to 40 per cent in chemical production, and whereas the order of participation in 1913 was United States 34 per cent, Germany 24 per cent, followed by Great Britain and France, the same order is maintained today, but America's share has risen to 47 per cent, while Germany's has fallen to 17 per cent.

The monograph then discusses in some detail the reasons for these changes and shows that chemical production is most economically carried out in single great units. One senses that Germany is believed to be the most favorably placed for the operation of such mass production, and that therefore an effort should be made to restore pre-war conditions. Speaking of aniline dyes, the monograph states, "This concentration in a single country was of decisive importance for the development of this industry into a remunerative large-scale industry. Only the custom of the entire world market or of a very large proportion of it could guarantee the aniline dyes industry sufficient return to render technical work on the scale described above an economic possibility." Nations are urged to look upon the chemical industry from the world, rather than from the national, economic point of view. Reference to the importance of the chemical industries to other lines of production is left out of consideration, as is also one of the most important points of all; namely, the recognition that a chemical industry has a value to a nation that cannot be measured merely by an economic standard and that the World War has taught a lesson that progressive nations are not likely soon to forget.

In the reply prepared by the Association of British Chemical Manufacturers, reference is again made to the fact that the United States of America still remains the only country which can be regarded as possessing adequate statistics, and the point is made that a discussion of the chemical industry from the world point of view is difficult, because of the difference in grouping products as chemical or non-chemical in different countries. Coal is regarded as the real, final, cheap raw material of the chemical industry, though it is not discussed in the German monograph. Furthermore, it is claimed that while overproduction in some lines and high tariffs are regrettable from a purely economic point of view, one finds himself in sympathy with the desire of countries, even the smaller ones, to render themselves somewhat independent as regards supplies of vital necessities. The expansion of a chemical industry leads to the development of numerous research centers, offering on the one hand opportunities for the trained chemist and on the other hand a further important training for the postgraduate chemist. The argument for the concentration of at least certain branches of the chemical industry in one country is met by reference to the example of the prosperous Swiss dyestuff industry which grew side by side with the German industry, and by insistence that the argument does not necessarily apply to other industries. "It cannot be contended, for example, that because in England and America as well as in Germany there are synthetic ammonia industries, none can succeed because the work is not concentrated in one country." It is also shown that prior to 1914 there was not the concentration of technic and manufacture in Germany which the German monograph appears to suggest, but that the industry then consisted of at least nine major firms, all engaged in vigorous competition.

It is too much to expect that countries which were compelled to establish their own chemical industries in order to secure supplies of chemical products will now consent to their curtailment, much less to their abandonment. Although a system whereby each country would make that for which it is best fitted and exchange these goods for others from lands better equipped to manufacture them is no doubt ideal in theory, it is very difficult in practice. However regrettable it may be from the point of view of some countries that chemical industries are developed within the borders of states desiring to become as independent as possible, that national tendency will no doubt persist even though it may not be best from the standpoint of world economics.

"The object of tariff barriers goes somewhat beyond that of protecting self-sufficiency, profit, or employment, for they render secure an outlet for the abilities and desires of educated workers and craftsmen and afford the workers an opportunity for the exercise of the greatest amount of skill." The British Association feels that a solution of the difficulties emphasized in the German monograph can probably be found in international agreements which may be concluded between the individual national industries after they have sufficiently amalgamated their own interests—a movement already well under way in Europe.

The example given to show the development of new competition which may easily change the position of a producing country or of a particular chemical is of special interest. Sulfuric acid is taken as the example and at least five reasons are given why the world production of sulfuric acid may be expected to decline. (1) In the superphosphate industry there is a tendency to produce elemental phosphorus from which phosphoric acid is made for the purpose of forming compounds with ammonia or other nitrogen bases or with potassium. (2) In the nitric acid industry the use of sulfuric acid for the decomposition of Chilean nitrate will be displaced through the manufacture of nitric acid for the oxidation of ammonia. (3) The production of hydrochloric acid from chlorine, produced as a by-product in the electrolytic manufacture of caustic, by combination with hydrogen, will decrease the demand for sulfuric acid. (4) The chemical principle of double decomposition will be used to eliminate the direct use of sulfuric acid as, for example, the manufacture of ammonium nitrate from sodium nitrate and the sulfate of ammonia, the sulfate radical being obtained by the interaction between gypsum and ammonium bicarbonate. (5) Catalytic processes taking place in the gaseous phase tend to eliminate the use of sulfuric acid. Such processes are the manufacture of formic and acetic acids and numerous other simple organic compounds.

The French document points out that, so far as world production is concerned, the situation has not improved since the war taught the various governments the necessity of national independence in matters chemical and that chemistry is fundamental to industry as well as to national defense. The rapidity of technical progress is stressed for, as we know, new processes which formerly were required to wait several years after discovery before application are now put to the test soon after their perfection. Science and technology are making such rapid progress that producing nations must be constantly on the alert. World conditions are changed and it would seem impossible to restore pre-war equilibrium.

The suggestion is advanced by the French that the first step is to conclude agreements between the industrialists themselves preliminary to interstate agreements. This might lead to the curtailment of new chemical industries in nations as yet without them, offering instead assurances that such products could be obtained on easy and advantageous terms, the free movement of raw materials on a liberal policy which would freely compensate those countries possessing monopolies, and finally a rationing of products in conformity with national and international requirements.

The Italian discussion offers proof of the possibility of development of a chemical industry even in circumstances unfavorable as regards raw materials, and stresses that after all "human ingenuity is the main factor of success." The details concerning the development of the chemical industry in Italy offer proof of this contention.

The Polish document, after emphasizing that "in all states which have given proof of their vitality and are developed economically and politically, the tendency to seek independence in the chemical industry was stimulated by the war," and that many essentials in civilization depend on the standard of chemical production, pleads for a freer movement of raw material and for lessened restrictions concerning the free movement of workers in search of employment. The point is also made that in countries without a chemical industry higher prices have always been demanded for the chemicals produced elsewhere and that "as long as there are armies with guns, rifles, and other arms, no government will be justified in leaving its country entirely without chemical weapons."

In laying aside this interesting document, which can be had for a dollar, we are reminded of a point made in "The German Alarm Clock," which appeared in THIS JOURNAL some ten years ago—namely, that for years after the war the effects of having awakened the world to the advantages of applied science would adversely affect German industry. Without saying so directly, the German monograph gives evidence of dissatisfaction with the change in world conditions, chemically speaking, which the new order of things has brought about and a desire for a rapid return to former world conditions. The old equilibrium is not likely to return, and people generally having come to see the vital necessity of a chemical industry, the document before us perhaps assumes it greatest importance as Exhibit A in future tariff discussions.

Blazing a Trail

"IF A man write a better book, preach a better sermon, or make a better mouse-trap than his neighbor, though he build his house in the woods, the world will make a beaten path to his door." When men come from Florida, California, Porto Rico, Maine, and many points much nearer; when the roster includes those from China, Czechoslovakia, Germany, and Great Britain; when the list shows presidents of corporations, directors of research, presidents of colleges, chairmen of departments, and representatives of various ranks in both industrial and academic organizations, one is forced to the conclusion that there must be something real in the idea upon which the experiment at State College, Pa., was conducted during July. This experiment—the Institute of Chemistry of the AMERICAN CHEMICAL SOCIETY—was based upon the belief that in the pursuit of their work men are forced to become specialists, but that in doing so they do not lose interest in their science as a whole, and that they would welcome an opportunity to exchange their experience as specialists with others who have likewise specialized. A simple case of profiting by a fair exchange, coupled with the notion that with the facilities to be found at State College one could make it, as one speaker said, an occupational vacation.

A more complete report will of course appear in our News Edition. Here we wish merely to stress the favorable comment made by those who were members of the Institute this year, many of whom came frankly skeptical, staying for a few days, and later returning for a longer period because they found something genuine which they did not wish to miss. The Institute to be held another year in a different locality will not necessarily follow along exactly the same lines, for experience teaches much and new environment and circumstances will alter parts of the program.

As the activities of the AMERICAN CHEMICAL SOCIETY grow there has been a multiplication in our publications in an effort to meet recognized needs. There has also been a growth in meeting activities—again to meet a recognized need. Thus the regional meetings have increased in prominence, and divisions have held extra meetings at their convenience. The Institute offers still another opportunity for discussion, but along different lines, since there is ample time to go thoroughly into all details on any topic. The morning conferences allowed an hour for discussion and on some occasions the group met for another two-hour period on the same question. But instead of being a mere addition to a list of meeting activities, it is possible that through the Institute an actual reduction may ultimately take place. Granted that the Institute becomes a permanent activity, is it not conceivable that the Colloid Symposium may find it advantageous to meet with it, that the Organic Symposium may do likewise, and that some of the more active divisions, such as Rubber, Petroleum, etc., may decide to hold one of their extra meetings in conjunction with the Institute, thereby increasing opportunities and convenience for all?

The members of the SOCIETY should be made to realize that this is one of their enterprises calling for their support and assistance, and that it should not be merely left in the hands of its committee.

Students at the Exposition

THE plans to enable students to take advantage of the Exposition of Chemical Industries as a factor in their education are developing along such favorable lines as to warrant further emphasis. A great deal of attention is being given to the selection of topics, as well as to the lecturers who will present them in the two courses—one available to beginning students, and the other arranged with special reference to more advanced classes. Adequate discussion through questions and answers is assured. A special feature this year will be the personal guidance of students through the Exposition. It is expected that many members of the American Institute of Chemical Engineers will coöperate in this feature, thereby making it possible for small groups of students to be conducted through the exhibits by men familiar with and experienced in the unit processes of chemical engineering and the equipment used therein.

We are glad to see this recognition given to those who are now students, but who will soon command important positions in industry, and bespeak for their encouragement the services of those who are asked to coöperate in this educational work, as well as the interest of professors generally who may be in position to urge attendance on the part of their students and help them derive the most that is offered by this unique plan.

Shirtless Sausage

LAST year when it was our privilege to publish the first announcement of commercial success in the manufacture of viscose sausage casings the daily press commented extensively upon these new "sausages in cotton shirts." We believe there will be equal interest now that sausages appear shirtless, thanks to a further development by the same group of investigators.

Noticing an occasional lack of adherence between viscose casings and the sausage, especially after a few hours, the chemists called upon practical sausage men to discuss the problem. They were met not with suggestions of how to insure such adherence, but with the inquiry, "Can you always make it behave that way?"

Subsequently it was found that under certain conditions, after a period of twelve hours, the viscose casing could be easily stripped from the link sausage and, because of an invisible layer, probably of colloidal material, the sausage would maintain its shape even under severe handling and cooking conditions. This cannot be done with the natural casing, and the result is an increased demand for link sausage which, thanks to science, can now be had without the slightest trace of any kind of casing.

This is not discovery through accident but another instance of the observation of small things which so frequently leads to substantial progress.

X-Ray Specifications

THERE are numerous examples of differences in industrial materials which record themselves in x-ray photographs but are not discernible by any of our chemical or physical methods of analysis. It is obviously not necessary to understand the actual differences which produce variations in these patterns to make use of this new information. We need not know the atoms or their arrangement so long as we know that the material represented by Photograph A is satisfactory, while that of B gives poor results in the factory.

Those pioneering in this field are encouraged by the serious consideration which the American Society for Testing Materials is giving the proposal that x-ray photographs be made a part of specifications. The suggestion appears both reasonable and practical, since the x-ray picture seems to be one of the immutable constants of materials. Its adoption will undoubtedly lead to increased accuracy in specifications and decrease in misunderstandings. The x-ray photograph is not yet universally applicable, but it is safe to say that when in doubt, try x-rays. The specialist can soon tell you whether or not their application will solve your particular analytical problem.

Opportunities in Carbon Dioxide

THE latest use for carbon dioxide as a refrigerant opens up new opportunities in research. If solid carbon dioxide is to be universally used, a satisfactory system of distribution from carefully located plants must be developed, or the solid must be produced in numerous localities where carbon dioxide is normally available. It looks like an opportunity for power plants, especially where there is off-peak power available. The difficulty lies in the recovery of the carbon dioxide from the flue gases. These gases may contain say 12 per cent CO_2, whereas gases prepared for the purpose run approximately 18 per cent. There is a real opportunity to devise economical methods of extracting carbon dioxide from the flue gases, utilizing off-peak power for liquefaction for the preparation of the refrigerant. There is also an opportunity to perfect improved methods for the manufacture of this gas as a primary product. It is another case of changed conditions calling for new developments, and proof of the well-known fact that, regardless of accomplishment, there is always much new work waiting to be done.

And Now Virginia

IT IS a great pleasure to list as No. 3 upon the roll of honor the Virginia Section of the AMERICAN CHEMICAL SOCIETY, which has forwarded a check for the Endowment Fund to the Treasurer. This represents a portion of the funds remaining after all business in connection with the memorable spring meeting of the SOCIETY at Richmond had been concluded, and follows the gifts of the Philadelphia and South Jersey Sections. It will serve to establish firmly a desirable precedent. We congratulate the Virginia Section upon the business management of the meeting and express the SOCIETY's appreciation for this addition to the Endowment Fund.

Chemical Processes for Re-refining and Decolorizing Dry-Cleaners' Solvent by Continuous Automatic Methods[1]

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Dry-cleaners are large consumers of light petroleum distillates. During use in the cleaning operation these solvents become contaminated by dirt and moisture, and become dark in color and odoriferous. The economical reclamation is a difficult technical problem. Purification processes now in use include steam distillation and processes utilizing caustic solutions and activated carbons and earths. A new process is described herein for use in conjunction with continuous centrifugal solvent clarification which permits simultaneously continuous decolorizing by means of concentrated sulfuric acid and a neutralizing treatment. Data are presented on the chemical and economic aspects of the new process in comparison with the others.

THE dry-cleaning industry is a large consumer of petroleum products whose problems appear to have received little attention from petroleum technologists. This industry now does a gross business of about $150,000,000,[2] and consumes about 100,000,000 liters (30,000,000 gallons) of petroleum annually in the cleaning operation.[3] On the average 0.5 kg. of "solvent" is consumed for each kilogram of goods cleaned. There are approximately four thousand dry-cleaning establishments in this country, ranging in size from the large "wholesalers," who clean 1,500,000 kg. or 1,000,000 or more "suit-equivalents" per year, to the small "retailer" cleaning only a few thousand kilograms annually.

Definitions

Dry-cleaning consists essentially in washing textiles in a suitable nonaqueous "solvent." So-called "wholesale" cleaners obtain their work chiefly from tailors and others who do not have their own dry-cleaning equipment. The "retailer" deals directly with the individual customer. In order to render the results stated in this publication more easily understood, the "suit-equivalent," equivalent to 1.5 kg. (3.3 lbs.) of textiles to be cleaned is a convenient unit, this being about the average weight of a man's three-piece suit. The articles submitted for dry-cleaning range from gloves to carpets, and it is not customary to weigh the goods cleaned.

The Process of Dry-Cleaning

In the process of dry-cleaning which is almost universally used in this country, the goods are washed with gasoline in a laundry type washer. Most of the excess solvent is then "extracted" by centrifugal force, and finally the last portion of the solvent, amounting to about 20 per cent of the dry weight of the goods, is evaporated by the use of air at about 80° C. (180° F.) in a drying tumbler. Many cleaners add some type of dry-cleaners' soap[4] to the solvent in the washer. Others add ammonia, mixtures of dry-cleaners' soap and ammonia, or even water. Data on the use of dry-cleaners' soap are presented in Table I.

Solvent Characteristics Required

Petroleum hydrocarbons used for dry-cleaning should conform to the following general requirements:

1—The solvent should not affect the strength, flexibility, smoothness, or luster of the textile fiber.

2—The solvent should not alter the dyestuffs used.

3—The solvent should not be injurious to plant workers.

4—The solvent should have a high initial boiling point to minimize evaporation losses and particularly the fire hazard.

5—The solvent should have a reasonably low end point to facilitate the removal of the last traces of solvent in drying.

6—The solvent should be free from colored or odorous constituents and from suspended solids or moisture which might be retained by the goods.

The first three of these requirements are apparently filled by any of the properly refined petroleum distillates.[5] Although these solvents can hardly be called non-poisonous,[6] they probably have as little effect on the human system as any available nonaqueous solvent.

The requirements of high initial point and low end point are not met by ordinary motor gasoline, which is the solvent in most general use at the present time. An effort is being made by the National Association of Dyers and Cleaners to promote the use of the so-called Stoddard type solvent,[7] which reduces evaporation losses and fire hazard without sacrificing ease of drying. This type of solvent has a flash point (Cleveland open cup) between 40.6° and 43° C., (105° and 110° F.) and users of solvent having a flash point above 100° F. (37.8° C.) are at present exempted from compliance with the New York State Labor Department Code.[8] The difference between this type of solvent and the usual winter grade of motor gasoline is clearly shown by the distillation curves (Figure 1) for the two solvents before and after the weathering which occurs during use in a dry-cleaning system.

The evaporation loss when using the Stoddard type of solvent is so much lower than when motor gasoline is used for cleaning that, this alone more than compensates for the slightly higher price charged for the Stoddard type of solvent.

Solvent Contamination

The removal of dirt, moisture, and color from the solvent and the elimination of any odor which might be retained by the goods are the dry-cleaners' most difficult problems. Until the advent of continuous centrifugal solvent clarification it was considered satisfactory to wash in contaminated solvent, relying on rinsing at least the light-colored goods in cleaners' solvent to prevent discoloration. The modern cleaner

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[1] Presented before the Division of Petroleum Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Tull, *Cleaners Dyers Rev.*, **10**, No. 9, p. 37 (February, 1927).

[3] *Natl. Cleaner Dyer*, **17**, 84 (August, 1926).

[4] Matthews, *Color Trade J.*, **15**, 79 (1924).

[5] Goldman, Hubbard, and Schoffstall, *Bur. Standards, Tech. Paper* **322** (1926).

[6] Engler-Höfer, "Das Erdöl," Vol. I, p. 786 (1913).

[7] Stoddard, *Can. Colorist Textile Processor*, **5**, 180 (1925).

[8] State of New York, Dept. Labor, Industrial Code, *Bull.* **29** (1926).

demands that the solvent in the washer be dry, fairly clean, light-colored, and free from objectionable odor at all times; and further that the solvent condition at the end of the washing period be such that no rinsing is needed.

The dirt picked up by cleaners' solvent is, of course, derived entirely from the goods cleaned. On the average, 100 kg. (65 suit-equivalents) of goods yield 1.6 kg. of dry solid dirt. The goods also contain considerable amounts of dark-colored substances which dissolve in the cleansing solvent. The extent of such contamination is shown by the following test, which indicated that 100 kg. (65 suit-equivalents) of average goods contained about 1.8 kg. of high-boiling substances soluble in the cleansing fluid:

Eighty kilograms of clothing were washed in about 300 liters of Stoddard type solvent. The initial color of the solvent was 10.

Note—In this paper, solvent colors are given in terms of the free iodine concentration (milligrams per liter) in an aqueous iodine-potassium iodide solution of equal color appearance. The solutions used contained two parts of potassium iodide for each part of iodine. Such solutions fade on standing, even in sealed tubes, and must be prepared the same day they are used.

Dirt (1.5 kg. dry basis) was removed from the solvent by continuous circulation through a centrifugal clarifier. At the end of the washing operation the color of the dirt-free solvent was 100. One-liter quantities of this solvent before and after use were steam-distilled at 100° C. The heavy ends left in the flask had the following characteristics:

	BEFORE WASHING GOODS	AFTER WASHING GOODS
Volume heavy ends, cc.	10	16
Neutralization value, mg. KOH per gram (A. S. T. M.)	0.7	6.6

The presence of small amounts of suspended solids or even of "dirt" in the cleansing fluid is not necessarily objectionable. The test data presented in Table I show that even fine white silks may safely be washed in solvent containing appreciable amounts of dirt, if no free moisture is present. If, however, the solvent contains as little as 0.1 per cent (by volume) of free water a large part of the dirt and moisture is picked up by the goods causing spots and general discoloration. The importance of guarding against the presence of free moisture in the cleansing solvent, which may contain a trace of dirt, cannot be too strongly emphasized.

Tests made in this laboratory indicate that the large amounts of unsaturated hydrocarbons contained in present-day motor gasoline may be responsible for some of the color and odor formed when this solvent is used. The varnish-like odor which such a solvent may develop is particularly objectionable, since it is retained by the goods after drying. This cannot be completely eliminated by distillation or by treatment with alkaline solutions, activated carbon, or combinations of these. Both color and odor, however, can be removed by suitable treatment with concentrated sulfuric acid.

Table I—Laboratory Washing Tests on White Silk Goods—Condition of Cloth after Washing and Drying

COLOR OF STODDARD SOLVENT USED	FILTERED DRY SOLVENT	DRY SOLVENT + 0.1% DIRT	SOLVENT + 0.1% DIRT AND 0.4% SOAP	SOLVENT + 0.1% DIRT AND 0.1% WATER	SOLVENT + 0.1% DIRT, 0.1% WATER, AND 0.4% SOAP
			SERIES I—MIXTURES OF NEW AND USED STODDARD SOLVENT		
Water-white (new)	OK	OK	...	Spots, wrinkles, and discoloration	Streaks, wrinkles, and discoloration
30	OK	OK	...	Spots, wrinkles, and discoloration	Streaks, wrinkles, and discoloration
50	OK	OK	...	Spots, wrinkles, and discoloration	Wrinkles and discoloration
100	OK	OK	...	Wrinkles and discoloration	Wrinkles and discoloration
			SERIES II—MIXTURES OF NEW AND ACID-TREATED USED STODDARD SOLVENTS		
Water-white (new)	OK	OK	Faint discoloration and wrinkles	...	Streaks, wrinkles, and discoloration
20	OK	OK	Faint discoloration and wrinkles	...	Streaks, wrinkles, and discoloration
60	OK	OK	Trace of discoloration and wrinkles	...	Streaks, wrinkles, and discoloration
100	OK	OK	Trace of discoloration and wrinkles	...	Slight wrinkles and discoloration

The new Stoddard type solvent is practically free from unsaturated compounds, and does not appear to develop appreciable amounts of either color or odor spontaneously, even when exposed to air in the presence of alkalies. The results of an examination of a 1926–27 winter motor gasoline and of a Stoddard type dry-cleaners' solvent by the method of Egloff and Morrell[9] are given in Table II.

Table II—Analyses of Stoddard Solvent and Motor Gasoline[a]

(Figures in per cent)

HYDROCARBON	STODDARD SOLVENT	MOTOR GASOLINE (1)	(2)
Unsaturates	0.5	6.5	7.0
Aromatics	7.3	7.2	4.4
Naphthenes	4.7	28.7	22.4
Paraffins	87.5	57.6	66.2

[a] Gasoline samples were purchased from local dealers and were not redistilled before analyzing.

Removal of Solvent Contamination

The removal of suspended solids and moisture from used cleaners' solvent is not particularly difficult. The centrifugal clarifier does this cheaply and effectively. Agglomeration by mixing with alkali solutions followed by gravity settling is another time-tried procedure, which, however, necessitates the provision of settling tanks holding twenty to fifty times the amount of solvent actually used in the washer, if serious accumulation of dirt in the cleansing fluid is to be avoided. Filtration is used to some extent in Europe, but because of the slimy nature of the solids to be removed and the necessity of minimizing solvent loss, this method would seem to be less desirable than either of the others. The Hele-Shaw "edge filter" has been recommended[10] for this service.

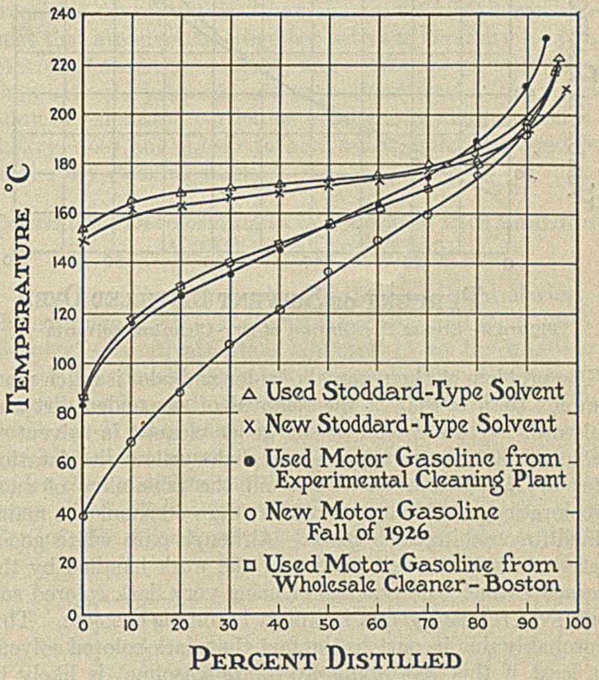

Figure 1—Distillation Curves for New and Used Dry-Cleaning Solvents

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[9] THIS JOURNAL, 18, 354 (1926).

[10] Hinckley, *J. Soc. Chem. Ind.*, 44, 117T (1925); Anon, *Industrial Chemist*, February, 1927, p. 67.

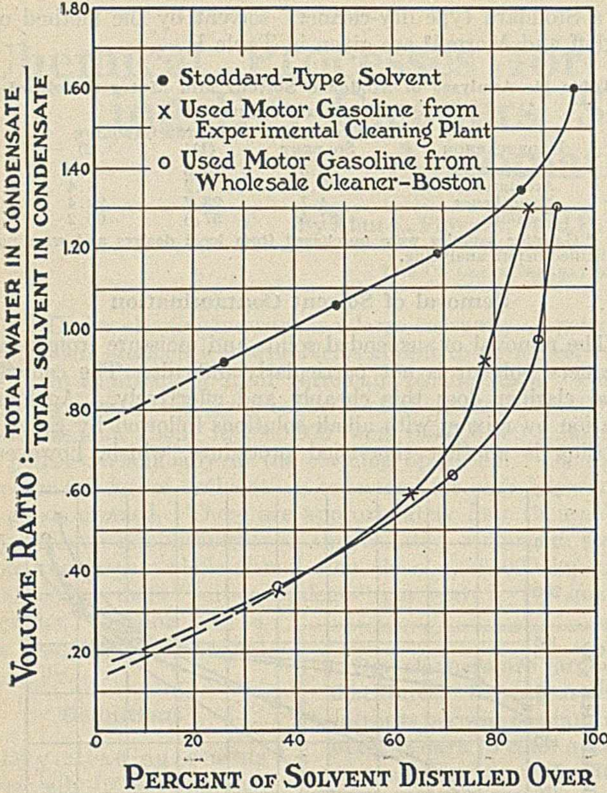

Figure 2—Steam Distillation of Dry-Cleaning Solvents

The problem of the removal of color and odor is much more complex than is that of the removal of suspended dirt and moisture. White cotton or silk goods cleaned in solvent of a color of 60 or more may show a slight yellow discoloration after drying (Table I). To avoid the possibility of such discoloration, a solvent color of less than 50 should be maintained for washing such goods. Although pure white goods represents only a small portion of the work handled by the average cleaner, the practice of using very dark colored solvent, even for dark goods, is rapidly becoming obsolete. This is probably due in part to the fact that dark-colored solvent (at least if this was originally motor gasoline) is likely to have a varnish-like odor, which is very difficult to remove from the goods in the drying operation.

Distillation is perhaps the most obvious means for purifying contaminated solvent, and has found wide application in this field. Batch distillation by the use of open steam appears to be the accepted procedure, probably because of the rather high finishing temperature which makes the use of steam in coils impractical, and because of the necessity of minimizing fire hazard and odor in the distillate. Laboratory tests (Figure 2) indicate that steam distillation under average dry-cleaning plant conditions will cost at least 5 to 10 mills per liter for steam, cooling water, and solvent loss, depending on the type of solvent in use and the degree of contamination. Distillation cannot eliminate volatile substances, nor does it remove the varnish-like odor commonly found in used motor gasoline, and the distilled solvent may also contain substances which cause it to cling tenaciously to traces of moisture after separation.

Batch *vs.* Continuous Contamination Removal

Until the present decade batch treatment of solvent to eliminate accumulated contamination was the accepted practice. Under these conditions the contaminating substances are contained in a relatively small volume of solvent, and a fairly high unit cost for reclaiming the solvent may be permissible and is apparently unavoidable. For this type of work steam distillation has so far been able to compete with proposed chemical processes for color and odor removal, particularly because of the simplicity of the process and apparatus involved.

In the modern cleaning plant the accumulation of large amounts of color, etc., in the solvent is no longer tolerated. While the cleaner who relies on the batch method of contamination removal may continue to use the cleansing fluid until its color has reached 250 or more, the cleaner who operates a continuous system for the removal of solvent contamination uses a solvent whose color varies only between the limits of about 20 to 60. The continuous removal of solvent contamination has numerous advantages from the point of view of the dry-cleaner, as well as from that of his customers, and the use of continuous clarifying and decolorizing systems of one type or another for handling cleaners' solvent is rapidly becoming well-nigh universal in this country.

The problem of continuous removal of color and odor from cleaners' solvent is fundamentally different from that of batch removal of such contamination. The system for continuous removal of color and odor receives solvent from the washer at a color of 60 or less and removes part or all of this color content before returning the solvent to the washer. It must therefore handle many times the volume of solvent that would be handled by a batch system washing the same quantities of goods. Under these conditions the cost of processing a liter of solvent must be very low indeed, and should preferably vary with the amount of contamination removed from the solvent during its flow through the processing system.

Steam distillation, at least with the type of equipment now used by dry-cleaners for distilling batches of dirty solvent, is far too costly for use as a continuous decolorizing process. It is also seriously handicapped by the fact that just as much steam and cooling water are required for distilling a liter of water-white solvent as for reclaiming a liter of solvent of color 500.

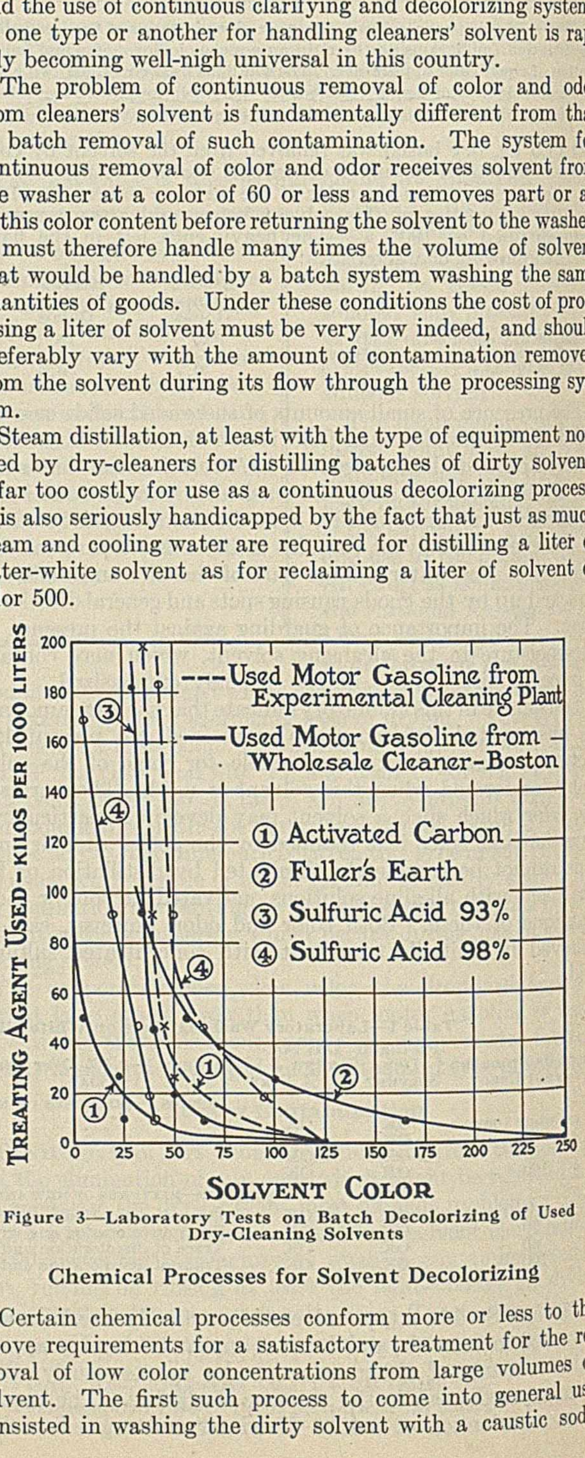

Figure 3—Laboratory Tests on Batch Decolorizing of Used Dry-Cleaning Solvents

Chemical Processes for Solvent Decolorizing

Certain chemical processes conform more or less to the above requirements for a satisfactory treatment for the removal of low color concentrations from large volumes of solvent. The first such process to come into general use consisted in washing the dirty solvent with a caustic soda solution and then with water. It was soon found, however, that this process did not prevent the slow accumulation of color and odor.

In 1924 work instituted at the Bureau of Standards by the National Association of Dyers and Cleaners[11] demonstrated that used cleaners' solvent could be reclaimed by the use of certain types of activated carbon in conjunction with aqueous alkaline solutions. Although this process was originally proposed for treating batches of contaminated solvent, it was soon found that the process could readily be applied in the continuous systems, which had previously used caustic solutions alone.

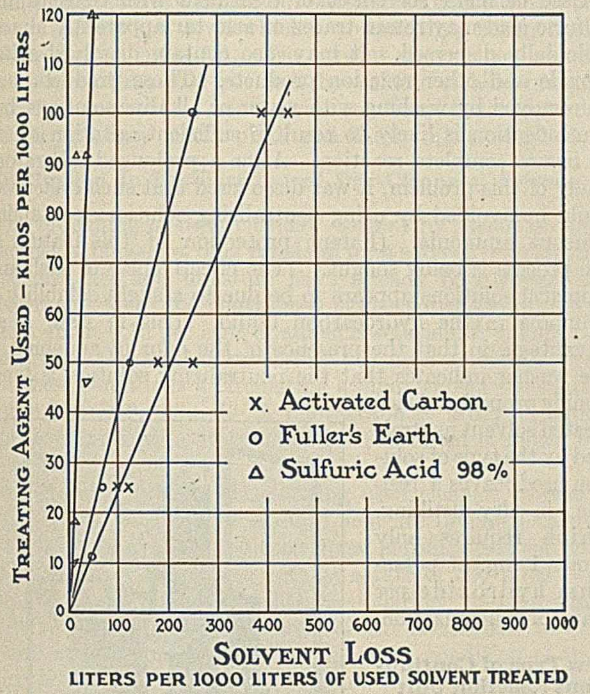

Figure 4—Laboratory Tests on Batch Decolorizing of Used Dry-Cleaning Solvents

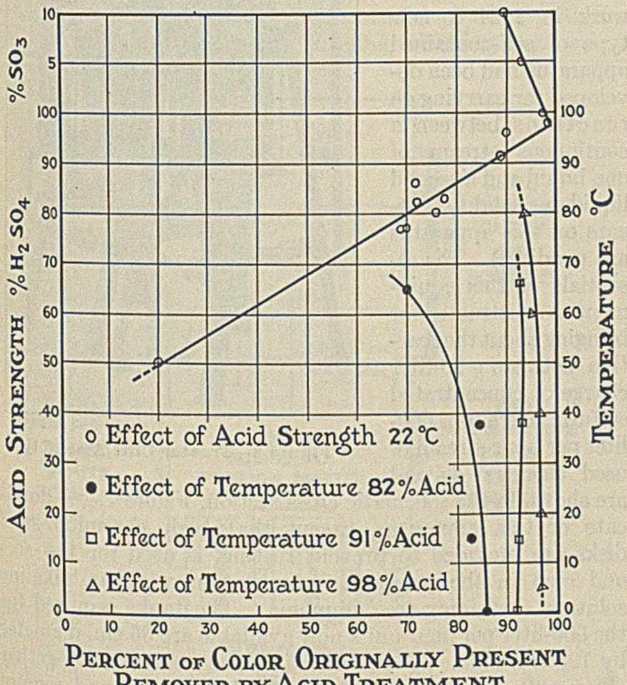

Figure 5—Effect of Acid Strength and Temperature on Decolorizing Used Dry-Cleaning Solvents

The activated carbon process for removing solvent contamination is essentially suitable for operation on the continuous system, rather than on the batch system, in that the cost of completely decolorizing a liter of badly contaminated solvent is quite high (comparable with the cost of steam distillation), while the cost of removing more or less completely a small amount of color from a large volume of solvent is low. (Figures 3 and 4)

Laboratory tests indicate that the activated carbon process will not completely remove the varnish-like odor from used solvent, and there is some evidence that gradual accumulation will occur in continuous systems using this process in conjunction with motor gasoline.

Numerous attempts have been made to utilize fuller's earth and the newer activated earths for decolorizing used solvents, and equipment for this purpose is on the market. Laboratory tests (Figures 3 and 4), as well as actual cleaning-plant trials, indicate that the relatively large quantity of such decolorizing agents required and the considerable losses of solvent that are involved, together with the necessity for proper control of moisture content, more than compensate for the simplicity of equipment and process involved. The regeneration of exhausted earths, as practiced in the petroleum industry, does not appear to be feasible under the conditions of the dry-cleaning plant.

Continuous Decolorizing in Conjunction with Continuous Centrifugal Clarification

Ever since the introduction of the centrifugal clarifier for the continuous removal of suspended dirt and moisture from cleaners' solvent, attention has been given the question of selecting or developing suitable processes and equipment for removing color and odor from the clarified solvent. Three years ago it was definitely recognized that such a color-removing process must be of the continuous type; also that under the conditions met in the average cleaning establishment the decolorizing equipment need only handle a fraction of the solvent stream passed through the centrifugal

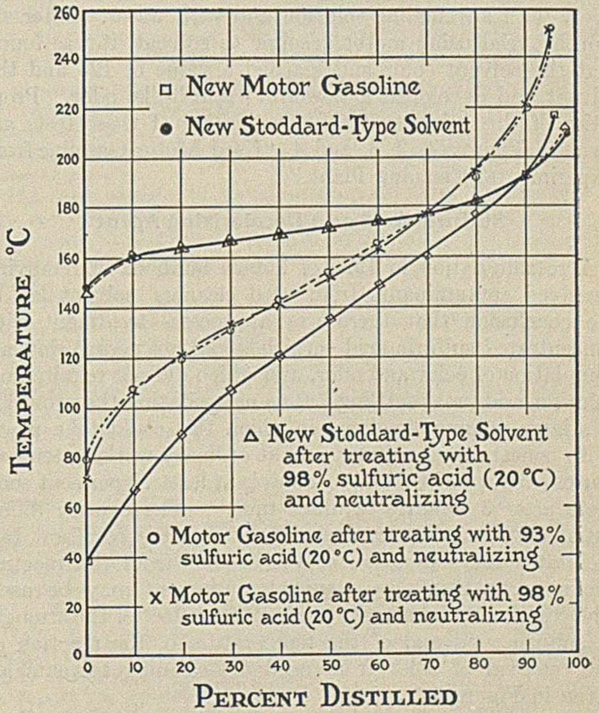

Figure 6—Effect of 93 and 98 Per Cent Sulfuric Acid on Distillation Curves of Motor Gasoline and Stoddard Type Solvent

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[11] Hubbard, *Bur. Standards, Tech. Paper* **280** (1925).

clarifier.[12] During the past three years intensive work along these lines has been under way.

An attempt was first made to utilize an activated earth as decolorizing agent. Equipment for this purpose was developed and finally tested under actual working conditions in a retail cleaning establishment, but this line of attack was subsequently dropped, for the reasons already indicated.

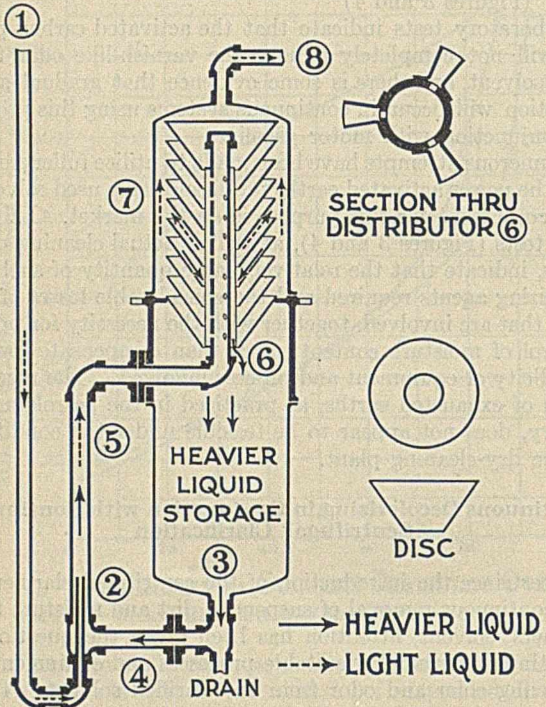

Figure 7—Schematic Cross Section of Continuous Treater

In 1925 an experimental dry-cleaning plant was established, washing overalls and other work clothes for a factory employing twelve hundred persons. In this plant equipment was developed for continuously washing the solvent successively with an alkaline solution and with water. After six months' trial using motor gasoline as solvent, it was found that the solvent color had reached a value of 125 and the solvent had developed a powerful varnish-like odor. Properties of this solvent at the termination of these tests are given in Figures 1, 2, 3, and 4, "Used Motor Gasoline from Experimental Cleaning Plant."

Sulfuric Acid as a Decolorizing Agent

A reëxamination in 1925 of known methods of removing dissolved contaminants from used cleaners' solvent led to the conclusion that there was a process—treatment with concentrated sulfuric acid—which would not permit slow accumulation of color and odor, and which did not require flocculation and "mat-settling," thus necessitating the provision of a large volume of solvent in which this could take place. With concentrated sulfuric acid at ordinary working temperatures (about 30° C.) the reaction is at least 70 per cent complete after 3 minutes' contact time.[13] The density differential between the cleaners' solvent and the resultant tars facilitates the separation of the solvent from the reaction products, so that very compact equipment may be used. The results of a laboratory study of the effect of the strength of sulfuric acid and of the temperature of the reaction on the removal of color from used dry-cleaning solvents are given in Figure 5.

The distillation curves in Figure 6 bring out a point of considerable practical importance in connection with sulfuric acid decolorizing when using motor gasoline for drycleaning. The high end point of acid-treated motor gasoline indicates that difficulty would be experienced in removing the last traces of this solvent from the goods in the drying operation. Work in the experimental cleaning plant fully confirms this: goods cleaned in acid-treated motor gasoline required two to three times the drying time needed when acid-treated Stoddard-type solvent was used. The sulfuric acid process therefore cannot be recommended for dry-cleaners who expect to continue the use of the motor gasoline type of solvent.

Used cleaners' solvent after treatment with concentrated sulfuric acid may retain traces of acid tar apparently almost colloidally dispersed. It may also contain dissolved sulfur dioxide and other reaction products. These products may be removed by washing with water or alkaline solutions, but emulsification is likely to result if sufficient agitation is used to insure complete reaction. After a prolonged laboratory study of this problem, it was discovered that such difficulties could be avoided by using neutralizing solutions containing aqueous ammonia. (Patent protection of this feature of the process is being sought.) The effectiveness of such ammoniacal solutions appears to be due to a slight solubility of ammonia in the hydrocarbon liquid. This in itself is an advantage, in that the presence of the odor of ammonia in the washer indicates that the neutralizing solution is functioning properly. Acid-treated solvent neutralized by the type of solution used leaves a residue in dry-distilling, which requires only about 1 mg. of potassium hydroxide per gram for neutralization.

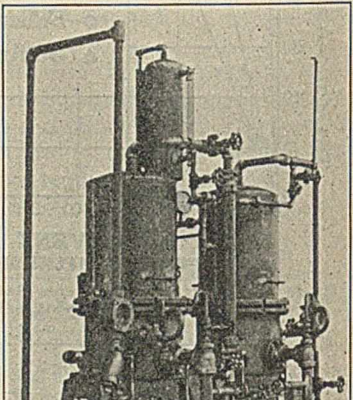

Figure 8—Treater Unit Assembly

New Type of Continuous Reaction Unit

In the course of the work in 1924 a new type of self-contained apparatus had been developed for carrying on reactions between a continuous stream of one liquid and a second liquid or a solid. (Patents on this apparatus are pending.) The essentials of this equipment as constructed for bringing about the reaction between a 20-liter charge of concentrated sulfuric acid and a 600-liter per hour stream of used cleaners' solvent are shown in the schematic cross section, Figure 7. A duplicate of this apparatus, except that high chromium-steel disks are provided to prevent rusting, is used for the second step in the process, neutralization with an alkaline solution containing free ammonia. The tanks required for the 600-liter per hour units now available are 35 cm. diameter by 125 cm. high. The acid-treater and neutralizer together (Figure 8) occupy a floor space 1.5 by 1 meter and require 2.5 meters of head room. In this equipment provision is

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[12] Flowers, U. S. Patent 1,545,091 (July 7, 1925).

[13] Engler-Höfer, "Das Erdöl," Vol. I, p. 543 (1913).

made for drawing fresh charges of chemicals into the respective tanks by establishing a partial vacuum in them by means of a small vacuum pump.

The principle of operation of this equipment is as follows: The solvent stream enters at (1), Figure 7, through the mixing nozzle (2). The chemical reagent flows from the storage space (3) through the pipe (4) and mixes with the solvent stream in the pipe (5). The mixture of the two liquids rises into the distributor (6) in much the same manner as the mixture of air and water rises to the surface in the air-lift pumping of deep wells. The distributor (6) sends the mixture into the disk-stack (7), which provides about 2.2 square meters of settling area in which the heavier component is required to fall a maximum of 7 mm. before it strikes a disk surface, on which it collects and down which it flows to drop finally back into the storage space (3). The solvent stream, now carrying not more than 0.05 per cent by volume of acid tar (or about 0.15 per cent of neutralizing solution), flows upwards past the periphery of the disks and finally out through (8).

Application to Decolorizing of Dry-Cleaners' Solvent

The re-refining of used cleaners' solvent by means of sulfuric acid is, of course, only practical for a solvent from which suspended dirt and moisture have already been removed. Furthermore, since the neutralized light-colored solvent may entrain about 0.15 per cent of aqueous solution, it cannot be admitted to the washer until this has been removed. To meet these conditions a circulating system, shown schematically in Figure 9, is used. A photograph of a dry-cleaning plant in which such a system has been installed is shown in Figure 10.

The present units for decolorizing used cleaners' solvent by means of concentrated sulfuric acid are designed to receive continuously from the centrifugal clarifier used solvent of a color of not more than 100, at a rate of 500 liters per hour, and to deliver to the centrifugal clarifier, and through this to the washer, this stream of solvent decolorized to between 0 and 20 color, depending upon the condition of the acid charge. When receiving solvents at an average color of about 40 and returning it at an average of about 10, the decolorizing operation costs about 0.5 mill per liter, as shown by data from eight months' experimental plant operation, during which time 5000 kg. of clothing, blankets, rugs, etc., were dry-cleaned.

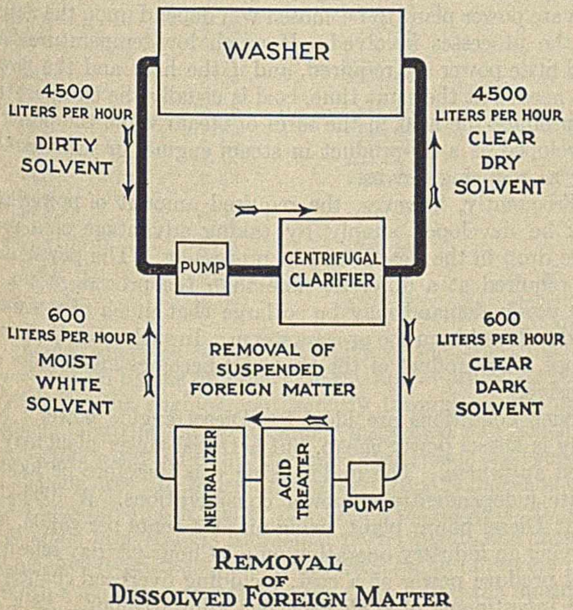

Figure 9—Schematic Diagram of Flow in Continuous Clarifying and Decolorizing System

The dry-cleaner is interested primarily in the solvent color which can be maintained when washing clothes at a given rate. Since the work done in the experimental cleaning plant represented only about $6500 gross income per year (at $1.00 per kilogram of goods cleaned), it affords only a little information in this connection. During eight months' operation, an average of 12 kg. of goods was washed per hour of decolorizing system operation, and an average solvent color of about 30 was maintained in the washer. Individual tests show that when washing men's dark winter clothes at a rate of 70 kg. per hour the color of the solvent in the washer may be as high as 250, while a washing rate of about 40 kg. per hour of average winter clothes, rugs, blankets, etc., may bring about a solvent color of about 50. Apparently a provisional capacity rating of about 30 kg. of average goods per hour of decolorizer operation may be made until further operating experience has been obtained with the units now being installed in dry-cleaning establishments in various parts of the country.

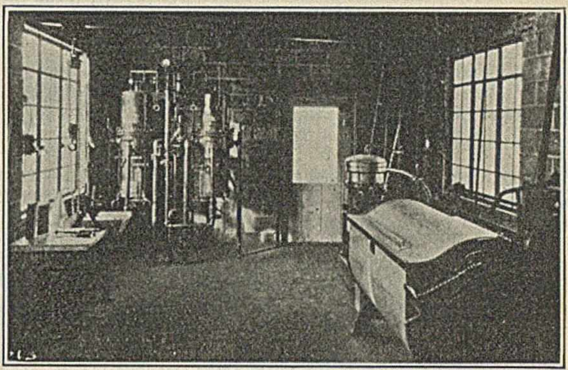

Figure 10—Dry-Cleaning Plant Equipped for Continuous Decolorizing by Means of Sulfuric Acid

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Spain Establishes Petroleum Monopoly

Establishment of an oil monopoly by Spain, announced in cabled advices to the Department of Commerce, will directly affect American concerns who do approximately 80 per cent of Spain's petroleum business. The text of the cablegram follows:

> A recent Spanish royal decree establishes a monopoly on the importation, manipulation, distribution, and sale of petroleum and petroleum products, included under items 36 to 48 of the Spanish customs tariff, prohibiting immediately the amplification of present installations or the creation of new ones.
>
> This decree provides for the expropriation of present holdings of domestic and foreign oil companies now operating in Spain, excluding foreigners entirely from the monopoly, but forcing the sale of all necessary equipment, reserving the right of refusal to purchase adjunct and accessory property.
>
> No mention is made of an intention to purchase existing stocks or good will. Spanish companies are given the option of cash reimbursement or acceptance of shares in the monopoly.
>
> The concession for the administration of the monopoly is to be for 20 years' duration, the object of the monopoly being to increase government revenue and to stimulate the Spanish refining industry, as well as for other purposes, such as the building of tanker fleets, utilization of national alcohol, etc.

The Department has information that Russian interests are penetrating European oil markets with products of their newly developed oil fields. Paralleling this movement is an apparent American overproduction which makes shipment of surplus to foreign purchasers desirable from the producers' viewpoint.

Recent reports to the Department of Commerce stated that a bill to form a French petroleum monopoly has been presented. In Italy state subsidies are granted oil operators. Poland is reported considering reviving its cartel, while Rumania has already nationalized the oil industry.

A report on Spanish petroleum importation in 1926, based on official Spanish statistics, reveals the commanding place occupied by American companies in Spain, which will be most seriously affected by the Spanish decree.

The Place of the Diesel Engine in Chemical Industry[1]

By Edgar J. Kates[2]

203 West 13th St., New York, N. Y.

DIESELS FOR PRIMARY POWER

IN CHOOSING a location for a chemical plant a number of factors must be considered. D. H. Killeffer[3] has succinctly indicated these factors in the following words:

> The ideal chemical plant location would be directly at the supply of raw materials, close to markets, immediately in the center of an area from which plenty of cheap, intelligent labor might be drawn, close to sources of power, bountifully supplied with water, far enough from habitations and near enough to sewage facilities to prevent undue expense from nuisance disposal, and finally in intimate contact with both raw materials and markets through adequate transportation facilities.

The primary reason for locating close to sources of power is, of course, to obtain cheap power. This is true whether the power source is coal, transported either by railroad or water, or central station electricity carried upon wires.

The importance of cheap power as compared with the other factors of cheap labor, raw material, and the like, depends upon the amount of power consumed per dollar's worth of product. In such industries as the electrolytic manufacture of aluminum, the grinding of logs into paper pulp, or the manufacture of ferromanganese, the power required is so great with respect to the value of the product that these industries, in order to be commercially successful, must locate where they can obtain power at minimum cost—close to favorable hydroelectric developments, such as at Niagara Falls and in parts of Canada and Norway.

In many chemical industries, however, the amount of power relative to the value of the product is not enough to dominate the other factors. Such plants will be located with more reference to raw materials or markets. Nevertheless, even in such industries the item of power is by no means insignificant, and any savings that can be made in power costs will be clearly reflected in the net earnings. For instance, a concern may have annual sales equal to its capitalization and be paying an 8 per cent dividend. Even though its power cost is only 10 per cent of the value of the product, a saving of but 20 per cent in the power item will permit the payment of 25 per cent more money in the form of dividends. It therefore behooves such industries to keep informed regarding the advances continually being made in the field of power production and to take advantage of the economies possible by utilizing modern Diesel engines.

Freedom of Location

There is one characteristic of Diesel engine power which commends it particularly to the chemical industry. This is the fact that a plant generating its own power by means of Diesel engines may be located practically anywhere and still have cheap power. Full advantage can therefore be taken of proximity to raw materials, to markets, to cheap labor, or whatever other considerations are influential in that particular branch of the industry. Thus the use of Diesel power results in a double saving—on the one hand a reduction in material-handling, labor costs, nuisance disposal and the like, and on the other, a decrease in the cost of power itself. The first-mentioned class of savings will in some cases far exceed the second.

Super-Power Possibilities Overrated

Super-power and giant-power projects have received so much attention, particularly in the political arena, that many have come to believe that it is only a question of a few years before electric power from falling water or from immense efficient steam stations will be available almost everywhere in our land, at a cost next to nothing. It is true that such power can be *generated* cheaply; the modern steam central station *produces* a kilowatt-hour for only 7 mills, including the fixed charges on the power house. Some hydroelectric projects favored with low construction costs and steady flow of water do still better. But the cost of *delivering* this power to the consumer is of a magnitude not generally appreciated. As a country-wide total, the investment in public utility transmission lines, distributing systems, and other things outside the power house itself is considerably more than the amount invested in producing the power. Furthermore, the cost of operating the distribution agencies, such as the upkeep of the wire systems and substations, and the loss of energy during transmission (averaging 19 per cent), are grave items of expense that must be paid out of the final price of the power to the consumer. Even with the present extent of transmission systems these expenses are so burdensome that the average price of electricity, obtained by dividing the gross revenue of the nation's electric public utilities by the number of kilowatt-hours sold, is 2.8 cents. With longer transmission systems the unit cost of distribution will increase, so that little, if any, of the economy at the power-generating end will reach the final consumer. This is one of the reasons why central station energy in a great many cases cannot compete with a private power plant.

Remote Locations Favor Diesels

In locations where transmitted electric power is not to be considered, either because, though available, it is too expensive and unreliable, or because the place is too remote to justify the cost of building a transmission line, the type of private power plant to be chosen will depend upon the nature of the processes involved. If much low-temperature heat and little power are required, and if the heat and the power are needed at the same time, coal is usually the cheapest fuel to produce the heat in the form of steam while the power is developed as a by-product in steam engines or turbines acting as reducing valves.

Frequently, however, the required amount of power cannot be developed simply by taking advantage of a pressure drop in the steam used in processing. The power may be required at a different time than the process steam, or the power demand may be so large that much of it cannot be developed from the process steam. In such cases the power is not a by-product of the heat and becomes much more expensive.

Such conditions are ideal for Diesel engine power. Not only is Diesel power cheap, but a Diesel power plant may be used anywhere. The undertaking can therefore be located quite independently of power considerations. A 1000-kilowatt Diesel power plant, using oil at 4 cents per gallon, and serving an industry operating on a 24 hour per day schedule, will produce power at a cost, including overhead charges on the investment, of 0.85 cent per kilowatt-hour. As a result of the high thermal efficiency, the fuel consumption is

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[1] Received April 19, 1927.

[2] Chairman Oil and Gas Power Division, American Society of Mechanical Engineers.

[3] This Journal, 18, 253 (1926).

low and the fuel cost is only 0.35 cent per kilowatt-hour. If, because of extreme inaccessibility or remoteness of the plant, transportation charges double the price of the fuel to 8 cents per gallon, the total cost of power becomes 1.20 cents per kilowatt-hour, by no means an excessive figure.

A steam turbine plant of corresponding size will use about 2.7 pounds of coal per net kilowatt-hour, which with coal at $5.00 per ton gives a fuel cost of 0.70 cent per kilowatt-hour and a total cost of 1.35 cents per kilowatt-hour. If the cost of coal is doubled because of extra transportation expense (and under the same conditions coal transportation is much more expensive than oil), the total cost of power in the steam plant rises to 2.05 cents per kilowatt-hour. The relative independence of the Diesel plant as regards variations in the cost of fuel is obvious.

Water Scarcity

In localities where water is scarce or expensive the Diesel engine has the advantage of a low water consumption. The water circulated through the jackets is about 9 gallons per kilowatt-hour, and as it is a simple matter to recool it and use it again, the water consumption can readily be limited to less than 0.5 gallon per kilowatt-hour. This is but a small fraction of the water required by a steam plant. In fact, the Diesel plant uses so little water that this consideration does not enter into the question, whereas with a steam plant it is paramount.

Diesel Reliability

The reliability of Diesel engines is today hardly questioned. Records of numerous plants running under various conditions have uniformly testified to a remarkably low percentage of time out for repairs. Table I shows a typical month's record of an oil pipe line installation comprising three pumping stations each containing three Diesel-driven pumps. The engines are required to be under heavy load continuously—i. e., 24 hours a day every day of the month. There are no spare units. The performance shown, 99.70 per cent, has been accomplished month after month with little variation.

Table I—Time Out for Repairs for Nine Diesel-Driven Pumps in Continuous Operation on Oil Pipe Line

(Typical month's record)

Installation	Time Out for Repairs and Adjustments *Hours*	Time in Service *Hours*	Time in Service Divided by Time Wanted *Per cent*
Station A:			
Unit 1	0.58	719.42	
Unit 2	9.08	710.92	
Unit 3	0.00	720.00	
Total	9.66	2150.34	99.55
Station B:			
Unit 1	4.68	715.32	
Unit 2	1.32	718.68	
Unit 3	0.93	719.07	
Total	6.93	2153.07	99.68
Station C:			
Unit 1	0.43	719.57	
Unit 2	2.47	717.53	
Unit 3	0.16	719.84	
Total	3.06	2156.94	99.86
Grand total	19.65	6460.35	Av. 99.70

Further evidence of the reliability of modern Diesel engines is given by the practice of many Diesel-driven ice plants of running the engines continuously throughout the entire summer, shutting down for minor inspection only when the ice storage room is full or for some other reason independent of the engines. In other lines of service still longer continuous runs have been made. In 1924 a non-stop of 201 days was made in a Kansas municipal power plant, and recently in another municipal plant a different make of engine completed a non-stop run of exactly 15 months, the shutdown even then having been quite voluntary.

Range of Sizes

Diesel engines can be obtained in a wide range of sizes suitable for most industrial applications. Most of the engines regularly manufactured range from 40 to 2000 kilowatts, but engines can be had as small as 10 kilowatts and as large as 10,000 kilowatts. Small engines have practically the same fuel efficiency as large ones, which is by no means the case with steam plants. Advantage can be taken of this characteristic by building power plants containing a number of Diesel engines to run simultaneously when carrying the maximum plant load. This not only insures greater flexibility in meeting variable conditions, but also makes it possible to add engines to the plant as the power requirements increase. In a steam plant, on the other hand, the fuel economy of large units is so much greater than that of small ones that it is common practice to put in a plant much larger than the present needs in order to secure better efficiency for the future. Such idle investment is avoided in the Diesel plant.

Plant Costs

On account of improvements in design and methods of manufacture, the cost of Diesel engines has declined quite remarkably in the last five years, and prices are generally lower even than pre-war figures. The cost of a complete plant depends upon a number of variables, such as freight, foundations, and type of building. However, as a first approximation, the cost of a 500- to 1000-kilowatt Diesel generating plant, complete except for the land and building, will be about $135 per kilowatt. This compares favorably with the cost of a high-grade steam plant of equal size, including boilers, stokers, stack, turbines, condensers, piping, draft fans, coaling equipment, and the other necessary auxiliary equipment.

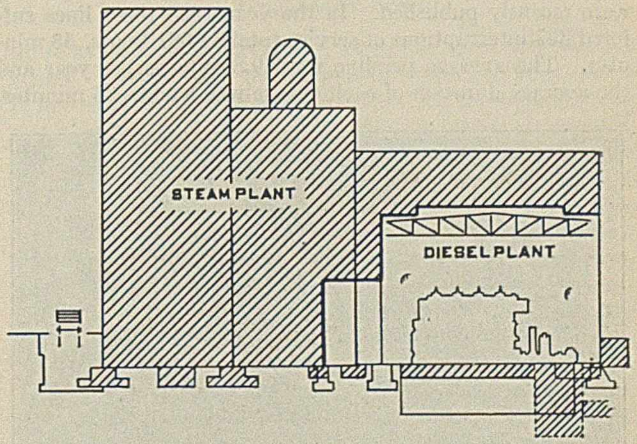

Figure 1—Relative Size of 1000-Kilowatt Steam and Diesel Plants (Same Scale)

The Diesel plant occupies much less ground space than a corresponding steam plant, and the building is smaller in all dimensions. The relative size of the two types of 1000-kilowatt plants is indicated in Figure 1, where they are brought to the same scale and superimposed.

Examples of Diesels Delivering Primary Power

Some typical instances of chemical industries using Diesel engines for primary power are shown herewith. In Figure 2 is illustrated a 500-kilowatt engine driving a cottonseed-oil mill in Texas. The three 300-kilowatt generating units shown in Figure 3 furnish power to a copper mine and milling plant in Cuba. A concern in Florida producing phosphates has obtained its power from a Diesel generating plant for fifteen years. The plant has grown to a capacity of 1200-kilowatts, the most recently installed unit, of 450 kilowatts, being shown

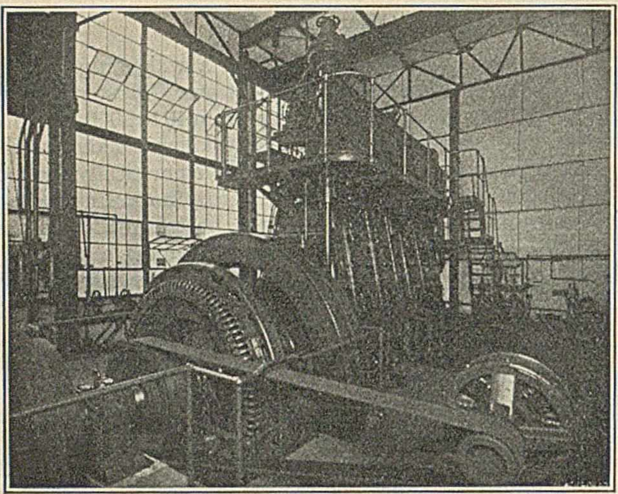

Figure 2—500-Kilowatt Diesel Engine Driving Cottonseed Oil Mill

in Figure 4. In spite of the age of most of the engines, the total operating cost is stated by the management to be 7 mills per kilowatt. This includes repairs, renewals, fuel, labor, and supplies, but no overhead.

DIESELS FOR SECONDARY POWER

As most users of purchased electricity know, high-tension power carried over long transmission lines is not entirely reliable. This type of power is subject to interruptions caused by lightning, wind, sleet, current surges, and similar line troubles. The frequency and duration of these outages vary widely. The line service records of several electric utilities operating 17 transmission line systems in different parts of the country were recently published. In the year 1925 these lines suffered 337 interruptions of service totaling 531 hours, 55 minutes. The average per line was 19.8 outages per year and the average duration of each outage was 1 hour, 35 minutes. The line having the best record reported only one outage lasting 12.5 minutes, while the worst record was 78 outages lasting a total of 181 hours, corresponding to an average duration of 2 hours, 19 minutes per interruption.

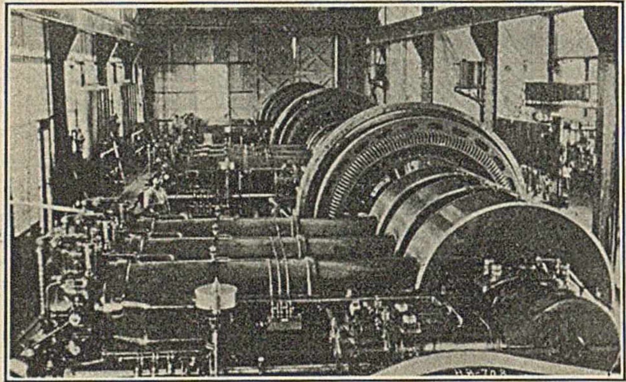

Figure 3—900-Kilowatt Oil Engine Plant for Copper Mining and Milling

Steady Power Required

In a number of chemical industries any interruption in processing is a serious matter. For example, in nitrating not only must the stirring be continuous, but the cooling water must flow constantly. In the nitration of benzene the temperature needs to be held below 60° C. in order to obtain a high yield of the desired product. If the cooling water supply fails, the resulting rise in temperature will allow undesirable and dangerous compounds to be formed. Furthermore, because of the higher temperature the speed of the reactions will increase, and this in turn will cause more heat evolution and still higher temperatures, finally putting the process entirely out of control and causing not only a loss of material but also a dangerous state of affairs. For these reasons a reserve source of power should be available for immediate use in case of an interruption in the electric service coming into the plant.

Another instance is the distillation of aniline under vacuum. A still may hold 25,000 pounds of aniline which is being evaporated at low temperature by keeping it under a vacuum of 29 inches. If a power interruption should permit a loss of vacuum the temperature would rise and the aniline would discolor rapidly.

In the disposal of sewage by the activated sludge method, continuous blowing of the sludge is necessary. If the air stops, the sludge settles upon the filter bed and penetrates the pores of the filtros blocks, making it difficult, if not impossible, to restore them to use. In a city the size of Pasadena, Calif., the filter bed contains about thirty-five hundred filtros plates costing about $2.00 each. The replacement of this filter bed, which might be the result of an interruption in the power supply, would involve not only an expense of $7000 for new plates, but also a considerable item for labor, as well as a shutdown for several days.

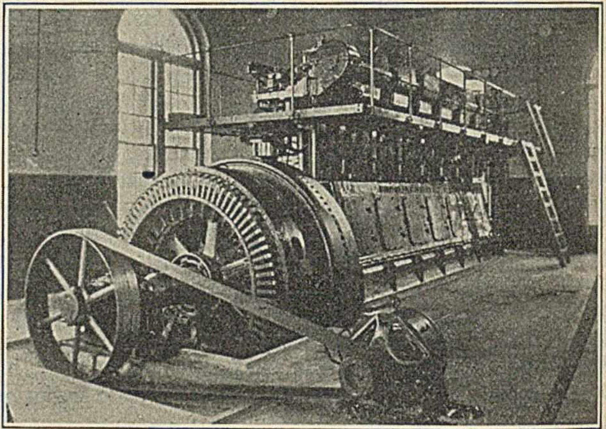

Figure 4—Modern Diesel Engine in 1200-Kilowatt Diesel Plant Producing Phosphates

An interruption in the power supply means great loss in an artificial silk factory. The liquid viscose is forced under pressure through a platinum orifice into an acid bath which causes it to coagulate into a thread. Each machine, of which a modern factory contains hundreds, holds about two hundred of these orifice plates, called spinnerets. If a power disturbance permits a loss in pressure of the viscose, the streams cease to emerge and the spinnerets clog. This may necessitate emptying the viscose and acid from each of the machines and removing the thousands of spinnerets in order that the orifices may be burned clean. Such repairs are costly not only in themselves, but also in the great loss of production that accompanies them.

A serious feature of transmission line outages is that they usually occur without any warning whatever, and when the power is off it is frequently impossible to learn when it will be restored. This uncertainty makes it difficult to decide whether to keep the labor force idle while waiting for the resumption of power, or whether to release the workers for a while.

In order to cope with these conditions many chemical industries that are dependent upon transmitted electric power require in the plant itself a reserve source of power in order to eliminate both the dangers and the monetary losses caused by power outages. For reasons which will be detailed later, the modern Diesel engine is admirably adapted to supplying such stand-by power.

Water Power

Other industries that are located on streams and develop their own water power are not troubled by transmission line interruptions, but are affected by the seasonal character of the energy from "white coal." It is expensive to build dams and other works for the purpose of utilizing merely the firm or steady year-round flow of the river; the initial cost per kilowatt capacity is too high and the resulting fixed charges per unit of output usually make the plan uneconomic. For this reason it is customary to install turbines and generators large enough not merely to use the minimum flow of the river during the dry season, but also to take advantage of the greater flow which exists during most of the year. In this case auxiliary power of some kind must be provided to take care of the deficiency in water power during the dry season. The great hydroelectric systems of California have found it necessary to provide auxiliary steam stations large enough to furnish 40 per cent of the maximum power demand.[4]

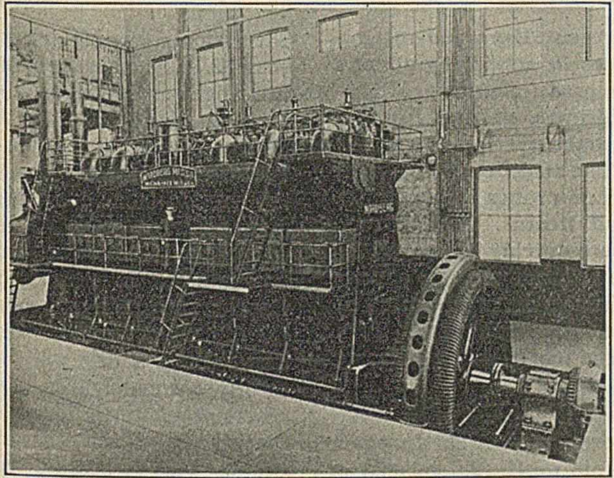

Figure 5—One of Three 2500-Kilowatt Diesels for Supplying Stand-By Power to Panama Canal

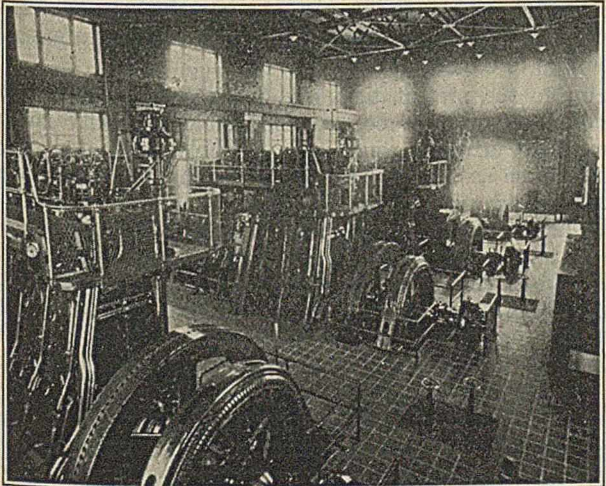

Figure 6—2000-Kilowatt Diesel Auxiliary Plant of Chicago Sanitary District

Diesels Often Ideal for Stand-By Power

To meet these needs for stand-by and auxiliary power the Diesel engine offers certain distinct advantages over other types of prime movers.

It is always immediately available for service. A Diesel plant can be started up from a completely idle and cold condition and put on full load within one minute. All that is necessary is to turn on the lubricating system and the compressed air used for starting. The engine immediately begins to fire and rapidly comes up to full speed, whereupon it is ready to receive its load. This contrasts strongly with a steam plant, whose banked fires require considerable time to develop full heat and whose turbines must be slowly warmed up to avoid heat distortions which might cause the blades to strike. Furthermore, the steam plant contains a large amount of accessory apparatus, such as boiler feed pump, condensing water pump, condensate pump, vacuum pump, and a multiplicity of valves, all of which need attention when starting up. The Diesel plant requires few auxiliaries, and with the possible exception of the jacket water pump, they are a part of the engine itself and automatically start and stop with it.

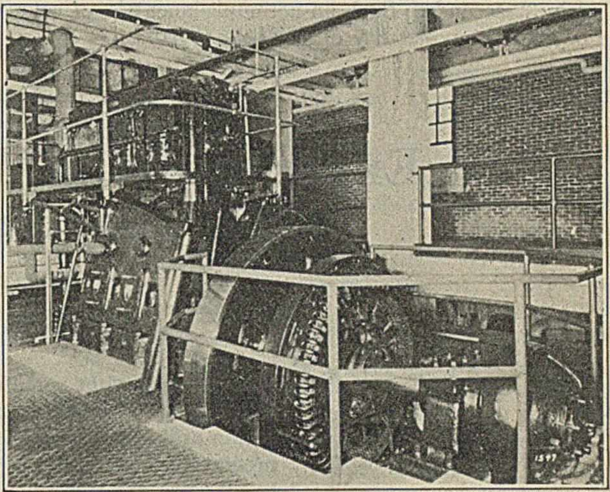

Figure 7—135-Kilowatt Stand-By Diesel in Harrisburg, Pa., Telephone Exchange

The Diesel stand-by plant involves no operating expense when idle. There is no consumption of fuel, nor is any attention required. The steam plant, on the other hand, requires boilers to be kept under steam at all times, which involves a considerable expense for fuel and operating attention.

When the stand-by plant is called upon for service the Diesel engine will produce power at low cost, one gallon of oil developing more than 11 kilowatt-hours. Assuming oil to cost 4 cents per gallon, the fuel cost is 0.35 cent per kilowatt-hour. This is considerably less than the fuel cost in an equivalent steam plant. Other operating costs, such as attendance and maintenance, are also lower in the Diesel plant.

There is no difficulty about getting suitable fuel for a Diesel engine. The range of satisfactory oils is very great, from kerosene on the one hand, to the heaviest crude and fuel oils on the other. In most localities several suitable grades of fuel are available, and that grade is chosen which will give the lowest power costs.

No licensed engineer is required to operate a Diesel engine. Consequently, for stand-by or auxiliary service no regular attendant is needed, one of the factory hands who has been trained in engine operation being called upon only when the engine must be run.

The complete reliability of modern Diesel engines, their moderate cost in comparison with an equivalent steam plant,

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[4] Markwart, "Aspects of Steam Power in Relation to a Hydro Supply." Paper presented at meeting of American Society of Mechanical Engineers, June 28 to July 1, 1926.

and their much smaller need of water are other features that commend them for this sort of service. These matters have already been treated in this article.

Examples of Stand-By Applications

The accompanying photos illustrate some of the uses of Diesels for stand-by and auxiliary power. Figure 5 shows a 2500-kilowatt unit which is one of three recently supplied to the Panama Canal to furnish stand-by service to the Gatun hydroelectric station, which normally furnishes power for the canal's operation. These engines operate on the low-grade fuel ordinarily carried in supply at the canal, which is known as "Bunker C." In the factory tests one of these engines was started and the full load of 2500 kilowatts applied in 32 seconds. Such an accomplishment is, of course, far beyond the possibility of any steam plant.

Figure 6 shows a plant with a capacity of 2000 kilowatts in four units installed by the Chicago Sanitary District to serve as emergency reserve and auxiliary to the district's hydroelectric plant. Shortly after it was placed in operation, in 1922, the coal shortage caused it to be operated at full capacity, and its economical record has resulted in its continued operation to relieve a less efficient auxiliary steam plant. The average fuel consumption at full load is better than 460 kilowatt-hours per barrel of oil.

A telephone exchange without electric power is helpless. Figure 7 shows a 135-kilowatt Diesel installed at the Bell Telephone Central Exchange in Harrisburg, Pa., to operate the switchboard and lighting system in case of failure of the purchased current supply. It is said that it has often been used.

Many chemical industries would benefit by similar applications of Diesel engines.

Experiments in Wood Preservation[1,2]

I—Production of Acid by Wood-Rotting Fungi

By Leo Patrick Curtin

Engineering Laboratories, Western Union Telegraph Co., New York, N. Y.

It is shown that certain representative wood-rotting fungi produce acidic substances in artificial nutrient media and also in wood. The production of acid immediately accompanies the growth of the fungus. In all cases the hydrogen-ion concentration was found to be of approximately pH 5. The acidic reactions were demonstrated with indicators of proper pH, notably sodium alizarin sulfonate and litmus. Methyl red, propyl red, and neutral red were quickly destroyed by *Fomes annosus*. The production of acid was also shown by the solvent action of the fungus on precipitates of calcium carbonate and strontium carbonate. This phenomenon makes possible the use of a new class of materials as wood preservatives.

About 93 per cent of the poles installed by the Western Union are creosoted. For several years this company has operated three plants for treating its poles. Chestnuts and cedars are butt-treated, while yellow pine is given a full-length creosoting under pressure.

These woods are the three principal sources of pole timber in the United States. The cedars are not members of the genus *Cedrus*, but are a group of conifers which are very much alike in their characteristics, the more prominent being *Chamoecyparis thyoides*, *Thuja occidentalis*, and *Thuja plicata.*

In 1925, according to U. S. Department of Agriculture statistics, 2,397,978 poles were treated with preservatives in the United States, 1,325,260 of these being cedars, 780,248 southern pine, and 276,030 chestnuts. Of these chestnuts, 150,000 were installed in Western Union lines.

A generation ago the chestnut was one of the principal sources of pole timber. With its gradual destruction by the chestnut blight it has become a less important factor. The decrease in the supply of chestnuts has been accompanied by a rapid increase in the use of yellow pine for poles of all kinds, and this wood is expected to be the principal source of pole timber in the not distant future. Yellow pine must be full-length treated to prevent its rapid decay both above and below ground. When properly treated, however, it is a very durable pole with excellent mechanical properties.

The cost of full-treating such poles is rather high, as the following typical instance will show: In 1925 a 20-foot yellow-pine pole, 11 cubic feet in volume, delivered at a Mississippi treating plant, cost $2.10. The same pole, full-length creosoted, f. o. b. treating plant, was worth $5.50. One dollar and twenty-five cents of the increase represented labor and other plant expenses, and $2.15 the cost of the creosote absorbed by the pole. It is seen that the creosote in the pole costs slightly more than the pole itself. Such a pole will absorb approximately 15 gallons of creosote, worth 14 cents per gallon. A chestnut pole of the same size requires but 35 cents worth (2.5 gallons) of creosote. This is because the chestnut is butt-treated only and also because its thin layer of sapwood absorbs a relatively small amount of creosote. The cedars are intermediate in their treating costs. They are similar to pines in having a fairly thick layer of sapwood and resemble the chestnuts in that the treatment is confined to the butt.

Up to the present time coal-tar creosote has been the leading preservative because it combines toxicity and a fair degree of permanence with desirable mechanical properties, such as waterproofing, fiber-binding, and lubrication. Its most serious disadvantages are its high cost and the difficulty of obtaining it in sufficiently great quantity to meet all demands. Coal-tar creosote is a by-product of the coke industry and constitutes but 3 per cent of the products of coal distillation. In spite of this and other drawbacks, no cheap organic preservative has been found to compete with it successfully.

The inexpensive preservatives are, in general, water-soluble inorganic salts such as zinc chloride, sodium fluoride, and copper sulfate. Such preservatives, in wood exposed to weather, are subject to loss by leaching and for this reason are not used where timber installations are expected to last more than ten or twelve years. On certain of the larger

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[1] Received March 12, 1927.

[2] In October, 1924, the Western Union Telegraph Company requested the writer to consider its wood-preserving problems and, if prospects appeared favorable, to conduct a research in that field. This paper is the first of a series describing this research.

railroads a tie is destroyed by mechanical shock in six to twelve years, and in such cases zinc chloride has met with some success, particularly in the more arid regions.

In 1925,[3] 167,642,790 gallons of creosote were used for wood preservation in the United States, 53.3 per cent of which was imported. This compares with a consumption of 13,048,539 gallons of petroleum and 26,378,658 pounds of zinc chloride in the same period. Other preservatives were consumed in relatively insignificant quantities.

The present cost of creosoting poles is a serious problem, which with the disappearance of the chestnut is certain to become more acute. A somewhat similar difficulty confronts the railroads and other users of creosoted wood. To meet this situation the Western Union Company decided to attempt the development of wood preservatives which would be (1) available in large quantity, (2) of high toxicity to low forms of vegetable and animal life, (3) at least as permanent as creosote, and (4) of low cost. The present is the first of a series of papers which will tell of the progress toward this goal.

Discussion

Leaving mechanical injuries out of consideration, the principal agents in the destruction of wood are rotting, due to consumption of parts of the wood by fungous organisms, and attack by insects.

It appeared probable that low-cost preservatives could be found only among inorganic substances. Petroleum, the most abundant and least expensive organic liquid, is strictly non-toxic, as will be shown in a later paper. It also seemed certain that the toxic agent must be in solution to kill fungi, since vegetable organisms cannot ingest solid particles. In the wood-preserving industry it is axiomatic that a substance must be soluble in order to be toxic. This idea is well expressed by Bateman and Henningsen, of the United States Forest Products Laboratory:[4]

> Research on the mechanism of the protection of wood by preservatives began with two working hypotheses; first, that any wood preservative must be capable of exerting a poisonous or toxic action on timber-destroying organisms, and second, that for the poisons to be effective they must be sufficiently soluble to exert a poisonous effect in the body fluids of the organism which they are intended to inhibit. In the case of timber-destroying fungi, at least, this means that the preservative must be soluble in water to the extent that the organism may be given a lethal dose.

It would therefore seem that high toxicity and permanence in an inorganic preservative are mutually exclusive properties; if the salt is highly toxic it must be fairly soluble, and if it is soluble it will be lacking in permanence when exposed to rains. If, however, it could be shown that a secretion of the fungus or some decomposition product of the material upon which it lives has capacity for dissolving certain salts of low solubility, the problem of obtaining an inorganic preservative which is both toxic and permanent would be greatly simplified.

For several years the writer has been of the opinion that the production of acidic substances is fairly common and perhaps general in all plants which do not contain chlorophyl. It has long been known that many bacteria, such as *B. lactis acidi* and *B. acetis acidi*, produce acids, and also that acidic products attend the growth of certain molds. Wood-rotting fungi are saprophytes, living on dead vegetable matter. Since they lack chlorophyl, they are unable to synthesize carbohydrate from atmospheric carbon dioxide. They are able, however, to hydrolyze, make soluble, and ingest carbohydrate and other solid organic material previously organized by higher plants.

The explanation of the method by which the fungus brings its food into solution has been that the organism secretes an enzyme or "ferment" which decomposes the solid carbohydrate into soluble substances. For example, Zeller,[5] in a study of the wood-rotting fungus, *Lenzites sepiaria*, mentions a dozen enzymes whose presence was detected in this organism—maltase, raffinase, emulsin, tannase, diastase, ligninase, cellulase, hemicellulase, pectase, pectinase, oxidase, and catylase.

The better known enzymes, such as invertase, have been studied very carefully. In the cases of certain others, however, the only proof of their existence is a chemical reaction, usually a hydrolysis, which might also be brought about by dilute acid.

While a search of chemical and mycological literature failed to disclose any direct evidence of the production of acid by wood-rotting fungi, there were a number of suggestive references, such as that by Sullivan[6] who, in a research on vanillin, recovered lignoceric acid by sublimation from rotten oak wood. Bray and Staidl[7] found that rotten wood contains considerable matter which is soluble in alkali. They did not show whether these acidic substances are produced by fungi, by atmospheric oxidation, or otherwise. Wehmer,[8] in a research which tends to show that lignin is the parent substance of coal, found humins in newspaper pulp in which a fungus had been growing. Rose and Lisse[9] showed that a sound specimen of Douglas fir contained 58.96 per cent of cellulose and 10.61 per cent of matter soluble in 1 per cent sodium hydroxide solution, while a fully decayed piece of the same wood contained 8.47 per cent of cellulose and 65.31 per cent of matter soluble in 1 per cent sodium hydroxide. As the lignin content had varied but slightly, it was evident that the alkali-soluble material had increased at the expense of the cellulose. Other investigators have likewise found that the cellulose is principally attacked, although one or two cases are known where the lignin was more readily destroyed by fungi.[10] Bray and Andrews[11] did some careful work on wood destroyed by *Fomes roseus*, *Lentinus lepideus*, and other fungi. In their opinion the material soluble in alkali comes from cellulose partially disintegrated by fungi.

Such alkali-soluble material need not be organic acid; in fact, it may be organic compounds commonly regarded as neutral substances. It probably consists mainly of carbohydrates of lower molecular weight than cellulose.

The reactions of many carbohydrates with alkali are well known. One need only mention the insoluble calcium salt, or pseudosalt, of dextrose, the soluble compound of calcium with levulose, the various alkaline-earth compounds with the higher sugars, and the numerous compounds of glycerol and other polyhydroxy alcohols with alkali and heavy metals.

Animals may be poisoned by a difficultly soluble substance, such as copper arsenite, because their acidic digestive juices bring the toxic material into solution. If it could be shown that acids are a by-product of fungous growth, then certain difficultly soluble salts might be brought into solution by these acids. Such salts should, of course, contain at least one ion which is toxic to fungi if they are to be of value in wood preservation. They should also be

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[3] Helphenstine, "Quantity of Wood Treated and Preservatives Used in the United States," U. S. Dept. Agr., Forest Service, 1925.

[4] Paper delivered at 21st Annual Meeting of American Wood Preservers Assocn., Chicago, Ill., February, 1925.

[5] "Studies in the Physiology of the Fungi," Pt. 2, Missouri Botanical Garden Annals, 1906.

[6] This Journal, **8**, 1027 (1916).

[7] *Ibid.*, **14**, 35 (1922).

[8] *Brennstoff-Chem.*, **6**, 101 (1925).

[9] This Journal, **9**, 284 (1917).

[10] Hawley and Wise, "The Chemistry of Wood," p. 295, Chemical Catalog Co., 1926.

[11] This Journal, **16**, 137 (1924).

salts of feeble acids, since the weak organic acids evolved by the fungi would have little solvent effect on a difficultly soluble salt of a strong acid, such as barium sulfate. It seemed probable that the fungus acids, if they actually exist, might dissolve such substances as zinc carbonate and copper arsenite but would have no solvent effect on the sulfides of these metals.

Experimental

Before commencing work with wood preservatives, it was essential that the correctness of the theory that wood-rotting fungi produce acids be fully demonstrated in the laboratory. There were practical difficulties, at least in the beginning, toward showing such reactions on wood. It seemed advisable, therefore, first to investigate the chemical reactions in nutrient media in which the growth is much more rapid than in wood.

Reactions in Nutrient Media—A great many cultures were made in which various indicators were dissolved in the nutrient jelly, the idea being that any acid produced by the fungus would react with the indicator and bring about the characteristic change in color. These tests showed conclusively that acid was produced by every fungus under trial. In all cases uninoculated samples of the nutrient jelly dyed with the indicator were kept for comparison. These sterile blanks retained their original basic color, showing that the indicator changes which occurred in the inoculated specimens were due solely to acid produced by the fungi.

The original cultures of the wood-rotting fungi were obtained from the U. S. Forest Products Laboratory. They included fungi which are common in rotting oak, chestnut, and other hard woods, as well as the coniferous woods. These and all other experiments with growing fungi were made under conditions of high asepsis to avoid infection of the cultures by air-borne spores of bacteria or fungi.

Reactions of Fungi in Agar–Malt Sirup Culture Medium

Fungus	Indicator	Original (Basic) Color	Final (Acidic) Color
Wood-rotting:			
Fomes annosus	Methyl orange	Yellow	No change
Fomes annosus	Congo red	Red	No change
Fomes annosus	Methyl red	Yellow	Indicator destroyed
Fomes annosus	Sodium alizarin sulfonate	Red	Greenish yellow
Fomes annosus	Propyl red	Yellow	Indicator destroyed
Fomes annosus	Litmus	Blue	Purplish red
Fomes annosus	Rosolic acid	Red	Pale yellow
Fomes annosus	Neutral red	Colorless	Indicator destroyed
Lenzites sepiaria	Methyl orange	Yellow	No change
Lenzites sepiaria	Sodium alizarin sulfonate	Red	Greenish yellow
Lentinus lepideus	Methyl orange	Yellow	No change
Lentinus lepideus	Sodium alizarin	Red	Greenish yellow
Polyphorus pilotae	Methyl orange	Yellow	No change
Polyphorus pilotae	Sodium alizarin sulfonate	Red	Greenish yellow
Polyphorus sulphureus	Methyl orange	Yellow	No change
Polyphorus sulphureus	Sodium alizarin sulfonate	Red	Greenish yellow
Mold:			
Rhizopus nigricans	Methyl orange	Yellow	Red
Rhizopus nigricans	Congo red	Red	Violet
Rhizopus nigricans	Sodium alizarin sulfonate	Red	Greenish yellow
Rhizopus nigricans	Litmus	Blue	Red
Penicillium	Methyl orange	Yellow	No change
Penicillium	Sodium alizarin sulfonate	Red	Greenish yellow

The tests shown in the accompanying table were made in a nutrient medium composed of 1.5 per cent agar and 2.5 per cent malt sirup. This gave a rigid gel containing about 3.5 per cent dry matter. The experiments proved conclusively that fungi growing in this medium liberate acid.

The change in the color of the indicator preceded the visible growth of the fungus by 1 or 2 mm. in the case of the wood-rotting organisms, and by 1 to 2 cm. in the cases of *Rhizopus nigricans* and several other mold fungi.

Looking through the bottom of a Petri dish culture dyed with sodium alizarin sulfonate, the jelly appeared as a brilliant red disk by strong transmitted light. A day or two after the fungus showed evidence of growth, a pale yellow spot appeared under the transplant. A few days later the culture showed a good-sized greenish yellow disk in the center surrounded by a wide red rim. In 2 weeks, or less, the entire culture had assumed a pale greenish yellow color with no trace of the original basic red.

While this greenish yellow color is characteristic of the alizarin sulfonic acid, to avoid any possibility of error the entire culture was melted in hot water and sodium carbonate solution added. This immediately restored the strong red basic color of the indicator, showing that the change in color was due solely to acid produced by the fungus.

All the cultures described above were repeated with an agar-starch culture medium and those listed under *Fomes annosus* were also repeated with a gelatin-sugar medium. Litmus, sodium alizarin sulfonate, and methyl orange were the only indicators used in these tests. The indicator reactions exactly checked those obtained with the agar-malt sirup cultures. The only differences noted were that the starch and sugar cultures gave less vigorous growths and the gelatin cultures tended to liquefy with the growth of the fungus.

Methyl orange is a very satisfactory indicator for testing many of the molds. It is too insensitive for those of the wood-rotting fungi which have been tried. Congo red is also lacking in sensitivity and in color is inferior to methyl orange. Sodium alizarin sulfonate is an excellent indicator for the wood-rotting organisms. It is less toxic than many other indicators and does not change color with carbon dioxide which is evolved in quantity by fungi.

Methyl red, propyl red, and neutral red are quickly destroyed by the fungi. The first two are yellow in the basic condition and all three are red in presence of sufficient acid. In the cultures of the methyl and propyl reds it was noted that after the fungus started to grow the bright yellow color quickly disappeared with no production of red. After the yellow color had vanished the cultures were melted, some being tested with alkali and others with dilute sulfuric acid. No trace of the indicator was found by these tests. As the uninoculated blanks had retained their yellow color unimpaired, it was evident that the fungus had destroyed the indicators.

Litmus is a satisfactory indicator for these reactions but not nearly so desirable as the alizarin sulfonate. Rosolic acid showed the usual acid reaction with the fungus, but was discontinued because of its tendency to fade, even in the uninoculated specimens. It is also very toxic, as might be expected from its phenolic nature, and for this reason it could only be used in very low concentrations.

Tests on Fungus Growing on Wood—While it appeared certain, because of the chemical similarity of the nutrient substances, that the acidic reactions found to accompany fungous growth in culture media also take place in rotting wood, it seemed desirable to demonstrate the correctness of this supposition by means of a fungus actually growing on wood. After several failures, proof was obtained in the following manner:

A number of sapwood sticks of short-leaf southern yellow pine and white cedar, about 15 cm. in length and 1 sq. cm. in cross section, were boiled for 3 hours in 0.05 per cent sodium carbonate solution to neutralize the acids occurring naturally in the wood. They were next boiled for 3 hours in water to remove excess sodium carbonate. The sticks were then soaked in sodium alizarin sulfonate solution until they were definitely red. After sterilization with steam at 15 pounds per square inch (1055 grams per sq. cm.) pressure, they were placed in 8-inch (20-cm.) test tubes in contact with a small block of wood on which was growing a pure culture of *Fomes annosus*.

It was not desirable to place the colored sticks in contact with a nutrient medium of the jelly type, as some of the material would penetrate the wood by capillarity and give reactions which might be credited to the wood itself. To avoid such a possibility, sticks of sterilized yellow pine about 15 cm. long were placed in test tubes in the bottom of which were 5 cc. of very stiff gel in which a pure culture of *Fomes annosus* was growing. The tubes were kept in the vertical position and the fungous growth gradually ascended the sticks. At the end of 6 weeks a dense growth of fungus completely covered all parts of the wood. Blocks about 1 cc. in volume were cut from the tops of these sticks and served as the inoculating medium in the tests with sticks colored with indicator. A plug of cotton in the top of the test tube served to bring the colored stick in firm contact with the mat of mycelium covering the inoculating block.

Growth soon commenced on the colored sticks and the acidic reaction was clearly apparent 24 hours later. The sticks were progressively decolorized, and after 3 weeks one-third to one-half of the lower ends of the sticks had lost their red color, the upper ends retaining their original appearance. Because of the toxicity of the indicator, the growth was frail and there was no difficulty in seeing the wood beneath it.

At this time the sticks were taken out for examination. Some of them showed no suggestion of redness in their lower parts, while several showed a few streaks of red because of deposits of indicator considerably below the surface. The sticks first described were held in ammonia fumes, which quickly restored the basic red color of the indicator. This step was necessary as the acidic greenish yellow color of alizarin sulfonic acid is scarcely detectable on yellow pine. The sticks which showed one or two streaks of red were then marked with a pencil to enclose areas having no trace of redness. Ammonia fumes restored the red color to all these sticks, including the areas so enclosed. Evidently, the production of acids by fungi takes place in wood as well as in artificial nutrient media.

ACTION OF FUNGUS ON CARBONATE PRECIPITATES—The production of acid in the agar–malt sirup gels was also shown by means of certain insoluble carbonates, notably strontium and calcium carbonates. A nutrient medium was prepared containing strontium chloride in solution equivalent to 1.5 per cent strontium carbonate. To this hot solution was added exactly sufficient sodium carbonate solution to precipitate the strontium as carbonate. Such gels without the precipitate of carbonate are translucent and transmit light very well. With the finely divided strontium carbonate precipitate, the culture assumes an opaque appearance somewhat resembling ground glass. Strontium carbonate is of low toxicity, and a transplant of *Fomes annosus* gave a slow but dense and vigorous growth in these cultures. As the growth of the fungus progressed, the opaque appearance disappeared and the jelly became translucent, indicating that the strontium carbonate had been brought into solution. After several weeks the entire culture medium had become translucent, showing no evidence of the presence of strontium carbonate. As with the indicator reactions, the translucent disk in the opaque culture increases in radius as the growth of the fungus progresses. Blank, uninoculated cultures, which also contained a precipitate of strontium carbonate, retained their opacity throughout the test.

This experiment was later repeated with cultures containing 0.75 per cent of calcium carbonate, with identical results. Solution of such difficultly soluble carbonates by the fungus acids is quite convincing and would in itself constitute proof of the existence of these acids, since there is no indication of solvent action by the nutrient medium itself.

Value of Research

A study of the indicator reactions shows that the acid solution produced by the wood-rotting fungi is of approximately pH 5. While this is a feebly acidic solution, it must be remembered that its action on rotting wood may extend over a period of several years. From this point of view the acid produced by the fungus may be of considerable help in making carbohydrate available for ingestion by the wood-rotting organism.

Nothing has been done to ascertain whether the acid liberated is a secretion of the fungus or a degradation product of the nutrient substance.

The production of acid by fungi may be of interest to botanists by clearing up a detail in connection with the peculiar vegetable organisms called lichens. The lichen is really two plants, generally a blue-green alga and a fungus, living in a symbiotic and, apparently, mutually helpful relationship. The alga contains chlorophyl and, by photosynthesis, obtains its needed carbohydrate from the atmosphere. The fungus extracts nutrient from the alga osmotically by means of hyphae, or directly by haustoria which penetrate the algal cells. The contribution to the partnership by the fungus is of a mechanical nature. Because of its tough, fibrous composition, it protects the more delicate alga and, by holding moisture, retards desiccation. If it could be shown that such fungi make mineral nutrient material available by liberation of acid, then the partnership would appear much more equitable than at present. It would help explain how the lichen, although composed of two delicate plants, is able to thrive on the rocks of arctic regions.

Trees Tested for Pulp Suitability

The suitability of 94 species of American woods for paper pulp has been tested experimentally by the Forest Service, Department of Agriculture, in an effort to find satisfactory woods to take the place of the decreasing supply of spruces, firs, and hemlocks.

The use of the more plentiful and less commonly used species of wood may be greatly increased, and expanded in the South, according to H. S. Betts, engineer of the Forests Products Division. At present, the spruces furnish 55 per cent of the wood consumed by the paper industry in the United States and, with the firs and hemlocks, furnish 77 per cent.

The Forest Service does not attempt to recommend definite species as substitutes for the three established woods, but only to report the results of treatment of the woods by various processes. The experiments are intended to serve as a guide for further investigation by the industry and indicate that:

> The sulfate process applied to the Southern pines, in combination with the gums and similar hardwoods of the South, will yield pulps which may be bleached by proper methods and used in the manufacture of book, magazine, and similar high-grade printing papers at reasonable manufacturing cost. The value of this experimental work is emphasized by the fact that the South is advantageously situated in respect to nearness to the publishing centers and availability of fuel, chemicals, and other raw materials. Not only has it enormous quantities of suitable woods available, but owing to climatic conditions the amount of wood which can be grown in the South is approximately 35 per cent of the potential productivity of the entire area of forest land in the United States. The growing capacity of unit areas is also very high.
>
> On the other hand, for pulps which require spruce, hemlock, and fir, woods of established value for making paper, there are stands in Oregon, Washington, and Alaska sufficient, under proper timber growing methods, to supply approximately 5,000,000 cords a year. It has been due largely to economic conditions that the extensive development of these pulp resources has so long been retarded.

Mechanism of the Steam-Carbon Reactions[1]

By E. W. Thiele and R. T. Haslam

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Four different kinds of carbon were treated with steam at various pressures in an effort to determine the mechanism of the reaction of steam and carbon.

ALL investigators who have considered the mechanism of the reactions between steam and incandescent carbon have assumed that the possible reactions were four in number:

$$\begin{array}{rcll} C + H_2O & = & CO + H_2 & (a) \\ C + 2H_2O & = & CO_2 + 2H_2 & (b) \\ C + CO_2 & = & 2CO & (c) \\ CO + H_2O & = & H_2 + CO_2 & (d) \end{array}$$

They have accordingly tried to decide which of these reactions take place, and to what extent. The previously suggested mechanisms, which are summarized by Haslam, Hitchcock, and Rudow,[2] while they explain the facts, are chosen from among many alternative explanations and rest on little more than judgment. These authors have made a more quantitative attempt to solve the problem, but they also have started with the four reactions (*a*) to (*d*), inclusive.

The present work was begun with the object of attempting to disentangle the effects of these reactions by a study of the effect of varying steam pressures. The results of the work indicate, however, that the facts cannot be explained completely in terms of the simple equations given above. The decomposition of water by steam involves a surface reaction of the same sort as that which Langmuir[3] and Rhead and Wheeler[4] have shown to be involved in the combustion of carbon. The observations which led to this conclusion may be stated thus:

If steam at atmospheric pressure is passed over a bed of hot coconut charcoal, graphite, or electrode carbon, a certain number of grams of steam will be decomposed per minute; and if the steam rate is sufficiently high the steam decomposed may be only a small part of the whole, so that the partial pressure of the steam does not change appreciably in passing through the bed. If steam be now passed through the same bed at half an atmosphere, the temperature and the number of grams of steam passing per minute remaining the same, it might be expected that the grams of steam decomposed per minute would be one-half or one-fourth as great, according as the reaction is of the first or second order (with respect to the steam). As a matter of fact, under these conditions the number of grams of steam decomposed remains nearly the same and the reaction behaves as if it were of the zero order.

With retort carbon above 1010° C. the results are still more striking. When the pressure of the steam is lowered in this case, the weight of the steam decomposed per minute actually increases very markedly. The reaction behaves as if it were of a "negative" order.

Note—The terms "zero order" and "negative order" are unusual, but only because the thing they represent is unusual; they are logical extensions of present usage. If the concentration of a substance is denoted by x and the rate of reaction changes as x^2, it is said to be of the "second" order with respect to that substance. If it changes as x^1, it is said to be of the "first" order. If, as in the present case, we have a reaction rate changing as $1/x$, that is, as x^{-1}, analogy requires that it be considered as of order "minus one." Where a change in x does not affect the rate, the rate may be said to change as x^0, since the value of x^0 is independent of the value of x. Such a reaction is therefore of "zero" order with respect to the substance in question.

The composition of the fixed gases resulting from the decomposition runs parallel to the apparent order of the reaction. Where the order of the reaction is zero, the composition is not much affected by pressure changes. Where the order of the reaction is negative, a reduction in pressure produces a large decrease in the amount of carbon dioxide formed, as compared with the carbon monoxide.

The effects here mentioned are produced whether the lowering of the steam pressure is produced by lowering the total pressure or by diluting the steam with an inert gas. It appears, though it is not certain, that lowering the partial pressure of the steam with the products of the reaction does not produce the same effects.

EXPERIMENTAL

Apparatus

The apparatus is represented in Figure 1. The reaction tube *A*, was of fused quartz, 36 inches long, about 7/8 inches internal diameter. It was supported vertically in the Hanovia tube furnace, *B*, 24 inches long, with tube of 2 inches internal diameter, by means of asbestos slate end pieces. The temperature was measured by a chromel-alumel thermocouple, *D*, which was wired to the outside of the reaction tube, the hot junction being opposite the fuel bed in the tube, the depth of the fuel bed in most cases being less than 3 inches. The voltage was measured by a Brown millivoltmeter of 1100 ohms resistance.

At the bottom of the reaction tube was a small roll of stiff nichrome wire. Above this was an alundum thimble, and above the thimble the tube was filled with pieces of porous porcelain plate. These furnished additional surface for the superheating of the steam and supported the fuel bed, which came next. Above the fuel bed the rest of the tube was filled with large porcelain, to hasten the exit of the reaction products.

The steam was provided by heating distilled water electrically. The boiler, *G*, was of Pyrex, the bottom being closed by a rubber stopper through which passed nichrome leads to the heater. The heater consisted of 10 feet of No. 30 chromel A wire having a resistance of about 50 ohms. Alternating current was used. The current in the heater was controlled by the rheostat, *H*, and measured by the ammeter, *J*.

In order to insure that the water evaporated should always be nearly equivalent to the electrical input, the boiler was surrounded by a steam jacket, the liter Erlenmeyer flask, *K*. In this flask water was boiled during the run, so that the temperatures on the outside and inside of the boiler were always very nearly the same. The flask was connected to the air condenser, *L*.

The reaction tube projected about 4 inches below the furnace, the exposed portion being lagged with asbestos, so that the heat conducted down the tube would keep the temperature above 100° C. The upper end of the reaction tube projected about 7 inches, and this portion was surrounded by an asbestos shield, inside which a Bunsen burner, *N*, was lighted to keep the water in the exit gases from condensing. The upper end of the tube was closed by a rubber stopper containing a thermometer, a capillary tube used as a gage connection, and a three-way stopcock, *X*, which permitted the products to be wasted or to pass into the absorption train.

The absorption train consisted of an empty distilling bulb, *P*, immersed in a beaker of water, to condense the bulk of the steam; two calcium chloride tubes, the second a catch; a tube filled with soda lime, or ascarite, to absorb carbon dioxide; and a calcium chloride tube as catch for the soda lime. The last absorption tube was connected through a three-way stopcock,

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[1] Received April 2, 1927. From a thesis submitted by E. W. Thiele in partial fulfilment of the requirements for the degree of doctor of science at the Massachusetts Institute of Technology.

[2] This Journal, **15**, 115 (1923).

[3] *J. Am. Chem. Soc.*, **37**, 1154 (1915).

[4] *J. Chem. Soc.* (*London*), **103**, 461 (1913).

W, to the sample bottle, *Q*, and to the carboy, *U*. The sample bottle was of 1 or 2 liters capacity, and was connected by a siphon tube with the water container, *R*. The sample collected was usually of from 500 cc. to 1 liter at atmospheric pressure.

The gage connection was connected to two gages, *S* and *T*. *S* was filled with mercury and open to the atmosphere, and *T* was filled with water. The carboy *U* was connected to a Richards pump for pressures below atmospheric or to a nitrogen cylinder for pressures above atmospheric.

Procedure

In making a run the furnace was brought up to temperature and the boiler started, the products being wasted through the cock *X*. After a sufficient purge, usually about 5 minutes, the cock *X* was turned and the gas passed through the train into the sample bottle. The cock *W* permitted evacuation of the train before beginning the run. In this way the air in the train at the start of the run was forced into the sample. Since the only source of oxygen in the sample was this air, the observed analysis could be easily corrected to the true gas composition. The water and carbon dioxide were determined by weighing, the other constituents by gas volume measurement. The accuracy of the work is shown by the closeness with which the gas analyses corresponded with the theoretical stoichiometric relationships.

Gas analyses were made with a Williams apparatus, except in the nitrogen runs, where a Burrell gas analysis apparatus was used. In some runs which were made at very low rates the buret of the Williams apparatus served as a sample bottle, special small U-tubes being used.

Kinds of Carbon Used

Four kinds of carbon were used:

(1) A steam-activated vegetable charcoal, called "52 minute Absorbite," from the Barnaby-Cheney Company. It contained 4.8 per cent ash. It was about 14 mesh.

(2) An arc-electrode carbon, crushed, three sizes being used. It was approximately the same as that used by Haslam, Hitchcock, and Rudow.[2]

(3) A natural graphite, from Sonora, Mexico, obtained through the courtesy of the U. S. Graphite Company. This material passed an 8-mesh screen and was retained on a 14-mesh screen.

(4) A retort carbon, obtained from the horizontal D type gas retorts of the Cambridge Gas Light Company. It contained 1.8 per cent ash and was used in two sizes, although most of the work was done with material of about 6 mesh.

Effect of Use on Carbon

To show the effect on the retort carbon of treating it with steam, three successive runs were made on one sample at atmospheric pressure and 1070° C., 20 grams of the carbon being used. Each run was preceded by a purge period. The results are given in Table I.

This decrease in the rate of reaction is much greater than the decrease in the amount of carbon present would warrant, since the total carbon gasified was less than one gram out of the 20 grams.

A similar experiment was made with 20 grams of arc electrode carbon at 1040° C. (Table I). In this case, however, the rate of reaction increased. The difference is probably due to the fact that the arc electrode carbon surface is comparatively smooth and dense, so that during the reaction the surface becomes rough and porous, the total active surface being increased. (The roughening was evident when the sample was removed from the reaction tube.) In the case of the retort carbon the material was already very porous.

Two successive runs with the active charcoal showed no difference whatever. No tests of this sort were made on the graphite.

In order to avoid the effects noted above, all runs were made either on fresh samples or on samples from which one run only had been taken.

It was found difficult to get check results on reaction rate within about 20 per cent variation from the mean. The great change in rate with slight changes in temperature was undoubtedly one cause of this. Slight variations in the samples or other factors may have contributed. To overcome this, two runs were made for every sample. The first or (*a*) run was a standardizing run, made at atmospheric pressure. The second or (*b*) run was made at the pressure which was being studied. The ratio of the second to the first has been used in studying the effect of pressure.

Table I—Effect of Steam on Carbon

RUN	H_2O PASSED	H_2O DECOMPOSED	CO_2 IN DRY GASES
	Mols per min.	*Mols per min.*	*Per cent*
	RETORT CARBON		
78*a*	0.0438	0.00233	20.2
78*b*	0.0445	0.00192	17.4
78*c*	0.0447	0.00176	16.1
	ARC-ELECTRODE CARBON		
94*a*	0.0956	0.00488	7.0
94*b*	0.0955	0.00636	6.1
94*c*	0.0977	0.00700	6.0

In a sense this amounts to determining the areas of surface on each fresh sample (in arbitrary units) by noting the rate at which it decomposes steam, all other variables being held constant, and then reducing all results to a common basis. Thus it eliminates the effect of variation in effective area of the samples. It also takes care of temperature variations from day to day, such as might arise from a slow change in pyrometer calibration. As a matter of experience this mode of procedure resulted in smooth curves.

If the rate of reaction of the fresh coke is denoted by *A*, and the rate for coke on which one run has been made is denoted by *B*, and if we use two subscripts to denote the temperature and the pressure in millimeters of mercury, the ratio method, as used where only one temperature is in question, may be described thus: Instead of comparing, for example,

$$A_{1000° C., 750 mm.}, A_{1000° C., 600 mm.}, A_{1000° C., 450 mm.}, \text{etc.},$$

we compare

$$\frac{B_{1000° C., 750 mm.}}{A_{1000° C., 750 mm.}}, \frac{B_{1000° C., 600 mm.}}{A_{1000° C., 750 mm.}}, \frac{B_{1000° C., 450 mm.}}{A_{1000° C., 750 mm.}}, \text{etc.}$$

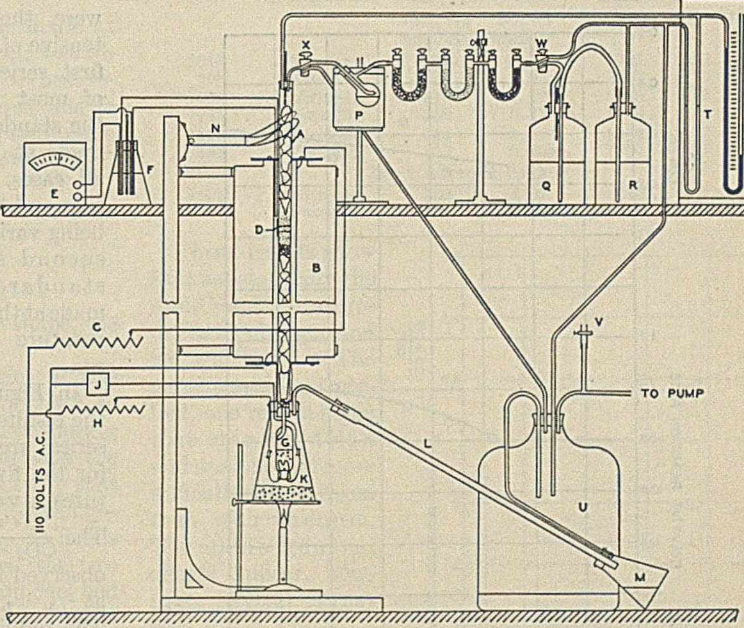

Figure 1

It will be noted that the first of these ratios is not in general equal to unity, on account of the change in coke with use.

Where the effect of temperature as well as pressure was under investigation, two procedures were used. Where the temperature did not vary widely, it was possible to make all the standardizing (*a*) runs at atmospheric pressure and one temperature, a whole series of (*b*) runs being made at various temperatures and at various pressures including atmospheric. In symbols, this method consists in finding the ratios:

$$\frac{B_{1010^\circ\text{C.},\ 250\text{mm.}}}{A_{1070^\circ\text{C.},\ 760\text{mm.}}},\ \frac{B_{1010^\circ\text{C.},\ 500\text{mm.}}}{A_{1070^\circ\text{C.},\ 760\text{mm.}}},\ \frac{B_{1010^\circ\text{C.},\ 760\text{mm.}}}{A_{1070^\circ\text{C.},\ 760\text{mm.}}},\ \frac{B_{1070^\circ\text{C.},\ 250\text{mm.}}}{A_{1070^\circ\text{C.},\ 760\text{mm.}}},$$

$$\frac{B_{1070^\circ\text{C.},\ 760\text{mm.}}}{A_{1070^\circ\text{C.},\ 760\text{mm.}}},\ \frac{B_{1125^\circ\text{C.},\ 250\text{mm.}}}{A_{1070^\circ\text{C.},\ 760\text{mm.}}},$$

or the like.

Where the temperature variation was wide, this procedure was not possible; and in this case all the (*a*) runs were made at the same temperature as the corresponding (*b*) run. In symbols, this consists in finding

$$\frac{B_{850^\circ\text{C.},\ 300\text{mm.}}}{A_{850^\circ\text{C.},\ 760\text{mm.}}},\ \frac{B_{950^\circ\text{C.},\ 300\text{mm.}}}{A_{950^\circ\text{C.},\ 760\text{mm.}}},\ \frac{B_{1050^\circ\text{C.},\ 300\text{mm.}}}{A_{1050^\circ\text{C.},\ 760\text{mm.}}}$$

The results obtained in this way give the general character of the effects, but small errors are introduced which are eliminated by the first method.

RESULTS

Experiments with Active Charcoal

These tests were made at 875° C. only, the ratio method being used. (Figure 2) The ratio $\frac{CO_2}{CO + CO_2}$ in the fixed gases from the (*b*) runs, which gives a measure of the change in composition of the gases as the pressure is lowered, is plotted using the same pressure coördinates. It will be seen that the rate of reaction falls off slightly as the pressure is lowered, but that the composition of the gases obtained is nearly the same.

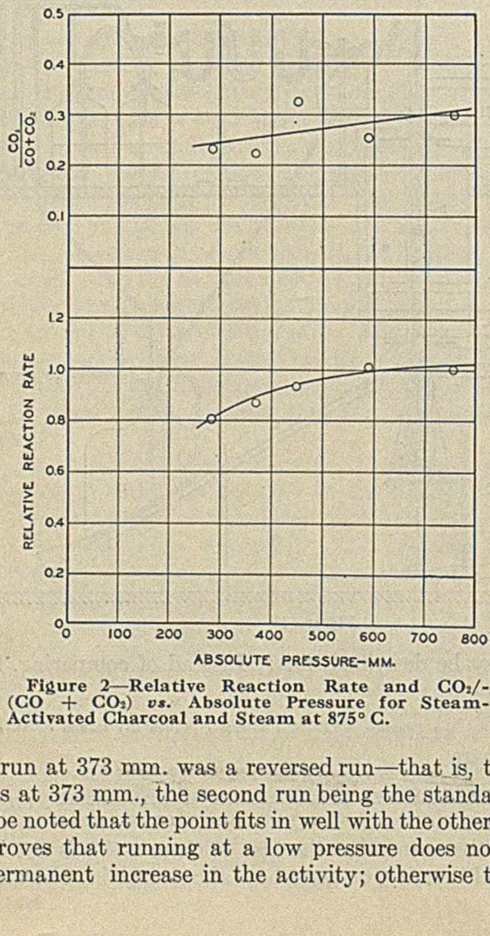

Figure 2—Relative Reaction Rate and CO_2/(CO + CO_2) *vs.* Absolute Pressure for Steam-Activated Charcoal and Steam at 875° C.

The run at 373 mm. was a reversed run—that is, the first run was at 373 mm., the second run being the standard run. It will be noted that the point fits in well with the other points. This proves that running at a low pressure does not cause any permanent increase in the activity; otherwise the rate during the second run would have been much more rapid than during the first.

Experiments with Graphite

The experiments with graphite were three in number. The standard (*a*) runs were made at the same temperatures as the (*b*) runs, which were all at about 335 mm. pressure. (Table II)

Table II—Graphite Experiments

Run	Temperature	Rate Ratio	CO_2 in Dry Gas	
			(*a*)	(*b*)
	° *C.*	(*b*)/(*a*)	*Per cent*	*Per cent*
110	845	0.785	12.5	10.9
99	960	0.895	14.0	12.6
111	1055	0.796	9.8	6.3

Thus in general the effect of lowered pressure, at all three temperatures, is similar to that with active charcoal, allowing for the fact that the carbon dioxide in a (*b*) run may be expected to be a little lower, as in the case of arc and retort carbon. Why the carbon dioxide should be greater at the intermediate temperature is not clear.

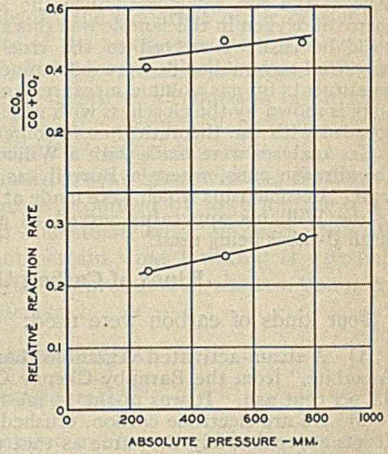

Figure 3—At 1010° C.

Experiments with Retort Carbon

These experiments were the most extensive of all. In the first series, which is of most importance, the standard run was made at 1070° C. in all cases, both pressure and temperature being varied. In the second series the standard run was made at the same temperature as the (*b*) run.

In Figures 3 to 7 the results of the first series are presented for the five temperatures investigated. The $\frac{CO_2}{CO_2 + CO}$ ratios observed in the (*b*) runs are plotted as before. The results at 1/3, 1/2, and 1 atmosphere are summarized in Figure 12. The nature of the results has already been indicated.

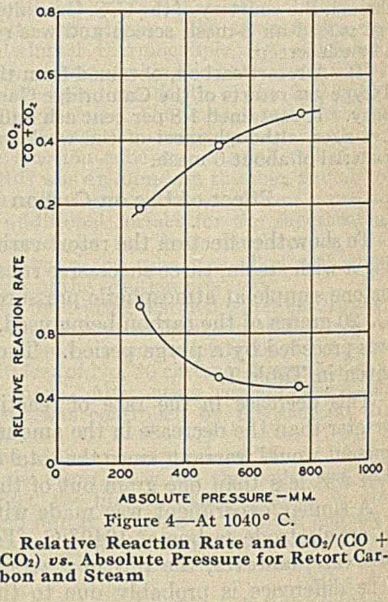

Figure 4—At 1040° C.

Relative Reaction Rate and CO_2/(CO + CO_2) *vs.* Absolute Pressure for Retort Carbon and Steam

To these data may be added the results of one experiment at 990° C. given in Table III.

Table III—Retort Carbon Data

Run	Pressure	H_2O Passed	H_2O Decomposed	CO_2 in Dry Gas
	Mm. Hg	*Mols per min.*	*Mols per min.*	*Per cent*
73*a*	767	0.0221	0.00180	23.6
73*b*	388	0.0243	0.00159	20.8

The results at 990° C. are therefore substantially the same as at 1010° C.

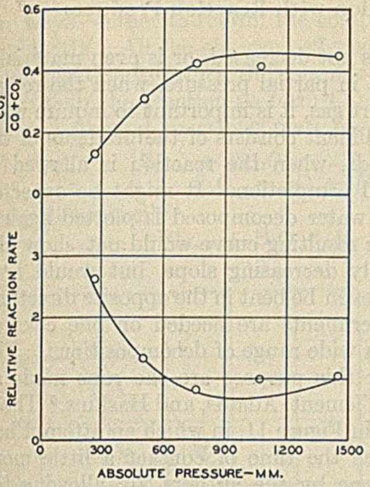

Figure 5—At 1070° C.

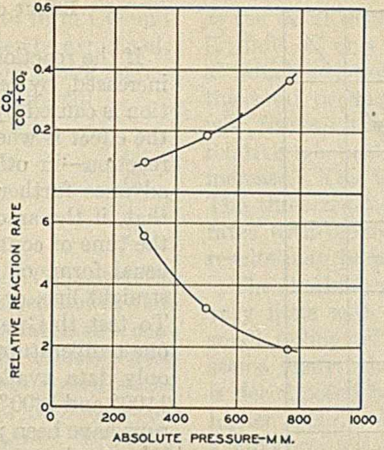

Figure 6—At 1095° C.

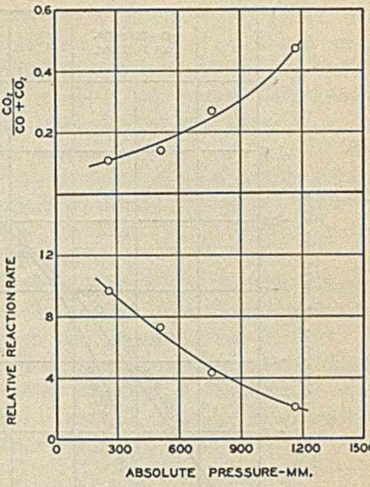

Figure 7—At 1125° C.

Relative Reaction Rate and $CO_2/(CO + CO_2)$ *vs.* Absolute Pressure for Retort Carbon and Steam

Experiments with Arc-Electrode Carbon

These experiments belong to two series. The first series was made at 1025° C. The runs were not made by the ratio method, but are single runs, made on fresh coke. There is included also a run made on a sample from which one run had already been made. The rate found in this case was reduced in the ratio in which successive runs at the same pressure were found to increase, as shown by run 97. The results are plotted in Figure 8. It will be observed that the points fall on a good curve, which indicates that with this carbon accidental variations are small. As usual, the $\frac{CO_2}{CO + CO_2}$ ratio is given, but these values are of course for fresh material.

In the second series the standardizing run was made at the same temperature as the (*b*) run. The (*b*) run was always made at a pressure of about 300 mm. absolute. These results were carried over a wide range of temperatures, and to assist in making this possible three sizes of carbon were used, the weights per piece of each size being as follows:

Mesh	Weight per Piece
	Grams
3 to 4	0.1659
4 to 6	0.0503
8 to 14	0.00444

Assuming these pieces to have the same average shape, the surfaces are in the ratio of 2.252:1:0.673.

In extending this series to the lower temperatures, it was found desirable to use a deeper fuel bed instead of the 2- to 2.5-inch fuel beds usually employed, as with these deeper fuel beds the points did not lie on the same line with the shallow fuel beds. The reason for this is undoubtedly that in the deep beds the temperature was not uniform throughout. Hence two figures, 9 and 10, are presented. In one is plotted temperature against the observed rates at the two pressures (not ratios). In this chart only the thin fuel bed results fall on the line. The rates are corrected for the varying surface. In the other chart the $\frac{CO_2}{CO + CO_2}$ ratio is plotted against the observed rate, both thick and thin fuel bed results being given.

There is only a slight indication (around 940° C.) of any such effect as is observed for retort carbon. For most of the range the high- and low-pressure rates are so nearly the same that they are indistinguishable on the chart. The $\frac{CO_2}{CO + CO_2}$ values also differ only slightly, as compared with the large variations produced in the case of retort carbon. Again it must be noted that, as run 94 shows, the carbon dioxide may be expected to be a little lower in the second run.

Effect of Nitrogen Dilution

Four experiments were made. Each of these paralleled a run made with vacuum, the only difference being that on the (*b*) run the lower steam pressure was produced by nitrogen instead of vacuum. The (*a*) runs were all made at the temperature given and at atmospheric pressure. The results are assembled in Table IV.

Table IV—Effect of Nitrogen Dilution

Run	Partial Pressure Lowered by:	Pressure	Rate Ratio	Temp.	CO_2 in Dry N_2-Free Gas
		Mm. Hg	(*b*)/(*a*)	° *C.*	*Per cent*
		Retort Carbon			
101*b*	Nitrogen	270	2.32	1065	9.7
85*b*	Vacuum	270	2.62	1065	6.1
100*b*	Nitrogen	318	1.17	1040	7.7
84*b*	Vacuum	260	0.87	1040	8.7
102*b*	Nitrogen	264	0.225	1010	17.4
83*b*	Vacuum	262	0.224	1010	17.0
		Arc-Electrode Carbon			
103*b*	Nitrogen	303	1.27	940	7.3
95*b*	Vacuum	305	1.03	940	7.1

These results show that substantially the same results are produced by nitrogen and by vacuum. The agreement is not perfect, one reason being that manipulation and analysis are more difficult with nitrogen than with vacuum. The same general effects appear, however, beyond question.

The Work of Others

The only work done at pressures other than atmospheric is that of Pexton and Cobb,[5] who used nitrogen for a diluent and found the reaction to be of zero order (thus agreeing with the present work); and that of Haslam,

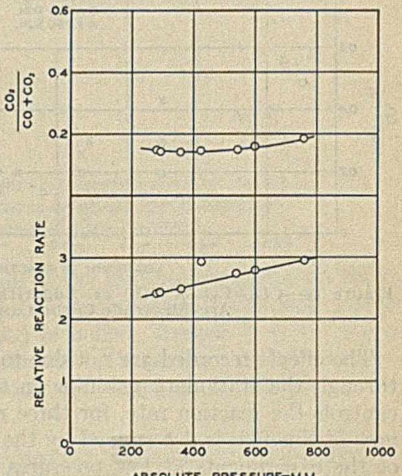

Figure 8—Relative Reaction Rate and $CO_2/(CO + CO_2)$ *vs.* Absolute Pressures for Arc-Electrode Carbon and Steam at 1025° C.

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[5] *Gas J.*, **161**, 163 (1924).

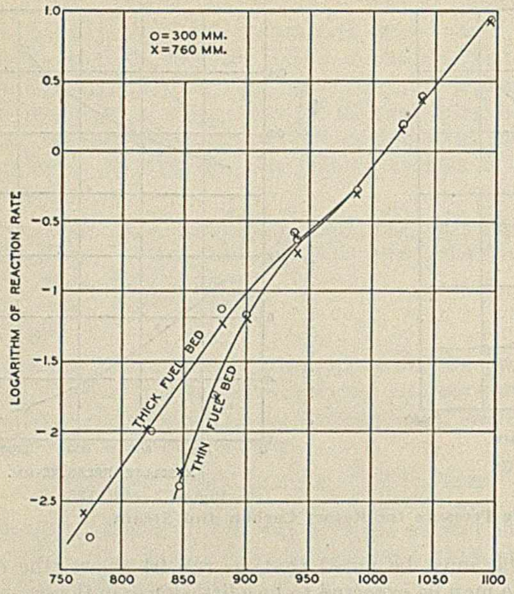

Figure 9—Logarithm of Reaction Rate *vs.* Temperature for Arc-Electrode Carbon and Steam

Hitchcock, and Rudow.[2] The results reported in the latter paper are entirely at variance with those obtained in the present work, in that the reaction seemed to be of the first order with respect to steam pressure (changes in which were produced by vacuum). The reason for the difference is not known; it was not the material used, for the arc carbon used in the present work was substantially the same as that used by these workers.

Discussion of Results

The results with retort carbon make it obvious that a difference in temperature between the inside and the outside of the tube cannot be the cause of the results. If such a difference arose because of the heat absorbed by the reaction, the effects would be in the opposite direction from the observed effects.

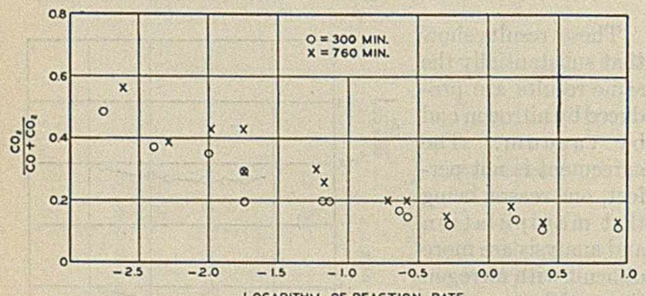

Figure 10—$CO_2/(CO + CO_2)$ *vs.* Logarithm of Reaction Rate for Arc-Electrode Carbon and Steam

The effects recorded are not due to the fact that diffusion through the stationary gas film on the surface of the coke controls the reaction rate, for three reasons: (1) The thickness of this film is determined by the mass velocity and most of the experiments at low pressures were run at the same mass velocity as the experiments at high pressures; (2) diffusion changes only slowly with temperature, whereas Figure 8, for example, shows that the rate of reaction doubles every 25 or 30 degrees; (3) reactions of this type controlled by diffusion must be very fast—combustion of carbon with oxygen, for example. The rates here in question are of an entirely lower order of magnitude.

Effect of Dilution with Reaction Products

If the reaction rate is not decreased, or is even materially increased, by reduction in partial pressure, when the reduction is caused by an inert gas, it is important to inquire what the effect is when the diluent consists of the products of the reaction—in other words, when the reaction is allowed to advance further toward completion. It might be expected that, if the amount of water decomposed is plotted against the time of contact, the resulting curve would not show the usual form, of gradually decreasing slope, but would be a straight line, or would even be bent in the opposite direction. To test this point experiments are needed on one coke at one temperature, over a wide range of decompositions. The only data available for this purpose are the runs made at 1100° and 1200° C. by Clement, Adams, and Haskins.[6] These runs have been plotted in Figure 11, in which an attempt has been made to determine the time of contact a little more accurately than was done by the authors, by allowing for the increase in volume during reaction.

It will be seen that the resulting points are by no means on a smooth curve. On the whole, however, the points would seem to indicate that the reaction rate falls off with decreasing partial pressure, in accordance with the ordinary theory.

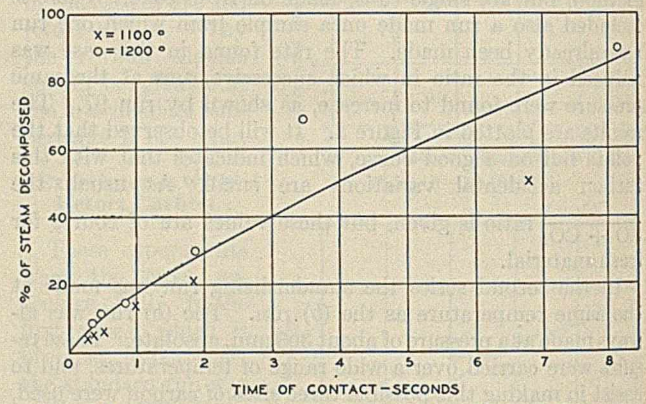

Figure 11—Per Cent of Steam Decomposed *vs.* Time of Contact (Data from *Bur. Mines, Bull.* 7)

Possibly the coke used by these workers would not show the effects exhibited by the samples used in the present work. It seems better to consider these experiments as evidence—somewhat imperfect, to be sure—that the effect of dilution with the reaction products is different from the effect of dilution with nitrogen.

PROPOSED MECHANISM

Much further work must be done before it will be possible to be certain as to the mechanism of this reaction and to explain the above effects fully. The following explanation, however, is offered as a reasonable hypothesis covering the observed facts.

It is well established that when oxygen or carbon dioxide reacts with carbon a surface complex of a very stable character is formed. This complex is usually represented as C_xO_y—which, in turn, breaks up into CO_2. It is natural to suppose that a similar complex is formed when steam reacts with carbon; and since the complex is stable nearly all the surface will be covered with it.

Nevertheless, since the C_xO_y complex does break up, there will always be on the surface a certain number of "bare" carbon atoms, not attached to the complex; and we suppose further that these bare atoms may react with the steam in

[6] *Bur. Mines, Bull.* 7 (1911).

two ways—either to reform the complex, or to form CO and H_2 directly. All the observed effects may then be explained, if the reaction by which the complex is formed is of a higher order than the reaction to form CO and H_2 directly.

The supposed reactions may be:

$$C_{bare} + 2H_2O = 2H_2 + C_xO_y \quad (1)$$
$$C_xO_y = aC + bCO_2 \quad (2)$$

or alternatively,

$$C_{bare} + H_2O = H_2 + CO \quad (3)$$

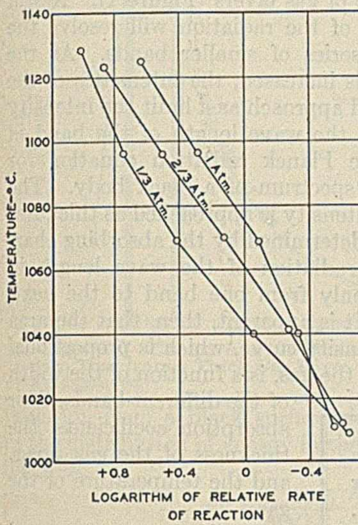

Figure 12—Temperature *vs.* Logarithm of Reaction Rate for Retort Carbon and Steam at Various Pressures

Reaction (2) is assumed to be much slower than (1), so that its rate controls the decomposition of steam by reactions (1) and (2); while (3) is supposed to be in many cases relatively less important than (1), because most of the surface is covered with the complex, C_xO_y.

If (3) is entirely negligible, then (2) predominates, and the reaction will be of the zero order with respect to steam. This is substantially the case with the arc-electrode carbon, charcoal, and graphite in the temperature and pressure ranges discussed in this paper, and also with retort carbon below 1010° C.

As the pressure of steam is reduced, the number of bare carbon atoms should increase as the inverse square of the steam pressure. As a result the water decomposed by reaction (3) increases as the steam pressure is decreased, whereas the water decomposed by the successive reactions (1) and (2) falls off only slightly at first. When a point is reached at which reaction (3) contributes a perceptible amount to the total products of the reaction, the steam decomposed will rise as the pressure falls, and at the same time the relative amount of carbon monoxide in the fixed gases will increase. This is just what is observed with retort carbon. The three reactions involved may well proceed at different rates with different carbons, so that the differences in the results may be easily explained.

The charts show that in the runs in which the rate changed very little with pressure the change was almost always a small falling off in rate as the pressure was lowered. It seems likely, therefore, that a small portion of the steam is decomposed by some other reaction, of the first or some higher order, and that the observed rates are the result of a superposition of the two effects.

SUMMARY

1—The type of carbon used greatly affects the mechanism, in degree at least, of the steam-carbon reaction.

2—With three very different kinds of carbon, the reaction with steam behaves as if it were of the "zero" order, with respect to changes in the partial pressure of the steam.

3—With retort carbon above 1010° C., the reaction behaves as if it were of a "negative" order.

4—When the reaction is of the zero order, the pressure of the steam has little effect on the composition of the fixed gases produced; when the reaction is of a negative order, increase in pressure lowers the CO content of the fixed gases very much.

5—These results are probably due to the formation of a chemically combined surface layer of the C_xO_y type. A particular mechanism covering the facts is suggested.

6—With retort carbon the rate of interaction of carbon and steam doubled every 25 to 30 degrees throughout the temperature range of 1010° to 1125° C.

Collapsing Strength of Thin Tubes and Pipes in Chemical Plants[1]

By W. F. Schaphorst

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SOMETIMES it is desired to compute the collapsing strength of tubes or pipes for ventilating chemical plants handling dust, gases, etc.—tubes that are made of thin sheet metal and that are large in diameter. The writer suggests the following method for determination of approximate values:

> Square the thickness of the metal in inches, multiply by 1600, divide by the square of the diameter of the tube in inches, subtract the quotient from one and then extract the square root of the difference. (This square root will always be less than one, of course. Thus, if the difference is 0.64, the square root will be 0.8.) Next subtract the square root from one and multiply the remainder by 500. The result is the collapsing pressure in pounds per square inch.

When written as a mathematical formula we have:

$$P = 500\left[1 - \sqrt{1 - \frac{1600\,t^2}{D^2}}\right]$$

where P = collapsing pressure, lbs. per sq. in.
t = thickness of sheet metal, inches
D = diameter of pipe, inches

This is a modification of the well-known Stewart formula, which was developed for greater thicknesses and heavier metals such as are used in boilers, flanged or screw piping, and large vacuum apparatus. It was derived by comparing the Stewart formula with the following test results:[2]

DIAMETER *Inches*	THICKNESS *Inch*	NOTICEABLE DISTORTION *Lbs. per sq. in.*	COLLAPSE *Lbs. per sq. in.*
12	0.0312	1.0	3.0
12	0.0375	1.0	3.5
12	0.05	2.5	7.5
15	0.0375	1.5	3.0
15	0.05	2.5	4.5
15	0.062	3.0	7.5
15	0.078	6.0	Uncollapsed at 10.0

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[1] Received March 30, 1927.

[2] Weeks, *Mech. Eng.*, **48**, 573 (1926).

Heat Transmission by Radiation from Non-Luminous Gases[1]

By H. C. Hottel

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The amount of heat transmitted from a gas to its bounding surface may be calculated when we know the gas and surface temperatures, the gas composition, and the shape of the apparatus. Figures 3, 5, and 6, together with equations (6) and (9), are sufficient to solve most problems involving this type of heat transfer. Three examples are given illustrating the method of using the plots.

THE importance of radiation from hot gases as one of the major factors involved in many problems of heat transfer has, until recently, been overlooked. Coefficients of heat transmission based on the assumption of convection as the mechanism controlling heat transfer have been reported for many types of industrial heat-transmission equipment in which radiation from the hot non-luminous gases was actually the controlling factor. Such coefficients, while satisfactory as long as their application is limited to apparatus similar to that which furnished the data, lead to false conclusions when conditions are different. Heat transfer by convection varies widely with gas velocity and size of gas passage, somewhat with temperature of gas, and almost none at all with gas composition. Heat transfer by radiation is independent of gas velocity, varies with the size of apparatus in a manner entirely different from convection heat transfer, and is highly sensitive to a change in temperature. It is obvious, then, that safe extrapolation of data necessitates the assumption of the proper mechanism of heat transfer. The role played by radiation from hot gases may be indicated by the fact that in cracking coils roughly 40 per cent of the total heat transferred is by radiation from the products of combustion; in open hearth furnaces, 90 per cent.

Although the general nature of thermal radiation from gases has been known ever since the early work of Julius, Paschen, and others, and has been studied by many investigators since, these experimenters have been interested more in the resolution of characteristic gas radiation into bands, groups, and families for the purpose of studying molecular structure, than in the quantitative determination of the total energy emitted by a gas. Not until the important investigation of Schack[1,2,*] was there any satisfactory attempt to determine heat transmission by radiation from non-luminous gases. It is the purpose of this paper to outline the method of using data obtained from investigations on the infra-red spectra of gases, in order to calculate the quantity of heat transmitted from those gases; to present charts for use in such calculations; and to indicate the method of using the charts for solution of problems in design of heat transfer equipment.

General Picture of Gas Radiation

If the radiant energy from a gas layer is passed through a prism to a receiving instrument capable of measuring energy intensity, and if the intensity is plotted against wave length, the resulting figure will not be a continuous curve similar to that obtained with radiation from a black body, but will consist of peaks or bands separated by wave-length regions from which there is apparently no radiation whatever, even with very great thicknesses of gas layers (Figure 1). A still greater spectral dispersion of the radiation will resolve the bands themselves into a series of smaller bands. As the thickness of the gas layer is increased, the intensities of the different bands increase and approach as a limit the intensity of black-body radiation at the wave length of the band in question, as given by the Planck radiation equation for energy distribution in the spectrum of a black body. The rate at which black-body intensity is approached as thickness of gas layer is increased is determined by the absorbing characteristics of the gas for radiation of the wave length in question, and varies not only from one band to the next, but even within a band. It is apparent, then, that the area under the wave length–intensity curve, which is proportional to the energy emitted from the gas, is a function of the width of the different bands, their absorption coefficients, the thickness of the gas layer, and the temperature of the gas.

Of the gases encountered in heat transmission equipment, carbon monoxide, the hydrocarbons, water vapor, and carbon dioxide are the only ones with emission bands of sufficient energy content to merit consideration. Moreover, carbon monoxide and the hydrocarbons are present in combustion products in such small amounts as to be negligible compared with water vapor and carbon dioxide. The last two, then, are the only ones we need consider. Their emission bands may be grouped into three spectral regions for each gas, which will hereafter be spoken of as the first, second, and third band of carbon dioxide or of water vapor, the wave length of the band increasing with band number.

Outline of Derivation

Let us consider a hollow evacuated space with walls in thermal equilibrium, the surface element dA radiating the quantity U of energy of wave length λ to the surrounding surface. As there is to be no change in temperature, the surrounding surface must radiate back the same amount of energy U to dA. If now a gas at the temperature of the space is introduced, there will be no change in temperature and the walls will continue to radiate the amount U towards dA. Let the gas absorb the portion U_1 of this energy. Then dA receives $U-U_1$ from the surrounding walls. Since its temperature has not changed, it must still be radiating the amount U, and must consequently receive a total of U. It follows that the gas itself radiates an amount U_1 to the surface dA, in order that the total radiation from walls and gas may equal U.

This conclusion—that the amount of energy radiated by a gas to a surface is equal to the amount of energy from the surface which is absorbed in passing through the gas—is a special form of Kirchoff's law. It enables one, on the assumption that absorption coefficient is independent of temperature, to use measurements of absorption of radiation from

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[1] Presented before the meeting of the American Institute of Chemical Engineers, Cleveland, Ohio, May 31 to June 3, 1927.

* Numbers refer to bibliography at end of paper.

a surface at temperature T by a cold gas, in determining the amount of radiation which the gas itself would emit were it at temperature T.

Since the ratio U_1/U is fixed by the absorbing characteristics of the gas and is independent of temperature provided absorption coefficients do not change with temperature, U_1 will follow the same law of temperature change that U, the radiation from a black surface, follows—i. e., Planck's law of the distribution of energy in the spectrum of a black body. That is,

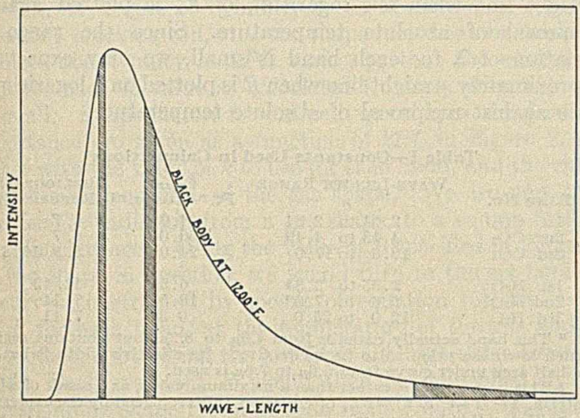

Figure 1—Comparison of Radiation from a Black Body with That from a Thick Gas Layer. Sharpness of Boundaries Exaggerated

$$E_\lambda = \frac{C_1 . \lambda^{-5}}{e^{C_2/\lambda T} - 1} \qquad (1)$$

in which E_λ is monochromatic radiation intensity (energy radiated from a unit surface throughout a solid hemispherical angle—E_λ is frequently defined in terms of unit solid angle, in which case the factor $1/\pi$ enters before the C_1 of equation (1)—above the surface, in unit time, in unit wave-length range) of wave length λ, T is absolute temperature, e is the natural base of logarithms, and C_1 and C_2 are constants. The radiation from an infinitely thick gas layer which absorbs in the wave-length range a to b, and consequently acts like a black body throughout that range of wave length, is given by the integral

$$R = \int_b^a E_\lambda . d\lambda \qquad (2)$$

in which R is radiant energy per unit time per unit of bounding surface, and E_λ is defined by equation (1).

To consider the effect of thickness of gas layer we must introduce the absorption law

$$J = J_0 \, e^{-kx} \qquad (3)$$

in which J is the intensity of beam of initial intensity J_0, after passage through a thickness of gas x; k is the absorption coefficient of the gas for the wave length in question. Since k varies widely throughout the spectral range a to b, it is not permitted to use an average value of k. The assumption of linear variation of k from a value of 0 to k_{max} throughout the range of the band leads to the equation

$$\frac{J_0 - J}{J_0} = 1 - \frac{1 - e^{-kx}}{kx} \qquad (4)$$

in which the left side is the fraction of radiation entering a gas, which is absorbed by passage through thickness x, when the maximum coefficient of the band is k. The validity of the assumption as to variation of k, and the derivation of (4) from (3) are discussed more fully in Appendix I of another paper.[3]

The effect of concentration of radiating constituent of the gas is the same as that of thickness of gas layer; i. e., a layer 1 foot thick, containing 10 per cent carbon dioxide and 90 per cent of a constituent not radiating at the wave length in question, will radiate the same amount as a layer 2 feet thick, containing 5 per cent carbon dioxide. This interchangeability of partial pressure and thickness of gas layer is valid so long as the total pressure of the gas is maintained constant,[4,5] and it is immaterial what inert constituent is used to maintain this constancy of total pressure. We may then substitute for x in equation (3) or (4) the term PL, in which P is partial pressure of radiating constituent in atmospheres, and L is thickness of gas layer in feet, giving k the dimensions, atmos.$^{-1}$ × feet^{-1}.

A combination of equations (2) and (4) gives

$$R = \left(1 - \frac{1 - e^{-kPL}}{kPL}\right) \cdot \int_b^a E_\lambda . d\lambda \qquad (5)$$

There remains to be considered the effect of gas shape on R. It will be remembered that E_λ of equation (5) refers to radiation throughout the total solid angle above the surface element dA, and since the L of equation (5) is a constant outside the integral sign, that equation represents the radiation from (or absorption of) a solid hemisphere of gas of radius L, located above the surface element dA, when the beam of radiant energy proceeds in all directions to (or from) dA. Actually, the length of path of the beam varies with the angle of incidence of the beam striking dA; and the relation between angle of incidence of beam and length of path through gas is a function of the particular gas shape being considered. Figure 2a shows a cross section through a bank of tubes, as encountered in cracking coils or water-tube boilers. The gas "seen" by a surface element on one of the tubes is shaded. This may be compared (Figure 2b) with the shape of gas seen by the surface element dA, as assumed in equation (5). The ratio of the energy radiated by the actual shape to that radiated by the hemisphere of radius L equal to a characteristic dimension (to be explained later) of the actual shape, will be called the shape factor, and be designated by ϕ. A more complete mathematical consideration of ϕ, and its evaluation for various gas shapes, is given in the paper already cited.[3] For our purpose it is sufficient to know that ϕ is a function of the shape of gas, and of the product term, kPL. Values for it are given in Figure 4. By multiplying the right side of equation (5) by ϕ, we obtain the true radiation from a gas mass of temperature T, characteristic dimension (or effective thickness) L, composition P, in the wave-length range a to b. It has already been mentioned that there are three such wave-length regions or bands for each of the two constituents, carbon dioxide and water vapor. We are now in a position to construct charts for calculations of heat transfer.

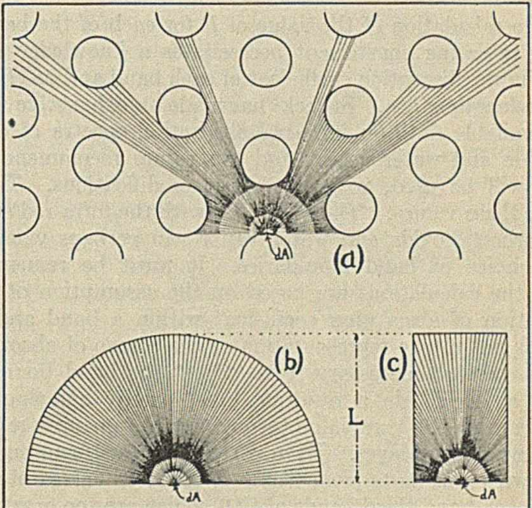

Figure 2—Path of Radiant Beam for Different Gas Shapes

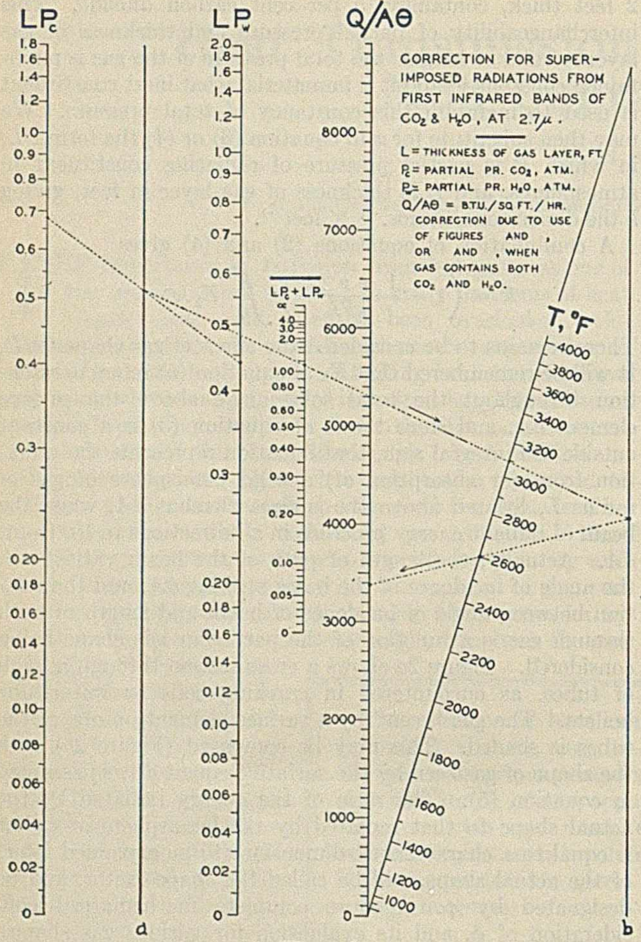

Figure 3

The calculation of the value of R for each of the bands of each radiating constituent necessitates a knowledge of the maximum absorption coefficient of each band and its effective wave-length width. Schack[2] has made an exhaustive survey of available data on infra-red absorption spectra of carbon dioxide and water vapor, and the values recommended by him will be used, with but slight modifications. Table I gives these values. Those familiar with the infra-red spectra of carbon dioxide and water vapor will perhaps wonder at the choice of band boundaries. It must be remembered that the calculations are based on the assumption of linear variation of absorption coefficient within a band and that this is not a true representation of the course of absorption. It is therefore necessary so to adjust the band boundaries used as to obtain a resulting band energy agreeing most nearly with the true value throughout the greatest range of thickness of gas layer. Even with such adjustment equation (5), with constants from Table I, predicts values of R for the second and third bands of CO_2, which are too great when PL is small. The measurements of total absorption of unresolved radiation by Angström, Gerlach, and Coblentz[13,14,15] provide a means of determining a correction factor for the two bands mentioned.[1,3]

Using the data of Table I to determine the R value for each band in accordance with equation (5), we could construct families of curves representing the radiation from the individual bands of CO_2 and H_2O. There would be one family of curves for each of the three bands of each constituent. Each curve in a family would represent the variation of R with temperature, for a constant value of PL, in which P is the partial pressure of the radiating constituent and L is the effective thickness (the meaning of this term will be considered later) of gas layer over the surface receiving the radiation. The choice of scales for R vs. T would be determined by the form of the Planck equation. The older Wien energy distribution equation, differing from that of Planck by the absence of the subtracted term "unity" in the denominator, is known to agree well with that of Planck when λT is small, and is of such form as to give a straight line when the logarithm of E_λ is plotted against reciprocal of absolute temperature. Since the range of variation of λ for each band is small, we may expect an approximately straight line when R is plotted on a logarithmic scale against reciprocal of absolute temperature.

Table I—Constants Used in Calculations

Band No.	Wave-Length Range μ	k_{max} Ft.$^{-1}$ atmos.$^{-1}$	Bibliography References
1st CO_2	2.64 to 2.84	4.9	6, 7
2nd CO_2	4.13 to 4.49	550.0	6, 7
3rd CO_2	13.0 to 17.0	24.0	8, 9, 10, 6
1st H_2O	2.55 to 2.84	6.5	11, 12
2nd H_2O	5.6 to 7.6[a]	13.5	7, 11
3rd H_2O	12.0 to 25.0	0.3[b]	7, 11

[a] This band actually extends from 4.8μ to 8.2μ, but contains regions of such low absorption as to be ineffective. Its effective width is but 1μ. One-half area under curve from 5.6μ to 7.6μ is used.

[b] This is an average, rather than a maximum value, as a result of which the term, $1-(1-e^{-kPL})/kPL$, of equation (5) is replaced by the expression $1-e^{-kPL}$ for this band only.

To obtain the total radiation to a square foot of bounding surface from a gas containing carbon dioxide, we would add the three R values for the three bands of the gas, one from each family of curves. If the gas contains both carbon dioxide and water, we are justified in adding all six band effects only under certain conditions. An inspection of Table I shows that the first band of CO_2 and first band of H_2O lie in the same wave-length range. Either constituent will consequently be somewhat opaque to the radiation from the other, and the total radiation to a surface, owing to the combined effect of the first bands of the two constituents, will be somewhat less than that obtained by adding the values as calculated independently by equation (5). The error introduced by the latter method will be negligible when the gas layer is thin or the percentage of radiating constituent low, but will be quite large for thick layers of gas or high percentage carbon dioxide and water vapor. The correction term to allow for this superimposed radiation is a complicated function of temperature, gas composition and thickness, and absorption coefficients of the bands in question. Figure 3 is an alignment chart† for the determination of this correction term, to be subtracted from the added R's as calculated by equation (5), or as read from Figures 5 and 6. It will be found that when

$$L(4.9\,P_{CO_2} + 6.5\,P_{H_2O}) < 0.3$$

the correction term is negligible. Although Table I would seem to indicate that there is some overlapping of the third bands of carbon dioxide and water vapor, the water vapor band is actually composed of a great number of small bands separated by non-absorbing regions, and the interference is negligible.

The determination of total radiation from a gas involves a consideration of its shape. Before adding the R's for the different bands, we must multiply each value by its corresponding shape factor, ϕ, which we have found is a function of the product term kPL, and which therefore varies from one band to the next as k varies. The shape factor of a gas mass is found to vary about the value, unity, and to approach unity at high values of kPL. The radiation from a tall, narrow cylinder (Figure 2c) of gas to unit area of its base will be less than that from a hemisphere (Figure 2b) to unit area at the center of its base, when the height of the cylinder equals the radius of the hemisphere. Consequently the shape factor will be less than 1.

Looking at the subject from another angle, the "effective thickness" of gas layer above the base of the narrow cylinder is less than that of the hemisphere of gas above the center of its base. When, however, the ratio of diameter to height of cylinder is large, ϕ for the cylinder will be greater than 1. By proper choice of effective thickness or characteristic dimension, L, of the gas shape in question; that is, by letting $L = \alpha_1 \times$ height of cylinder, or $\alpha_2 \times$ clearance between tubes in a cracking coil, etc., the shape factor can be made to oscillate about unity as kPL varies, so that the correction term for each R value as calculated from equation (5) will be small. Shape factors for different gas shapes of industrial importance are given as a function of kPL in Figure 4, together with the value of k to use for each band, and the characteristic dimension L of the gas shape. We are now able to calculate radiation from a gas shape, to a square foot of bounding surface. Using the value of L specified in Figure 4 for the shape in question, we would turn to the six families of curves constructed by means of equation (5), and read the R for each band, at the temperature of the gas and of the surface, subtracting the low from the high value for each band. Each resultant R would then be multiplied by its corresponding shape factor as read from Figure 4, and these final values of R added. The last step would consist in multiplying the result by the black-body coefficient of the receiving surface, which will usually lie between 0.6 and 0.9.

It is apparent that the method just outlined is exceedingly tedious and, in the case of a gas containing both carbon dioxide and water vapor, would involve the reading of six pairs of values from the families of curves representing individual band radiation, their subtraction by pairs, the multiplying of the six resultant terms by six corresponding terms as read from Figure 4, and the subtraction, in some cases, of a correction term for superimposed radiation from Figure 3. A simplification is almost indispensable from an engineering standpoint. Fortunately, this is possible without appreciable sacrifice of accuracy. If there were no shape factor consideration, nothing would prevent the three R values for the three bands of one constituent from being added before being plotted as a function of T and of PL. This would be equivalent to assuming ϕ to equal unity throughout. We have already found that by proper choice of L for a gas shape its ϕ may be made to oscillate about unity with a maximum deviation of about 10 per cent. For example, if we consider the radiation from a gas sphere to a unit element of its surface, ϕ will vary from $^2/_3$ to 1 as kPL varies from zero to infinity, if the diameter of the sphere is used for L. If, however, we use $^2/_3$ diameter as the effective thickness, L, of the gas layer, ϕ passes from 1 through a minimum value of 0.955 and back to 1. Likewise, in the case of a gas between parallel planes a distance D apart, ϕ varies from 2 to 1 when L equals D; whereas, if we let L equal 1.8 times D, ϕ varies from 1.111 through a minimum of 0.94 and back to 1. In a similar manner, by proper choice of L, the shape factor for any shape may be made to stay close to 1. The assumption of unit shape factor for all three bands of a gas then leads to small errors which partly counterbalance, and which are well within the accuracy of the constants of Table I. Figures 5 and 6, based on this assumption, present the total R due to all three bands. (The constants of the Planck radiation equation, used in calculating Figures 5 and 6, are those given in International Critical Tables.) ΣR for carbon dioxide will be designated by C; ΣR for water vapor by W. The scales used are those already mentioned as justified by the form of the Planck equation, except that the temperature scale has been labeled in ° F. instead of ° R, for engineering convenience. After making the assumption of $\phi = 1$ in calculating Figures 5 and 6, the only further use we make of Figure 4 is to determine the proper value to use for L, the effective thickness of the gas layer, and to find by inspection how great an error is introduced by the use of the total radiation charts instead of those giving individual band radiations.

The total heat exchange by radiation from a gas to its bounding surface is given by the equation

$$Q/\Theta = p.A\{(C_g - C_s) + (W_g - W_s) - (K_g - K_s)\} \quad (6)$$

in which the subscripts g and s refer to the value of C, W, or K at the mean gas temperature, T_g, or the mean surface temperature, T_s, respectively. p is the black-body coefficient of the receiving surface. K is the correction sometimes necessary for superimposed radiation of carbon dioxide and water vapor, determined from Figure 3.

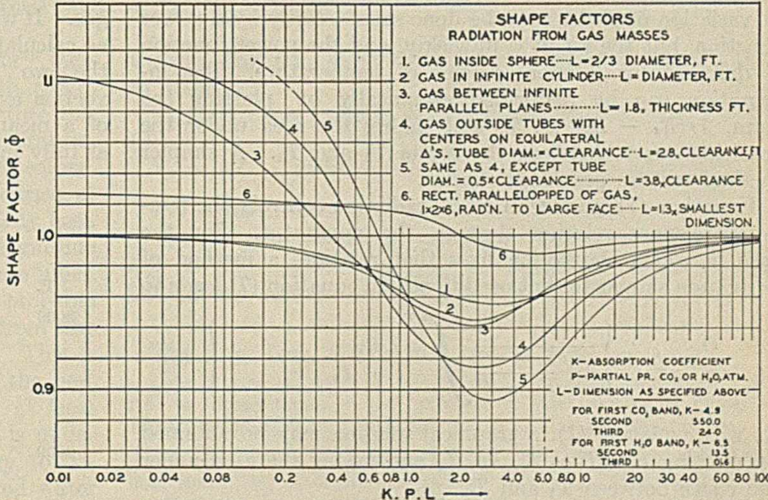

Figure 4—Shape Factors and Equivalent Thickness of Gas Layers

When there is a large drop in temperature of gas from entrance to exit end of passage, the question arises as to the proper average gas temperature to use for T_g, in terms of entrance and exit gas temperatures. A little consideration leads to the conclusion that the temperature-space relation through the gas passage will differ, depending on whether radiation or convection is controlling, and that Q/Θ consequently will vary with the type of heat transfer controlling, for fixed terminal conditions. Let us first consider the case in which radiation is so large compared with convection that it practically determines the temperature-space relation in the apparatus. Let the mass of gas flowing through per unit time $= V$, specific heat $= s$, inlet gas temperature $= T_1$, exit temperature $= T_2$, and average surface temperature $= T_s$. Let $C_T + W_T - K_T$, the total radiation at temperature T, be designated by R_T. Consider a differential length of passage of surface area dA, with the gas falling in temperature from T to $T - dT$. Then

$$dQ/d\Theta = Vs.dT = p.dA.(R_T - R_s)$$

$$Vs = \frac{\int_o^A p.dA}{\int_{T_2}^{T_1} \frac{dT}{R_T - R_s}}$$

For Vs we may substitute $Q/A\Theta/(T_1 - T_2)$, obtaining

$$\frac{Q}{\Theta} = p.A.\frac{T_1 - T_2}{\int_{T_2}^{T_1} \frac{1}{R_T - R_s}.dT} \quad (7)$$

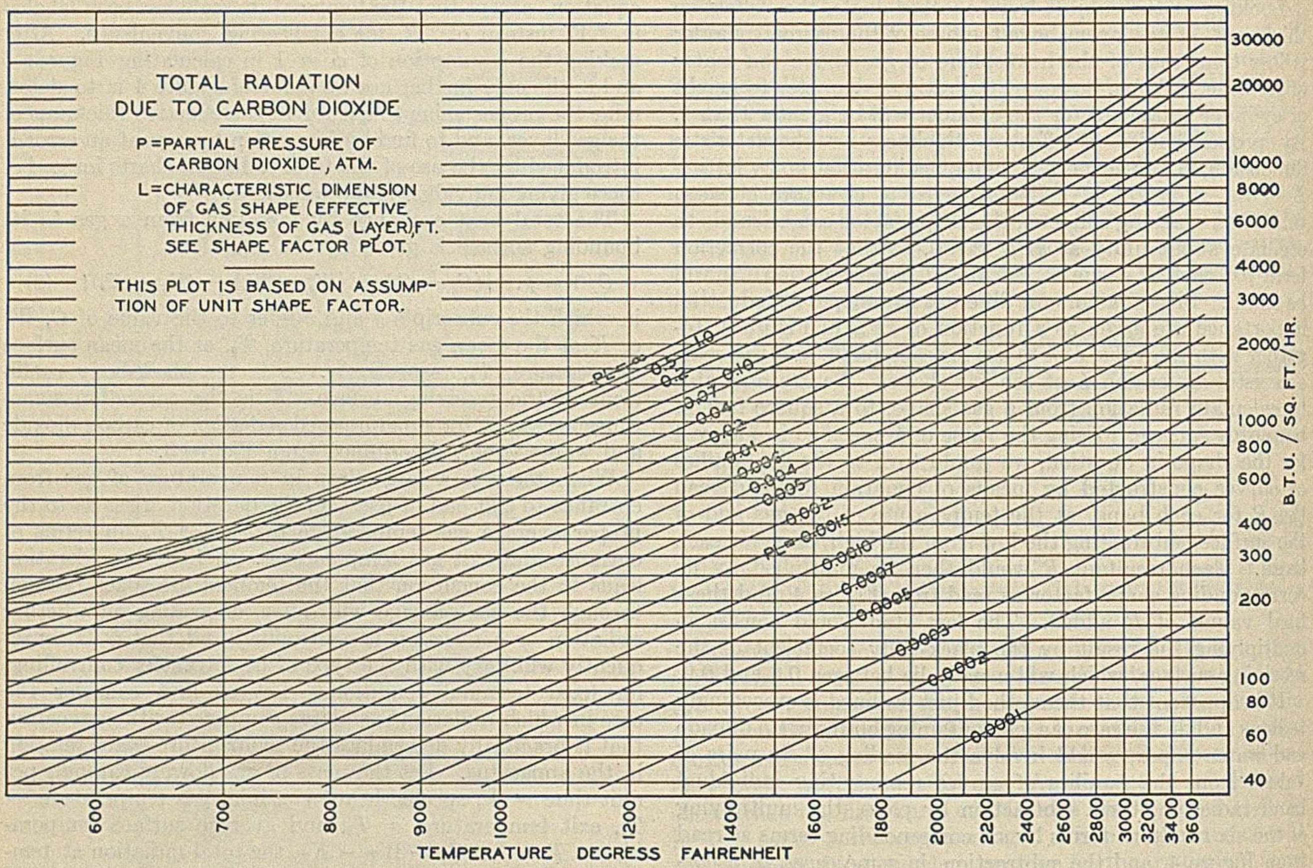

Figure 5—Total Radiation from Carbon Dioxide

which is the desired relation. To integrate the denominator we must express R_T as a function of T. Over a short range of variation of T this may be done satisfactorily by a power function, but the result is unwieldy, and the power function is different for different ranges of temperature. The integration can be performed graphically by plotting the term, $1/(R_t - R_s)$ vs. T, and taking the area under the resulting curve, between the limits T_1 and T_2. A simpler method will be presented shortly.

Equation (7) gives Q/Θ when radiation controls the temperature-space relation through the apparatus. For the case in which convection fixes that relation, a method of derivation similar to that used to obtain equation (7) leads to

$$\frac{Q}{\Theta} = p.A \left\{ \frac{1}{\log \dfrac{T_1 - T_s}{T_2 - T_s}} \int_{T_2}^{T_1} \frac{R_T}{T - T_s}\, dT - R_s \right\} \quad (8)$$

As with equation (7), a graphical solution may be obtained by plotting $R_T/(T - T_s)$ vs. T, and taking the area under the curve between T_1 and T_2.

The determination of Q/Θ by use of equation (7) or (8) is tedious, and the question arises as to whether it is possible to use a mean temperature of gas, expressed as a function of T_1, T_2, and T_s. Two methods, with a semi-mathematical basis, both lead to results which are poorer than the empirical method of using for gas temperature in equation (6), the temperature of the surface T_s, plus the logarithmic mean temperature difference of gas and surface. In other words,

$$T_g = T_s + \frac{T_1 - T_2}{2.3 \log \dfrac{T_1 - T_s}{T_2 - T_s}} \quad (9)$$

Table II presents a comparison of the true value of $Q/A\Theta$, calculated graphically by equation (7) or (8), with the value obtained by using gas temperature as defined by equation (9), and by using the arithmetic mean temperature of the gas. It will be noticed that $Q/A\Theta$ based on a gas temperature as calculated from equation (9) lies, in every case, between the two "true" values. Since neither radiation nor convection ever controls to the exclusion of the other, the use of a mean gas temperature as defined by equation (9) is as fully justified as the use of equation (7) or (8).

Table II—Comparison of Values of $Q/A\Theta$

T_1 °F.	T_2 °F.	T_s °F.	Factor[a]	$Q/A\Theta$ as Calcd. by Eq. (7) or (8)	$Q/A\Theta$ Using T_g as Defined by Eq. (9)	$Q/A\Theta$ Using Arithmetic Mean T_g
3000	2000	0	R	5660	5840	5950
			C	5842		
		1000	R	4955	5020	5290
			C	5062		
		1500	R	3617	3670	4090
			C	3698		
		1800	R	2368	2385	3085
			C	2445		
2000	1000	0	R	1550	1695	1860
			C	1785		
		600	R	1296	1369	1669
			C	1469		
		800	R	1025	1070	1480
			C	1168		

[a] Factor controlling temperature-space relation: R = radiation, C = convection.

Before illustrating the use of the plots, let us consider briefly their probable accuracy. The assumptions involved in their derivation are (1) that the course of absorption through a band may be expressed as a linear function of wave length, provided a compensating adjustment of band boundaries is made, (2) that the absorbing characteristics of the gas do not change with temperature, (3) that the shape factor is 1. The first assumption undoubtedly leads to errors of considerable magnitude.[2] The second assumption is necessary to make use of absorption coefficients determined

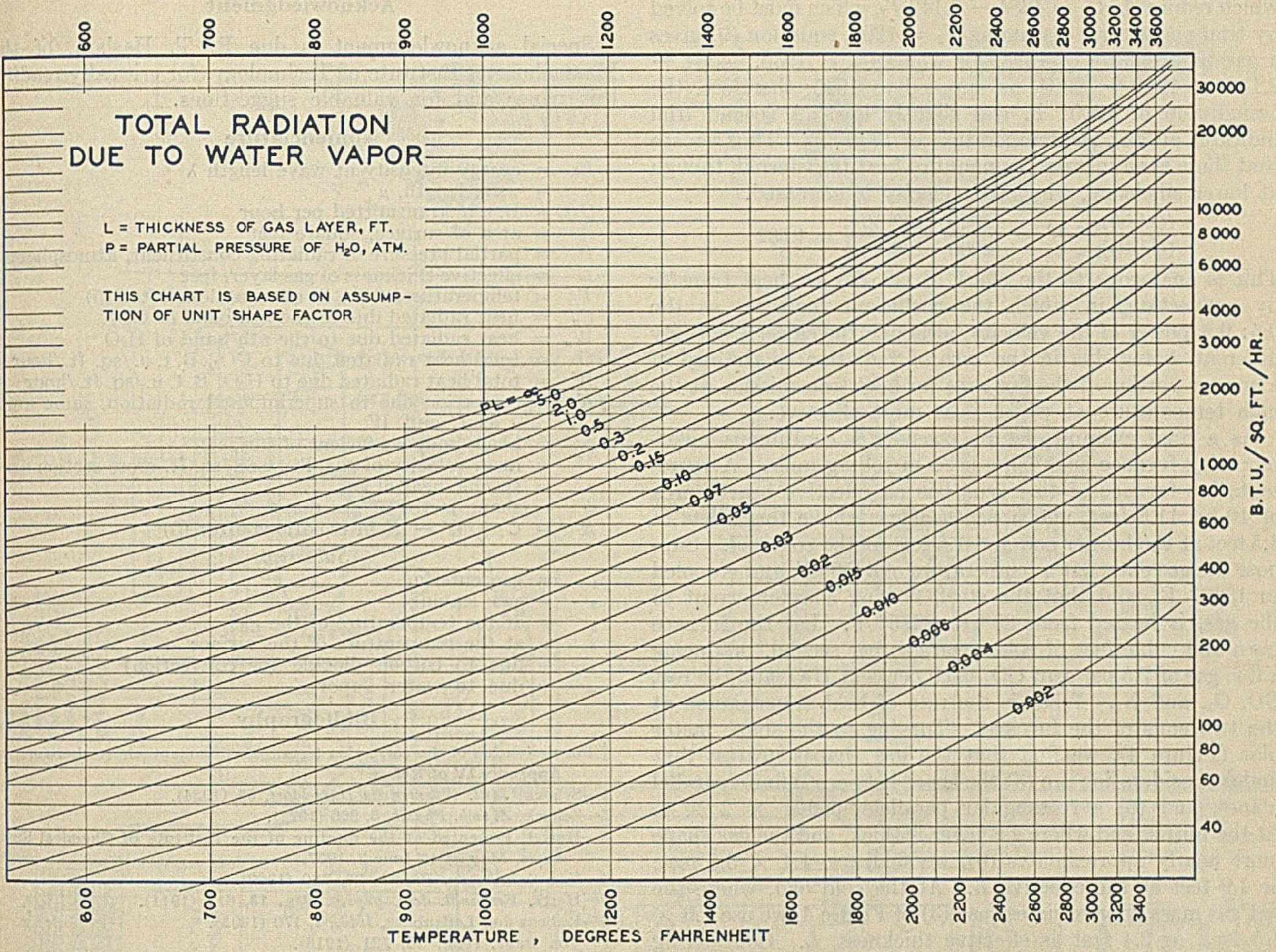

Figure 6—Total Radiation from Water Vapor

at room temperature. The work of Eva von Bahr[16] indicates that there is an increase in absorption with rise in temperature, at least up to 900° C. By neglecting this increase and using values obtained at room temperature, we obtain minimum values of $Q/A\Theta$, provided, of course, that the absorption coefficient does not again decrease at high temperatures. The third assumption has already been considered, and leads to errors of much smaller magnitude than the other two. The data on carbon dioxide are much more reliable than those on water vapor. It is probable that the maximum error in determining $Q/A\Theta$ from the plots is not over 30 per cent, and probably less. This is greater than the error involved in using many of the best equations for heat transfer by convection, but it at least leads to results in the right neighborhood. Work is under way at the Massachusetts Institute of Technology to determine the total radiation from carbon dioxide and water vapor at high temperatures, to provide a more accurate basis for Figures 5 and 6.

Heat Transfer Calculations Illustrating Use of Plots

Since the principles involved in heat transfer by radiation from gases are different from the more familiar ones used in convection heat transfer, a few representative examples will be given to indicate the use of the charts.

As a first example let us consider a gas flowing with a mass velocity of 0.4 pound per second per square foot, carbon dioxide content 20 per cent, no water vapor, specific heat 0.3, through a 6 by 6 inch square duct, the gas entering at 2000° F. Suppose an average surface temperature of 800° F. Assuming all the heat to be transferred by radiation from the gas, how long would the flue have to be to cool the gas to 1000° F.?

To determine average gas temperature, we use equation (9).

$$T_g = 800 + (2000-1000)/2.3 \log (2000-800)/(1000-800) = 1358° \text{ F.}$$

$$PL = (6/12) \times 0.20 = 0.1.$$

Using Figure 5 we read, for $PL = 0.1$, $C_{1358} = 1450$, and $C_{800} = 380$. Then, assuming a black-body coefficient of 0.9 for the surface of the duct,

$$Q/A\Theta = 0.9\ (1450-380) = 963 \text{ B. t. u./sq. ft./hour.}$$

The total heat transferred per unit time is

Q/Θ = mass velocity × cross sectional area × specific heat × rise in temperature = $0.4 \times 3600 \times 0.25 \times 0.3 \times (2000-1000) = 108{,}000$ B. t. u./hour given up by the gas.

Then the necessary area is 108,000/963 = 112 square feet, corresponding to a flue length of 56 feet. The equivalent coefficient h_r, as used in convection heat transfer calculations, is 963/average Δt = 963/558 = 1.73, which is of the same order of magnitude as we would expect h_c to be under such conditions, indicating that roughly half the total heat transferred would be due to radiation. It is to be remembered that the expression of heat transfer by radiation in the form of a coefficient is a purely artificial procedure, used simply for comparison with h_c.

Suppose it is desired to find the effect of doubling the mass velocity of the gas in the above duct, maintaining the same entrance gas temperature and average surface temperature and flue length. We have the equation

$$0.9\ (C_g - C_{800}) = \frac{0.8 \times 3600 \times 0.25 \times 0.3 \times (2000-T_2)}{112}$$

which reduces to $C_g = 4284 - 2.142\ T_2$, which must be solved by trial and error. Assuming $T_2 = 1200$, equation (9) gives a gas temperature of 1528, for which $C_g = 1935$. $4284 - 2.142 \times 1200 = 2094$, as opposed to 1935; therefore, the assumption of 1200° F. was slightly low. A second trial indicates an exit gas temperature of 1230° F. Thus we see that there is an increased amount of heat transferred, though at lower efficiency, when the velocity is increased.

$$\frac{(Q/A\Theta)_{v\,=\,0.8}}{(Q/A\Theta)_{v\,=\,0.4}} = \frac{(2000-1230)0.8}{(2000-1000)0.4} = 1.532$$

This is analogous to the effect of velocity on heat transfer by convection, in which the coefficient increases as the 0.5: 0.8 power of the velocity, although the cause is entirely different, being due in the case of radiation to the use of a greater portion of the flue area for heat transmission at the high temperature at which it is most effective.

As a final example, let us consider a continuous billet-reheating furnace such as is used in rolling mills. A representative furnace of this type has an effective hearth area of 40 by 11.5 feet, and a depth of gas above the billets of 3.5 feet at the burner end and 1.5 feet at the cold end. Suppose the gas enters at a temperature of 3450° F. and is cooled to 1300° F., and that the steel, flowing countercurrent to the gas, is heated from 80° to 2275° F. Let the furnace burn 100 cubic feet of coke-oven gas per second, producing a flue gas of 7.5 per cent CO_2, 20.0 per cent H_2O, and the rest CO, O_2, and N_2. What is the rate of heat transmission at the two ends of the furnace? Turning to the shape factor plot (Figure 4), we find that the gas shapes nearest that under consideration are (3) the space between infinite parallel planes, and (6) a rectangular parallelepiped $1 \times 2 \times 6$. At the burner end where gas layer is thick, and the gas shape more nearly approximates (6), we shall use 1.4×3.5 feet, or 4.9 feet as the effective L. At the cold end, where the flat gas mass approximates case (3) of Figure 4, we use 1.6×1.5 feet, or 2.4 feet as effective thickness, L. Considering first the burner end, $P_cL = 0.075 \times 4.9 = 0.37$, and $P_wL = 0.20 \times 4.9 = 0.98$. Using Figures 5 and 6 for gas and steel temperatures of 3450° and 2275° F., respectively, and $p = 0.8$, we have, on substituting into equation (6),

$$Q/A\Theta = 0.8\{(17500-7000) + (25000-9600) - (6900-2300)\} = 17{,}050 \text{ B. t. u./sq. ft./hour}$$

It will be noticed that for this case the correction due to superimposed radiation is appreciable, owing to the high values of PL. As a matter of interest, the value of the coefficient of heat transfer, as used in convection, may be obtained for comparison:

$$h_r = 17050/(3450-2275) = 14.5$$

If we use the Weber equation[17] for convection coefficient of gases flowing inside conduits, the result obtained is $h_c = 1.58$. It is apparent, then, that at the hot end of the furnace about 90 per cent of the total heat transferred is by radiation from the hot gases. At the cold end of the furnace, however, conditions are reversed. At this end, $P_cL = 0.18$, $P_wL = 0.48$, $T_g = 1300°$ F., $T_s = 80°$ F. On substitution into equation (6), we find $Q/A\Theta = (0.8)(1500-0+1800-0-150+0) = 3150$. The equivalent $h_r = 2.46$, while the value of h_c from the Weber equation is 2.44. Consequently, at this end of the furnace heat transferred due to convection and that due to radiation are about equal. The over-all H due to convection and gas radiation combined (obtained by adding the individual h_r and h_c) varies from about 16 at the hot end to 5 at the cold end of the furnace. Actual experimental data on a furnace such as that described here indicate average over-all coefficients ranging from 5 to 12, six out of seven of them lying above 10. Such high values would not have been expected on the assumption that all the heat was being transferred by convection.

Acknowledgment

Special acknowledgment is due R. T. Haslam, of the Massachusetts Institute of Technology, for critically reading this paper and for valuable suggestions.

Nomenclature

E_λ = energy intensity at wave length λ
λ = wave length, μ
Q/Θ = B. t. u. transmitted per hour
A = area of surface, square feet
P = partial pressure of radiating constituent, atmospheres
L = effective thickness of gas layer, feet
T = temperature, ° F., in all equations after (5)
C_n = heat radiated due to the nth band of CO_2
W_n = heat radiated due to the nth band of H_2O
C = total heat radiated due to CO_2, B. t. u./sq. ft./hour
W = total heat radiated due to H_2O, B. t. u./sq. ft./hour
K = correction due to superimposed radiation, same units as C and W
p = black-body coefficient of surface
V = mass velocity of gas, lbs./sec./sq. ft. cross-section area
s = specific heat of gas
ϕ = shape factor of gas mass
R = $C + W - K$ in equations after (5)

Subscripts

$_1$ = gas entering
$_2$ = gas leaving
$_g$ = at the temperature of the gas
$_s$ = at the temperature of the surface
$_c$ = due to carbon dioxide (or convection)
$_w$ = due to water vapor

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† For derivation of the correction term and alignment chart therefor, see Appendix IV of Ref. 3.

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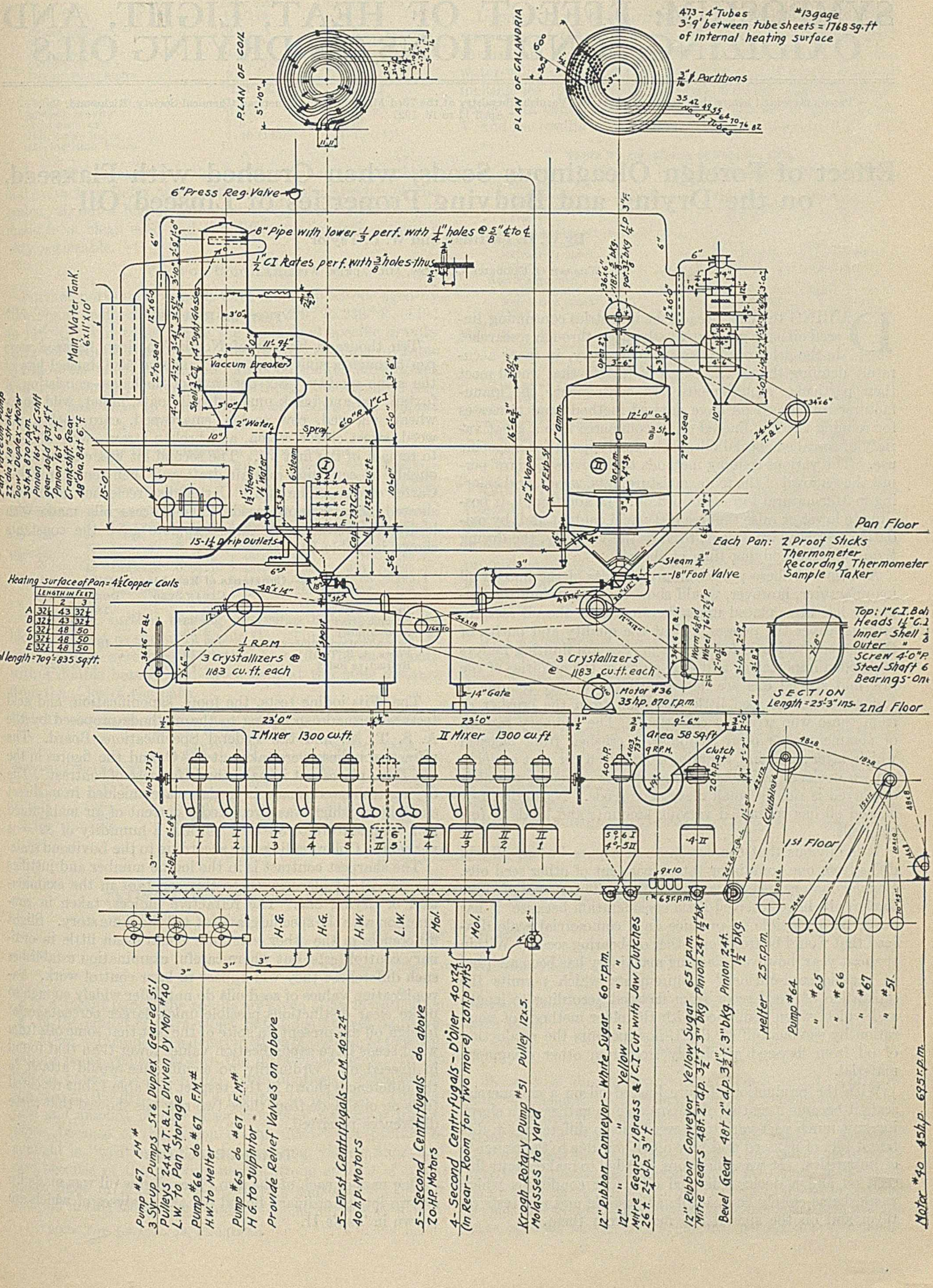
Information Storage

We are indebted to Dan Gutleben, an engineer of the Pennsylvania Sugar Company, for the chart (page 895), selected from a drawing many feet in length, which illustrates the application of the engineer's language to the storage of information. The original outline represented a beet sugar factory from the beet storage sheds to the sugar storage house. The purpose is to fix systematically the statistical information for use in the drafting room, in the erection work, and as a permanent record of the operators. The outline is in fact a flow sheet for the entire factory, carrying descriptions of apparatus and other equipment. The descriptions indicate the salient features with shop numbers and manufacturers' names for identification. As all the equipment is arranged in order, the information is automatically indexed. Some plants store their statistical information in volumes written in the language of Noah Webster, but in this outline, which presents the facts in the language of the engineer, may be found practical suggestions which can be applied in many industries and to various branches of the chemical industry.


PLAN OF COIL
5'-10"
PLAN OF CALANDRIA
473 - 4" Tubes #13 gage
3'-9" between tube sheets = 1768 sq. ft. of internal heating surface
$\frac{3}{16}$" ℓ Partitions
No. of Tubes 35 42 49 55 64 70 76 82
6" Press Reg. Valve
8" Pipe with lower $\frac{1}{3}$ perf. with $\frac{1}{4}$" holes @ $\frac{5}{8}$" ℄ to ℄
$\frac{1}{2}$" CI Rates perf. with $\frac{3}{8}$" holes thus
Main Water Tank 6'x11'x10'
Pan Vaccum Pump 22" dia x 18" stroke "Dow" Duplex-Motor 35 h.p. 870 r.p.m. Pinion 16 t. 4" f. 6 shft gear 40 t. d. 93 t 4" f. Pinion 16 t 6" f. Crankshaft Gear 48" dia. 84 t 6" f.
2" to seal
Vaccum Breaker
Shell $\frac{3}{4}$" C.I. (4 Sight Glasses)
2" Water
Spray
6'-0" R
1" C.I.
I
1½" Steam
1¼" Water
15-1¼ Drip Outlets
Cap = 737 Cu. ft.
= 1274 Cu. ft.
Heating surface of Pan = 4½" Copper Coils
LENGTH IN FEET
1 2 3
A 32½ 43 32½
B 32½ 43 32½
C 32½ 48 50
D 32½ 48 50
E 32½ 48 50
Total length = 709' = 835 sq. ft.
II
12" Vapor
1" amm.
12'-0" o.s.
10 r.p.m.
2" to seal
34"x 6"
24"x 6" T.&L.
Pan Floor
Each Pan: 2 Proof Sticks
Thermometer
Recording Thermometer
Sample Taker
Steam $\frac{3}{4}$"
18" Foot Valve
48"x 14"
$\frac{1}{4}$ R.P.M.
3 Crystallizers @ 1183 cu. ft. each
3 Crystallizers @ 1183 cu. ft. each
15" Spout
14" Gate
Motor #36 35 h.p. 870 r.p.m.
Worm 6 t.p.d. Wheel 76 t. 2$\frac{1}{4}$" P.
Top: 1" C.I. Bolt
Heads 1$\frac{1}{4}$" C.I.
Inner Shell
Outer "
Screw 4'-0" P.
Steel Shaft 6
Bearings - One
SECTION
Length = 25'-3" ins.
2nd Floor
I Mixer 1300 cu. ft.
II Mixer 1300 cu. ft.
23'-0"
23'-0"
Area 58 sq. ft.
9 R.P.M.
Clutch
40 h.P.
20 h.P.
I 1 I 2 I 3 I 4 I 5 I 6 II 5 II 4 II 3 II 2 II 1
5 I 6 I 4 II 5 II
4 II
1st Floor
9x10
65 r.p.m.
H.G. H.G. H.W. L.W. Mol. Mol.
3"
Pump #67 F.M. #
3 Syrup Pumps 5x6 Duplex Geared 5:1
Pulleys 24x4 T.&L. Driven by Mot #40
L.W. to Pan Storage
Pump #66 do #67 F.M. #
H.W. to Melter
Pump #65 do #67 F.M. #
H.G. to Sulphitor
Provide Relief Valves on above
5 - First Centrifugals - C.M. 40"x24"
40 h.p. Motors
5 - Second Centrifugals do above
20 H.P. Motors
4 - Second Centrifugals - D'Oller 40x24
(In Rear - Room for two more) 20 h.p. Mts
Krogh Rotary Pump #51 Pulley 12x5.
Molasses to Yard
12" Ribbon Conveyor - White Sugar 60 r.p.m.
12" " " Yellow " " "
Mitre Gears - 1 Brass & 1 C.I. Cut with Jaw Clutches
26 t. 2¼ d.p. 3" f.
12" Ribbon Conveyor Yellow Sugar 65 r.p.m.
Mitre Gears 48 t. 2" d.p. 3½" f 3" bkg Pinion 24 t 1½" bk.
Bevel Gear 48 t 2" d.p. 3½" f. 3" bkg. Pinion 24 t.
1½" bkg.
Melter 25 r.p.m.
Pump #64
" #65
" #66
" #67
" #51.
Motor #40 45 h.p. 695 r.p.m.

SYMPOSIUM: EFFECT OF HEAT, LIGHT, AND OXIDIZING CONDITIONS ON DRYING OILS

Papers presented before the Section of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927

Effect of Foreign Oleaginous Seeds, when Crushed with Flaxseed, on the Drying and Bodying Properties of Linseed Oil

By W. H. Eastman and W. L. Taylor

William O. Goodrich Company, Milwaukee, Wis.

DURING the past decade the industries consuming linseed oil have made great advances, through researches in the fields of physics and chemistry, in more accurately defining the specifications of the oils that would meet their particular requirements. In consequence the manufacturers of linseed oil have devised methods and processes for refining the raw linseed oil of commerce into a great variety of so-called special oils, each one designed for a specific use. The various refining methods thus developed now permit the removal of the foots, moisture, fats, waxes, and coloring matter natural to raw linseed oil. In addition, it is possible to lower or raise the free fatty acid content and, by oxidation and heat treatment, to vary the viscosity, the drying time, and the bodying time of the oil.

A review of these process improvements of the linseed oil manufacturer, however, would show that heretofore the emphasis has been placed upon the treatment the oil receives after it leaves the presses. That the quality and purity of the flaxseed which is fed to the presses are limiting factors of decided importance, and that many of the qualities of the raw and special oils are determined before any refining is started, have received little attention from the crusher or from those who write specifications. The ordinary raw oil of commerce has been customarily crushed from flaxseed which, after screening, contains from 3 to 6 per cent of dockage—a dockage which on account of the screening methods employed is rich in small oleaginous seeds. Naturally, raw linseed oil has contained varying amounts and kinds of foreign oils.

It is obvious that the constants of a pure linseed oil will differ from one containing 3 to 6 per cent of other seed oils. Regular factory tests have shown this. The effects of these foreign oils have received little consideration because it has never been possible to produce on a commercial scale flaxseed that would be free from other oil-bearing seeds. Within the past year, however, cleaning machinery has been adapted to the flaxseed-crushers' requirements which permits the separation of weed seeds from flaxseed according to length and which, when combined with the older methods of separation by sieving and air draft, now permits the production of oil from flaxseed absolutely free from other oleaginous material.

With the production of pure linseed oil on a commercial scale it became a matter of importance to gather data showing how much past variations were due to differences in different lots of flaxseed and how much was due to the presence of impurities. It was, therefore, decided to make a pure linseed oil and a dockage linseed oil under conditions which would be as closely comparable as possible and run tests on them and on the special oils made from them.

Tests on Raw Oils

Ten thousand bushels of North American flaxseed were run through a split spout to obtain two 5000-bushel lots of the same quality. Six per cent of dockage—consisting of foxtail, red and black mustard, wild oats, millet, wild buckwheat, pigweed, cow cockle, smartweed, corn cockle, rag weed, sweet clover, vetch, and broken straw—were allowed to remain in the first lot. The second lot was cleaned thoroughly by screening and air draft and then sent through a Carter disc machine and a Carter disc recleaner until tests showed no oleaginous seeds. Old-process oils made with hydraulic presses from these two lots gave the constants shown in Table I.

Table I—Constants of Raw Linseed Oils

	Clean Seed	Dockage Seed
Iodine number	189.5	185.6
Specific gravity	0.9343	0.9341
Acid number	1.38	1.96
Saponification number	189.4	188.6
Foots, A. S. T. M.	0.75	1.1
Refractive index	1.48 (051)	1.48 (028)

The Wijs iodine tests, the foots, saponification, and acid tests were made according to the methods proposed by the A. S. T. M. and the Federal Specifications Board. The refractive indices were taken at 25° C. and the figures in the last three places put in parenthesis for ease of contrast. The drying tests were made in a glass case shielded from direct sunlight in which was circulated a current of air maintained at a temperature of 30 ± 2° C. and a humidity of 32 ± 4 per cent. Color readings are according to the Lovibond scale.

The sharpest contrast is in the iodine number and justifies the important place given to this constant in the examination of drying oils. The refractive indices, taken in conjunction with the specific gravities, tell the same story. Slight differences in the other constants would mean little in ordinary control tests, but where careful examination establishes such differences they will appear in later control work. Saponification values of seed oils do not differ widely enough to make clear distinctions possible unless larger percentages of foreign oil are present, in spite of the fact that some oils from weed seeds have saponification values lower than that found in linseed oil. Ordinarily no significance would attach to the differences shown in this respect in Table I, but repeated tests on oils made from these two raw oils showed that these differences persisted.

Tests on Boiled Oils

One part of each of the two types of raw oil was made up as two lots of ordinary boiled oil, the analyses of which are shown in Table II.

Table II—Constants of Boiled Oils

	CLEAN SEED	DOCKAGE SEED
	Lot 119	Lot 121
Iodine number	179.8	175.7
Specific gravity	0.9416	0.943
Acid number	4.12	4.95
Refractive index	1.48 (182)	1.48 (178)
Drying time, hours	9	9.5
	Lot 120	Lot 122
Iodine number	181.4	177.4
Specific gravity	0.9394	0.9412
Acid number	3.6	4.37
Refractive index	1.48 (143)	1.48 (145)
Drying time, hours	10	11

As would be expected, the iodine number, acid number, and refractive index vary with the specific gravity of the boiled oil, but a higher iodine number persists with the oils made from clean seed and the difference in drying time is very noticeable.

Tests on Blown Oils

Further portions of the oil were made up as oils aged by blowing at temperatures ranging from 300° to 240° F. (149° to 116° C.), but to as nearly the same final specific gravity as factory conditions allow. The differences given in Table III show the effects of heat and air upon the refractive index and acid number. The refractive index is much more sensitive to heat than to oxidation and oil with a high original index will show a high final index.

Table III—Constants of Blown Raw Oils

BLOWING TEMPERATURE °C.	°F.	LOT	SEED	SPECIFIC GRAVITY	REFRACTIVE INDEX	IODINE NUMBER	ACID NUMBER	SAPONIFICATION NUMBER
149	300	33	Clean	0.9509	1.48(330)	169.4	2.37	195.9
		41	Dockage	0.9516	1.48(289)	167.2	2.75	193.8
138	280	34	Clean	0.9515	1.48(291)	169.1	2.73	194.9
		42	Dockage	0.9504	1.48(271)	168.3	2.89	193.2
127	260	35	Clean	0.9504	1.48(263)	170.7	2.70	195.7
		43	Dockage	0.9511	1.48(260)	168.1	3.32	195.3
116	240	36	Clean	0.9511	1.48(264)	170.4	2.65	195.4
		44	Dockage	0.9506	1.48(247)	169.3	3.12	195.3

In general, further heating intensifies differences in the blown raw oils, as shown in Table IV. Tubes of oil from the eight batches were heated at the same time in an oil bath with a double bottom and tubes kept at the same distance from the sides of the bath.

Table IV—Constants of Blown Raw Oils Heated for 90 Minutes at 560–600° F. (293–316° C.)

BLOWING TEMPERATURE		CLEAN SEED		DOCKAGE SEED	
°C.	°F.	Refractive Index	Viscosity *Poises*	Refractive Index	Viscosity *Poises*
149	300	1.49(239)	57	1.49(209)	52
138	280	1.49(220)	46	1.49(111)	28
127	260	1.49(224)	55	1.49(082)	20
116	240	1.49(265)	76	1.49(150)	31

Tests on Varnish Oils

In order to make a further study of bodying qualities the remainder of the original raw oils was made into a neutral varnish oil, thoroughly bleached to produce an oil of the water-white class, and refrigerated so that it would stand in melting ice for 12 hours without showing any cloudiness. Some data concerning these varnish oils are given in Table V, and the results of varnish tests made on them in Table VI.

Table V—Constants of Varnish Oils

CONSTANT	CLEAN SEED	DOCKAGE SEED
Varnish Oil:		
Iodine number	189.8	185.6
Refractive index	1.48(033)	1.48(023)
Color	7.7 R	7.3 R
Supreme (water-white class):		
Iodine number	189.7	185.7
Refractive index	1.48(041)	1.48(026)
Color	3.3 R	3.4 R
Arctic supreme:		
Iodine number	191.6	186.7
Refractive index	1.48(046)	1.48(034)
Color	3.2 R	3.3 R

Table VI—Varnish Tests

	CLEAN SEED	DOCKAGE SEED
A—LIGHT VARNISH: TIME, 90 MINUTES; HEAT, 560–600° F. (293–316° C.)		
Varnish	1.49(141)	1.49(098)
Supreme	1.49(122)	1.49(030)
Arctic supreme	1.49(067)	1.49(026)
B—HEAVY VARNISH: TIME, 150 MINUTES; HEAT, 560–600° F. (293–316° C.)		
Varnish	1.49(398)	1.49(352)
Supreme	1.49(379)	1.49(280)
Arctic supreme	1.49(294)	1.49(274)

Table VI suggests an interesting relationship between the viscosity of a heat-treated oil as shown by the refractive index and the higher melting point fats and the iodine number of the original oil. It indicates that of two oils with the same proportion of high melting point fats the one with the higher iodine number will body faster.

Conclusion

The investigation shows the variations which may be expected in oils made from the same crop from the same district, if greater or less amounts of dockage seeds are allowed to remain mixed with the flaxseed at the time of crushing, and further, that these variations cause differences which will affect the processes of the linseed-oil consumer. Thus far all the writers' work with pure linseed oils and linseed oils containing a proportion of dockage oil demonstrates that there is an appreciable difference in their constants, that these differences are maintained in the refined oils made from them and are often magnified in later blowing and heat treatments.

Absorption of Ultra-Violet Light by Paint Vehicles

By George F. A. Stutz

NEW JERSEY ZINC COMPANY, PALMERTON, PA.

IN A recent paper[1] the results are given of an investigation of the action of ultra-violet radiations on wet paint vehicles. Included is a determination of the degree to which various paint vehicles absorb the ultra-violet light. In the present paper this absorption determination is extended to the case of the dry films of a number of vehicles. The nature and amount of this absorption is of particular importance, because of the action of the ultra-violet portion of sunlight in "weathering," or decomposing, vehicle films; and also because of the growing use of strong sources of ultra-violet light in accelerated weathering apparatus. To further aid in this study, the change in the absorption caused by exposure of the films to sunlight and the mercury arc is also determined.

Method

Because of the relatively high opacity of all vehicles to ultra-violet light, it is necessary to examine them in very thin films. A film thickness of 0.02 mm. or less is required in most cases in order that sufficient light will be transmitted to make accurate measurements possible. Most satisfactory results were obtained by flowing out thin films of the vehicles on transparent plates. For this purpose plates of fused quartz and Corning glass G 980 A were used. The vehicles were allowed to dry in diffused daylight, in the laboratory,

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[1] Stutz, THIS JOURNAL, **18**, 1235 (1926).

and no attempt was made to control the humidity conditions. The film thickness was determined by means of a Randall-Stickney micrometer thickness gage. This measurement is only accurate to within about 10 per cent, the extreme thinness, as well as the non-uniformity, of the films making a more accurate determination impossible.

The quartz spectrophotometer described in the previous paper was used to measure the ultra-violet transmission of the films. At least four different thicknesses of each film were used. The degree of absorption was calculated using the relationship

$$I = I_0 10^{-kt}$$

where I = intensity of transmitted light
I_0 = intensity of incident light
t = film thickness in centimeters
k = coefficient of absorption

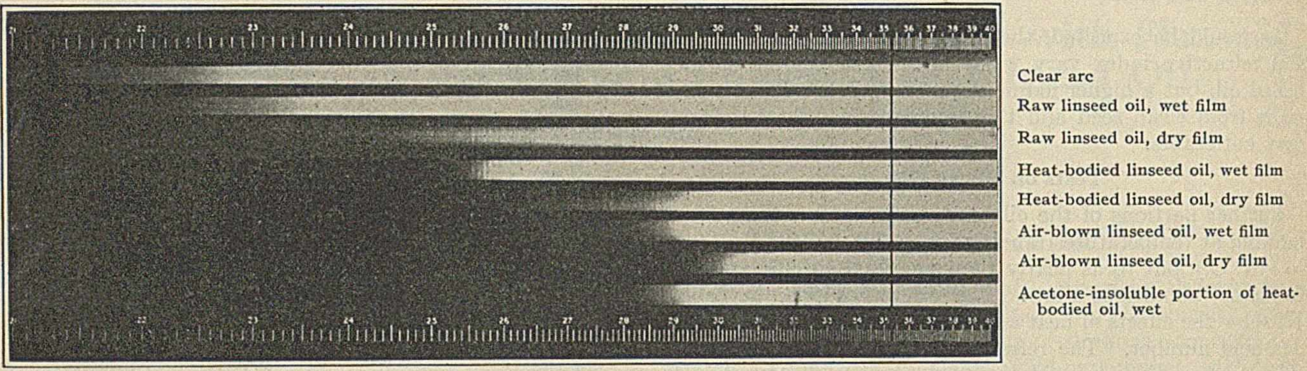

Figure 1—Spectrograms of Tungsten Spark under Water, Taken through Films of Vehicle Approximately 0.02 mm. Thick

Table I—Ultra-Violet Absorption by Oils

Age *Days*	Exposure[a] *Hours*	Transmission at 0.01 mm. Thickness in Per Cent at Wave Length: 3655	3131	3023	2968	2804	2655	2536	2400	2300
RAW LINSEED										
Wet film		98.7	92.7	89.3	86.3	76.3	73.5	70.8	42.2	35.0
5	...	98.5	87.0	85.0	80.0	63.0	54.9	37.1	27.5	25.1
115	...	76.7	48.5	43.2	39.8	29.1	27.0	21.1	17.8	15.5
115	5 U. V.	91.6	72.4	66.0	60.9	44.7	38.4	31.5	26.9	24.5
RAW LINSEED + 5 PER CENT LIQUID DRIER										
Wet film		97.9	86.1	80.5	80.0	67.2	57.2	51.1	34.4	29.4
5	...	98.4	74.1	71.2	69.0	45.7	35.5	20.7	18.2	18.0
115	...	72.4	34.6	32.3	30.9	21.4	15.1	12.6	10.9	10.9
115	5 U. V.	86.1	62.4	53.5	51.9	31.6	27.0	20.0	17.0	15.8
RAW LINSEED + 5 PER CENT LIQUID DRIER										
40	...	75.7	35.2	29.5	29.5	13.7	8.0	7.8	6.0	5.8
40	16 Sun.	98.0	68.0	51.2	48.0	21.5	13.8	11.5	10.0	10.0
RAW LINSEED + 5 PER CENT LIQUID DRIER										
2 years	...	10.9	3.0	2.4	2.1	1.2	1.0	0.85	0.65	0.52
2 years	22 U. V.	35.5	14.1	12.3	10.9	6.5	5.1	4.9	3.2	2.5
ALKALINE-REFINED (REFRIGERATED) LINSEED + 5 PER CENT DRIER										
Wet film		97.5	85.7	84.2	81.6	65.1	60.8	51.6	27.5	23.4
5	...	97.5	74.0	61.5	60.0	39.8	21.1	15.8	14.9	14.4
115	...	69.1	32.5	24.2	22.8	18.2	15.1	14.0	12.5	11.8
115	5 U. V.	87.1	65.1	57.0	53.4	39.3	32.0	27.1	23.0	21.6
40	...	64.1	26.7	19.0	19.0	9.2	7.1	4.7	3.0	2.3
40	16 Sun.	88.3	55.0	44.0	43.0	18.9	11.1	8.5	6.2	5.3
ACID-REFINED LINSEED + 5 PER CENT LIQUID DRIER										
Wet film		94.0	83.0	79.2	78.5	65.6	64.0	56.6	34.9	33.5
5	...	98.4	84.1	70.8	70.0	50.7	37.2	30.6	22.1	19.3
115	...	76.7	53.7	43.0	37.8	28.0	24.5	21.0	17.8	15.5
115	5 U. V.	91.8	78.5	69.1	66.1	49.0	42.0	38.0	34.3	29.2
AIR-BLOWN BODIED LINSEED, VISCOSITY 9 POISES										
Wet film		72.0	25.1	22.6	16.2	8.1	3.2	0.60	0.50	0.50
5	...	72.4	34.7	24.3	17.0	8.0	3.1	0.51	0.2	0.2
115	...	70.8	25.4	17.8	14.2	6.5	2.55	0.43	0.2	0.2
115	5 U. V.	80.3	44.6	30.0	26.3	17.0	8.32	7.2	7.0	6.8
3 years	...	10.6	2.13	1.72	1.36	0.77	0.59	0.55	0.41	0.48
3 years	22 U. V.	50.9	25.4	22.1	17.2	10.9	9.6	6.9	4.5	3.9
HEAT-BODIED LINSEED, VISCOSITY 4 POISES										
Wet film		98.0	80.0	76.1	72.1	38.2	19.1	7.5	3.7	3.5
5	...	93.8	58.3	36.0	31.0	10.1	6.0	4.0	3.5	3.2
115	...	65.2	29.2	18.0	11.6	7.1	4.6	3.5	2.9	2.8
115	5 U. V.	74.1	32.4	16.6	10.0	6.1	4.4	3.5	2.7	2.8
3 years	...	27.0	5.9	4.8	4.2	2.9	2.4	0.4	0.2	0.2
3 years	22 U. V.	44.7	13.8	12.6	10.7	4.4	3.1	1.4	1.3	0.90
HEAT-BODIED LINSEED, VISCOSITY 9 POISES										
5	...	84.5	46.4	43.0	32.2	14.9	5.95	0.80	0.70	0.80
5	48 U. V.	73.5	30.9	24.4	21.4	5.90	2.00	1.10	0.64	0.41
CHINA WOOD OIL WITH DRIER										
5	...	88.1	45.7	41.7	34.3	16.3	5.25	3.05	1.62	1.49
	48 U. V.	88.9	49.6	45.0	38.5	21.5	12.5	7.60	6.50	5.75
PERILLA OIL										
5	...	85.5	46.8	39.6	28.5	8.6	3.2	1.8	1.72	1.68
	48 U. V.	91.8	60.5	54.0	44.2	22.1	13.6	9.60	8.50	5.95
TREATED POPPYSEED OIL										
5	...	88.1	71.6	68.1	52.2	21.6	16.9	8.50	2.04	0.50
	48 U. V.	85.7	59.3	54.8	51.6	41.0	33.4	29.3	22.4	19.5
TREATED SOY BEAN OIL										
5	...	94.4	76.5	64.1	55.0	29.0	20.9	16.3	9.9	2.0
	48 U. V.	95.3	68.4	62.0	57.4	49.0	44.7	42.8	33.0	28.4

[a] U. V.—ultra-violet; Sun.—sunlight.

From the average value of *k*, determined at the several thicknesses, the percentage transmission of a film 0.01 mm. thick was calculated. These values are recorded as a measure of the transparency of the films. The figures are given at a film thickness of 0.01 mm., because the differences existing between the several vehicles are best shown at this thickness.

The exposure of the films to ultra-violet light was carried out in a cabinet held at 40° C. by blowing through it a current of cool air. The films were placed 30 cm. (12 inches) from a 15-cm. (6-inch) Cooper-Hewitt quartz Uviarc. The exposures to sunlight were made on clear days in August, 1926.

Results

To show that the ultra-violet absorption by oil films is continuous, the spectrograms shown in Figure 1 were taken. The source of light is a tungsten spark under water, giving a continuous spectrum down to 2140 Å.[2] The light from this source was passed through a film of the vehicle approximately 0.02 mm. thick and dispersed in a Hilger E-4 quartz spectrograph. The increase in opacity of linseed oil on drying is shown, as well as the relative opacities of raw, heat-bodied, and air-blown oils.

The transmission values, as determined with the quartz spectrophotometer, for linseed and other oils, are recorded in Table I. Values for the wet films of several of the oils are also given, corresponding to the results previously recorded.

Note—The values of *K* recorded in the previous paper are relatively high in some cases, owing to an inaccuracy in the determination of the thickness of the wet films.

Curve 1 shows the transmission of three typical linseed oils. Curve 2 gives the transmission of several other paint oils. Different samples of any one kind of oil vary somewhat in ultra-violet transparency. The results given are characteristic of oils of the several classes and types named.

The results for varnishes are recorded in Table II, and Curve 3 shows the transmission of several of these varnishes. The seven varnishes used are the ones on which Nelson and Schmutz have reported accelerated weathering results.[3]

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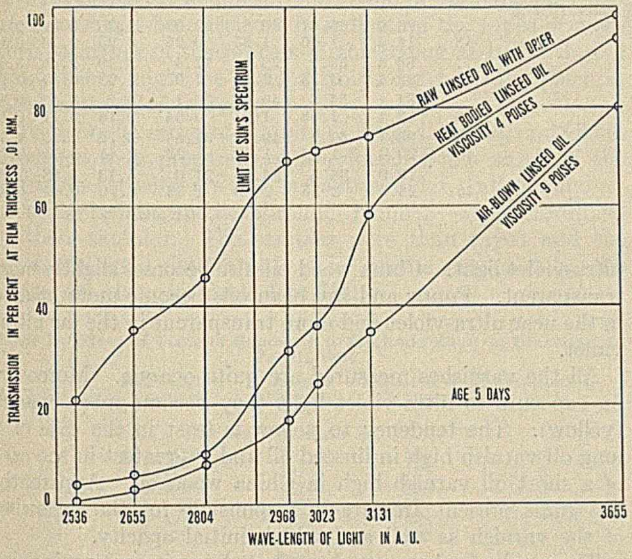
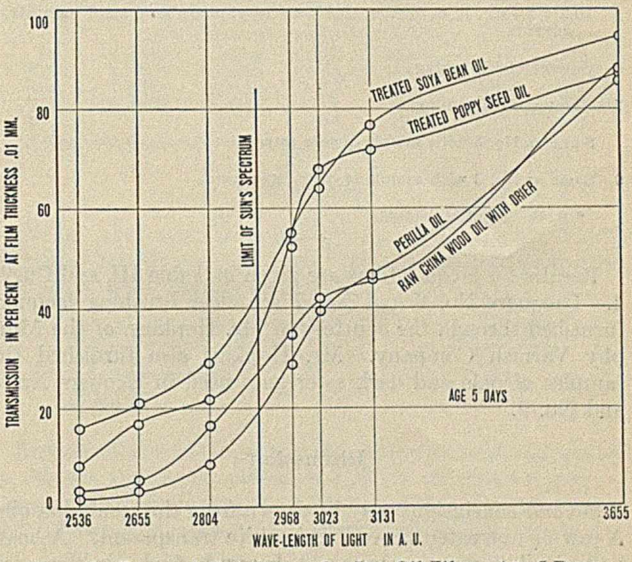
[2] Fulweiler and Barnes, *J. Franklin Inst.*, **194**, 83 (1922).

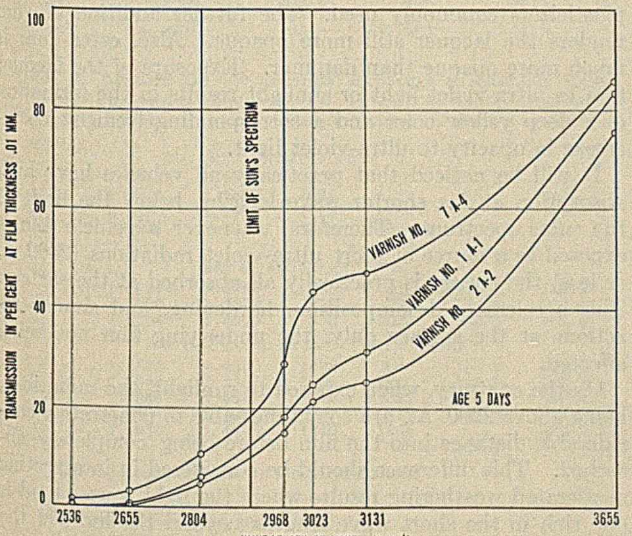
[3] Nelson and Schmutz, *Proc. Am. Soc. Testing Materials*, **24**, Pt. II, 920 (1924).



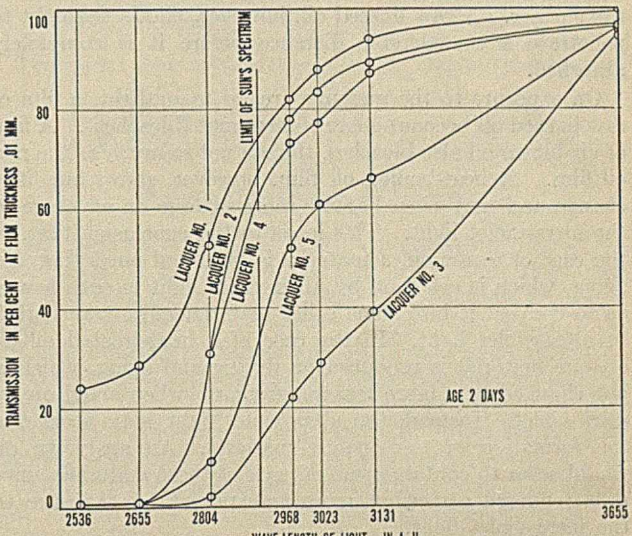
Curve 1—Transmission Curves for Dry Linseed Oil Films, Age 5 Days



Curve 2—Transmission Curves for Dry Oil Films, Age 5 Days



Curve 3—Transmission Curves for Dry Varnish Films, Age 5 Days



Curve 4—Transmission Curves for Dry Lacquer Films, Age 2 Days

Table II—Ultra-Violet Absorption by Varnishes

No.	Gum	Age	Length in Oil[a]		U. V. Exposure	Transmission at 0.01 mm. Thickness in Per Cent at Wave Length:								
			Tung	Linseed		3655	3131	3023	2968	2804	2655	2536	2400	2300
		Days			*Hours*									
A-1	Limed rosin	5	7	10	..	83.2	31.3	24.8	18.0	6.3	0.73	0.19	0.17	0.20
		7			48	59.4	15.7	13.3	9.8	2.6	0.56	0.20	0.16	0.16
A-2	Limed rosin 50%; Congo 50%	5	10	0	..	75.3	25.4	21.6	14.3	4.90	0.40	0.05	0.03	0.04
		7			48	54.5	18.3	14.6	10.1	2.7	0.44	0.08	0.05	0.05
A-5	Ester 50%; Kauri 50%	5	1	5	..	79.4	25.1	21.6	12.0	3.6	0.23	0.08	0.07	0.06
		7			48	58.6	15.7	10.6	7.6	1.6	0.18	0.03	0.03	0.03
A-3	No. 1 Kauri	5	0	25	..	75.8	37.1	29.8	23.4	9.2	1.3	0.28	0.20	0.20
		7			48	67.6	31.8	23.8	17.1	7.2	2.1	0.9	0.35	0.40
A-7	Ester 50%; Congo 50%	5	14	35	..	75.8	29.5	25.1	16.4	6.1	0.20	0.02	0.03	0.03
		7			48	70.8	28.2	22.0	14.1	3.6	1.0	0.36	0.16	0.15
A-6	Limed rosin	5	72	28	..	75.2	25.1	20.5	13.1	4.3	0.33	0.04	0.06	0.05
		7			48	55.8	17.5	14.4	10.0	4.5	1.40	0.67	0.36	0.25
A-4	Ester	5	36	0	..	85.8	47.3	43.3	28.8	10.7	2.3	0.23	0.40	0.23
		7			48	66.5	22.6	21.1	15.1	4.93	1.32	0.40	0.18	0.10

[a] By length in oil is meant the number of gallons of oil per 100 pounds of gum.

Table III—Ultra-Violet Absorption by Lacquers

No.	Composition	U. V. Exposure	Transmission at 0.01 mm. Thickness in Per Cent at Wave Length:						
			3655	3131	3023	2968	2804	2655	2536
		Hours							
1	17% 1/2 sec. R. S.[a] cotton, 83% solvents	..	100.0	94.0	88.0	82.0	52.7	28.5	24.5
		48	45.5	10.5	7.5	6.5	3.4	1.0	0.32
2	14.1% 1/2 sec. R. S. cotton, 16.6% tricresyl phosphate, 69.3% solvents	..	97.0	89.5	83.6	78.0	31.0	0.51	0.50
		48	16.1	1.70	1.60	1.45	0.04	0.03	0.03
3	10.7% 1/2 sec. R. S. cotton, 12.7% tricresyl phosphate, 10.9% ester gum, 65.7% solvents	..	94.4	38.9	29.0	21.9	2.00	0.53	0.50
		48	8.80	0.31	0.18	0.10	0.02	0.01	0.01
4	9.8% 1/2 sec. R. S. cotton, 11.5% tricresyl phosphate, 9.6% dammar gum, 69.1% solvents	..	96.6	87.1	80.3	73.3	30.5	0.4	0.3
		48	18.6	2.1	1.7	1.3	0.35	0.07	0.06
5	10.3% 1/2 sec. R. S. cotton, 12.1% tricresyl phosphate, 5.2% dammar, 5.2% ester, 67.2% solvents	..	96.0	66.8	60.8	52.0	8.9	0.32	0.32
		48	14.6	1.66	1.35	0.95	0.25	0.10	0.10
6	Commercial brushing	..	86.6	39.1	28.0	17.4	5.19	2.48	3.08
		48	22.4	3.13	2.43	2.07	1.08	0.56	0.70
7	Commercial brushing	..	81.4	54.8	49.0	36.1	16.2	1.12	0.83
		48	12.4	1.08	1.01	0.64	0.16	0.11	0.10
	Same as No. 3 with sample of pale ester gum	..	93.1	59.2	49.9	31.5	5.75	1.53	1.33
		48	20.3	1.86	1.32	1.22	0.41	0.05	0.05
9	Same as No. 3 with sample of dark ester gum	..	70.9	38.5	34.2	24.0	5.13	1.88	1.80
		48	26.0	3.35	2.60	1.32	0.70	0.61	0.35

[a] R. S.—regularly soluble.

Results for lacquer films are given in Table III and Curve 4. Lacquers No. 6 and No. 7 are clear brushing lacquers furnished through the courtesy of Mr. Hopkins, of the Murphy Varnish Company. Mr. Hopkins also furnished the samples of pale and dark ester gum used in lacquers No. 8 and No. 9.

Discussion

Several conclusions may be drawn from the results on oils. A raw or untreated linseed oil is quite transparent. A heat-bodied oil is more opaque. A heavy-bodied, air-blown oil is still more opaque. In general, then, in the case of a bodied oil the ultra-violet light is absorbed almost entirely at the surface. A raw linseed oil, however, allows the light to penetrate a considerable distance before it is completely absorbed.

On exposure to the mercury arc, or to sunlight, a film of raw linseed oil becomes more transparent (bleaches). A film of air-blown oil also bleaches, though not so much as the raw oil film. A heat-bodied oil film, however, shows but little change and may even become more opaque on exposure to the ultra-violet light. This leads to the conclusion that, in the case of a raw oil, a material is produced on drying and aging, which is acted on by ultra-violet light in such a way as to convert it into some other material more transparent to ultra-violet light. In the case of a heat-treated oil an opaque material is produced on drying and aging, which is not changed to a more transparent form when acted on by ultra-violet. Instead, the ultra-violet light may accelerate the formation of the opaque material. An air-blown oil would seem to contain some of each of these materials since it is rendered somewhat more transparent by exposure to the ultra-violet light.

Perilla oil becomes more transparent on exposure to the ultra-violet light. China wood oil also becomes slightly more transparent. Poppy and soy bean oils become more opaque in the near ultra-violet and more transparent in the far ultra-violet.

All the varnishes measured are quite opaque. Moreover, on exposure to ultra-violet light they become more opaque (yellow). The tendency to yellow is least in the case of a long oil varnish high in linseed oil and is greatest in the case of a short oil varnish high in China wood oil. Apparently the gums present are largely responsible for the yellowing of the varnish as well as its high initial opacity.

The results for lacquers show that clear nitrocotton is quite transparent. The addition of a plasticizer renders it more opaque at the shorter wave lengths. This is true of all the plasticizers commonly used. The further addition of gum renders the lacquer still more opaque. Also, ester gum is much more opaque than dammar. Exposure of the lacquer film to ultra-violet light or sunlight results in the formation of a deep yellow color and a corresponding tremendous increase in opacity to ultra-violet light.

It will be noticed that practically all vehicles have high absorption at the shorter wave lengths, below the limit of the sun's spectrum. Therefore, whenever a vehicle film is exposed to a source of short ultra-violet radiations (2800 Å. or less) the energy is practically all absorbed at the surface. This accelerates decomposition, hardening, and similar reactions at the surface only, the underlying film not being affected.

On the contrary, when exposed to sunlight, the radiations, being above 2900 Å., are sometimes able to penetrate a considerable distance into the film before being completely absorbed. This difference should be considered in interpreting accelerated weathering results where the light source used is one rich in the short wave lengths beyond the limit of the sun's spectrum.

Acknowledgment

The author wishes to acknowledge the assistance and criticisms of the members of the Research Division of the New Jersey Zinc Company, and the aid rendered by his assistant, C. Hall, in making the observations.

Action of Cathode Rays on Drying Oils

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The production of high-voltage cathode rays outside of the generating tube has been described by Coolidge[1] and some experiments with these rays outside of the generating tube are described by Coolidge and Moore.[2] In a description of this work[3] it was mentioned that castor oil exposed to the rays was changed to a solid.

The relations which occur when drying oils are thickened by heating are quite different than those when the oil is thickened by the action of ultra-violet light, and these differ from the actions when the oil is oxidized by blowing. It was believed that this thickening by the action of high-voltage cathode rays might be of service in indicating the types of reactions occurring in the process of thickening and that during raying there might be actions which did not take place in other methods of bodying.

Accordingly, series of samples of linseed, perilla, and China wood oils were prepared as described. Some or all of the constants—specific gravity, refractive index, iodine number, molecular weight, and hexabromide number—were determined on these samples. The samples were than rayed and the constants again determined. The results produced by the raying are given in Table I to III.

Table I—Effect of Time of Exposure to Cathode Rays on Linseed and Perilla Oils

Exposure *Minutes*	Refractive Index	Iodine Number	Molecular Weight	Hexabromide Number
		SET 1—LINSEED OIL		
0	1.4776	187.6	762	37.6
1	1.4778	187.4	781	22.6
2	1.4780	187.4	832	22.3
3	1.4782	187.6	870	24.3
5	1.4786	185.5	883	19.5
10	1.4799	181.0	967	21.6
		SET 5—PERILLA OIL		
0	1.4804	205.5	785	47.8
1	1.4805	205.5	810	42.2
2	1.4806	202.6	817	41.1
3	1.4808	202.3	834	38.8
5	1.4812	198.7	878	37.0
10	1.4819	195.3	925	31.2

Table II—Linseed Oil—50 Seconds' Exposure to Cathode Rays

After Heating *Hours*	Refractive Index Before	Refractive Index After	Molecular Weight Before	Molecular Weight After	Iodine Number Before	Iodine Number After
			SET 2—HEATED AT 293° C.			
[a]	1.4776	1.4810	970	856	177.2	...
1	1.4836	1.4842	1096	1132	148	147
2	1.4890	1.4895	1728	1989	117.5	112.6
2.5	1.4903	...	2330	Insoluble gel		
			SET 3—BLOWN AT 138° C.			
[a]	1.4781	1.4788	788	818	184.0	183.7
3	1.4790	1.4800	833	929	175.6	173.2
9	1.4796	1.4820	893	1025	160.5	159.3
			SET 4—HEATED AT 293° C. WITH UMBER			
[a]	1.4825	1.4830	1038	1046	155.2	144.2
0.5	1.4855	1.4857	1209	1220	142.2	128.8
1.0	1.4886	1.4892	1540	1571	135.9	120.3
1.25	1.4901	1.4904	1617	1658	132.0	114.7
1.5	1.4910	1.4915	1840	1904	...	103.2
1.75				Gel	129.8	

[a] Time required to raise oil to temperature used.

Table III—Perilla and China Wood Oils—50 Seconds' Exposure to Cathode Rays

After Heating *Hours*	Refractive Index Before	Refractive Index After	Molecular Weight Before	Molecular Weight After	Iodine Number Before	Iodine Number After
			SET 6—PERILLA OIL HEATED AT 293° C.			
[a]	1.4806	1.4811	790	891	201.4	196.6
1.25	1.4869	1.4873	1123	1207	157.4	155.3
1.75	1.4900	1.4906	1388	1527	143.4	142.5
2.25	1.4917	1.4920	1719	1959	134.1	Gel
2.75			Solidified			
			SET 7—PERILLA OIL AIR-BLOWN AT 293° C.			
[a]	1.4808	1.4812	785	864	200	195.7
0.5	1.4850	1.4852	1078	1131	161.2	162.5
0.92	1.4888	1.4892	1440	1524	151.6	142.1
1.10	1.4906	1.4910	1753	1857	131.7	131.8
1.24			Solidified			
			SET 8—CHINA WOOD OIL HEATED AT 190° C.			
[a]	1.5148	1.5144	873	888	...	157
0.5	1.5134	1.5132	991	1020	...	157
1.0	1.5116	1.5114	1098	1160	155.1	153.8
1.5	1.5103	1.5100	1371	1453	146.1	145.6
2			1994	Gel		

[a] Time required to raise oil to temperature used.

Materials

Perilla oil of suitable purity for research work was kindly furnished by Maximilian Toch. It had the following characteristics when used in this work:

Specific gravity at 15.5°/15.5° C.	0.9358
Refractive index at 25° C.	1.4804
Iodine number, Wijs (30 minutes)	205
Hexabromide number	47.8
Acid value	3.08
Molecular weight	765

Linseed oil derived from selected northwest seed was treated to remove the break, chilled to 6.6° C. to separate part of the saturated glycerides, and filtered cold. This oil showed the following characteristics when used in this work:

Specific gravity at 15.5°/15.5° C.	0.9355
Refractive index at 25° C.	1.4776
Iodine number, Wijs (30 minutes)	187.6
Hexabromide number	37.6
Acid value	4.38
Molecular weight	760

The *China wood oil* had the following characteristics:

Specific gravity at 15.5°/15.5° C.	0.9405
Refractive index at 25° C.	1.5160
Iodine number, Wijs	163
Browne heat test minutes	9.5

Preparation of Sets of Samples

Set 1—Two and a half cubic centimeters of linseed oil were placed in a glass Petri dish of 10 cm. diameter. The dish was fastened to a shaft inclined at an angle of 27 degrees and rotated at about 60 r. p. m. The center of the Petri dish was 5 cm. from the window of the cathode ray tube. In all cases the tube was operated at 250,000 volts (maximum) and 1 ma. The oil spread itself quite evenly over the bottom of the Petri dish in a layer about 0.3 mm. thick. Five samples were exposed 1, 2, 3, 5, and 10 minutes.

Set 2—Six hundred grams of linseed oil were heated at 293° C. in a 1000-cc. three-neck Pyrex flask with mechanical stirring at 200 r. p. m. Air carrying moisture equivalent to 62.6 per cent relative humidity at 25° C. was passed over

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[1] *J. Franklin Inst.*, **202**, 693 (1926).

[2] *Ibid.*, **202**, 722 (1926).

[3] *J. Chem. Educ.*, **3**, 1369 (1926).

the surface at the rate of 4.25 liters per minute. Samples taken when the temperature reached 293° C. and after 1-, 2-, and 2.5-hour intervals were exposed for 50 seconds to the cathode rays in exactly the same manner as described for set 1.

Set 3—One thousand grams of linseed oil were heated at 138° C. and air carrying moisture equivalent to 50 per cent relative humidity at 25° C. was blown through the oil at the rate of 5.6 liters per minute by a bubbler tube with fine holes. Samples taken at the start and after intervals of 3 and 9 hours were exposed to the cathode rays for 50 seconds.

Set 4—One hundred and ninety-four kilograms of aged linseed oil were heated in a wrought-iron kettle with 1.6 kg. of umber. The oil, which had been blown previous to use, had the following characteristics:

Iodine number, Wijs (30 minutes)	161
Saponification value	186.9
Acid value	3.64
Specific gravity at 15°/15° C.	0.9884

The umber contained $Fe_2O_3 + Al_2O_3$, 50.22; SiO_2, 17.98; Mn_3O_4, 15.76; and volatile matter 14.74. Two hours were required to raise the temperature to 293° C. The oil was stirred with a ladle. Samples were taken when just up to 293° C. and after time intervals of 0.5, 1, 1.25, 1.75, and 2 hours. These samples were exposed to the cathode rays for 50 seconds.

Set 5—Perilla oil was exposed for 1, 2, 3, 5, and 10 minutes in exactly the same manner followed for linseed oil (set 1).

Set 6—Five hundred grams of perilla oil were heated to 293° C. and held at that temperature in a 1000-cc. three-neck Pyrex flask. The oil was stirred at 200 r. p. m. A stream of pure dry nitrogen was passed over the surface at the rate of 4.25 liters per minute. Samples withdrawn at specified times were exposed to the cathode rays for 50 seconds.

Set 7—Five hundred grams of perilla oil were heated to 293° C. and air blown through it at that temperature at the rate of 4.25 liters per minute from an air bubbler. The air carried H_2O equivalent to a relative humidity of 50 per cent at 25° C. The oil set to a gel in 1.75 hours. Samples withdrawn at specified times were exposed to the cathode rays for 50 seconds.

Set 8—Two hundred and fifty grams of China wood oil were heated at 190° C. in a 500-cc. three-neck Pyrex flask and stirred mechanically at 200 r. p. m. Air carrying moisture equivalent to 62.5 per cent relative humidity at 25° C. was passed over the surface at the rate of 2.26 liters per minute. Samples were withdrawn when the oil reached 190° C. and at 30-minute periods thereafter. The samples were exposed to the cathode-ray stream for 50 seconds in the same manner as in other runs.

Discussion of Results

In set 5 the over-all decrease in hexabromide number corresponds to 0.166 gram of hexabromide per gram of oil, which in turn corresponds to a decrease per gram of oil of $\frac{278.24}{757.74} \times 0.166 = 0.0609$ gram of that linolenic acid which forms an insoluble hexabromide.

If the linolenic acid underwent a change whereby one ethylene linkage was closed, then the decrease in iodine absorbed would be 2 × 126.93 grams for 278 grams of linolenic acid or $\frac{2 \times 126.93}{278.24} \times 0.0609 = 0.0556$ gram of iodine for the 0.0609 gram of linolenic acid. The actual decrease in iodine number is 0.102 gram of iodine per gram of oil, which is nearly twice this value and might be accounted for on the assumption that two of the three ethylene linkages in each molecule of linolenic acid were closed.

The samples were too small to permit the determination of specific gravity or viscosity. It was believed, however, that the change in specific gravity would be indicated by the change in refractive index, which was accordingly determined. It was found that the raying increased the refractive index in all samples of linseed and perilla oils and decreased it in the case of China wood oil.

The molecular weight increased steadily in all cases. It is noticeable that the gain in molecular weight for equal exposure is in a general way dependent on the molecular weight of the sample exposed to the rays; thus, in sets 1, 5, and 3 the molecular weight gain is from 15 to 30 for samples having low molecular weights—e. g., 762, 785, and 788. The corresponding gain for samples having molecular weights of double this value and upwards is more nearly 100 to 200 points for the same exposure (50 seconds), except in set 4, in which driers were boiled into the oil. In this set the molecular weight gain on exposure is smaller but increases steadily with increase in the molecular weight of the successive samples.

The iodine number decrease is greatest in this set, which contains driers. In the raying process a considerable amount of ozone is produced in the air. Some of the reactions which occur during the raying are affected by this, particularly with oils containing iron.

In set 1 there is a sharp drop in hexabromide number without any change in iodine number in 3 minutes' exposure. The increases in molecular weight and refractive index are very small in this period. This seems to be best explained as a change in the linolenic glyceride to an isomer which does not yield solid hexabromide. Further evidence supporting this premise is obtained from the results in the raying of China wood oil. The samples up to 1.5 hours were homogeneous. No gel could be detected. After 50 seconds' exposure to the cathode rays all samples contained gel lumps easily noticeable by rotating the sample tube. These lumps dissolved in benzene, giving solutions which when poured through dry filter paper did not leave gel lumps on the paper. Further, the molecular weights are relatively low. This behavior would not be inconsistent with the idea of change to β-eleostearic acid, and it seems difficult to explain the results in any other way.

The identification and properties of the different isomers of linolenic acid is a task far from complete, but there is evidence that the drying of oils is somewhat dependent on the relative proportions of these isomers.

In order to see whether the rate of drying of the oils before and after exposure to the cathode ray discharge would support the idea of isomeric change, drops of linseed and perilla oils before raying and after raying for 1, 2, 3, 5, and 10 minutes were put on a glass plate and the plate was then inclined so that the drops ran down to the edge, making series of thin films the width of the drop. The glass plates were dried in an oven at 60° C.

The time required for the oil, without driers, to become dry to touch or to dry hard was found to decrease in a regular manner as the time of exposure to cathode rays increased up to 10 minutes. Perilla oil, without driers, rayed for 10 minutes was dry to touch in 2 hours and hard in 5 hours. Linseed oil rayed for 10 minutes was dry to touch in 3 hours and hard in 6 hours at 60° C. Raw perilla and linseed oils, without driers, flowed on the same glass plates at the same time were wet and not much changed when the progressively thicker films from rayed samples were all dry.

In another set, raw linseed oil in an oven at 75° C. required 8 hours to become dry to touch, whereas the same oil rayed for 10 minutes was dry hard in 4 hours. Raw perilla oil was dry to touch after 7.5 hours and the same perilla oil rayed 10 minutes, was dry hard in 3.5 hours.

Raw linseed oil on glass in the open room at 20° C. became dry after 45 hours; raw perilla after 43 to 44 hours. The same linseed oil rayed 10 minutes was dry at the end of 24 hours. The same perilla oil rayed 10 minutes was dry at the end of 24 hours.

Aside from any support given to the premise of isomeric change during the raying process, these results are not without significance in the treatment of drying oils for various purposes.

In all cases the oils were greatly bleached by the raying process. The linseed oil samples in sets showed progressive decrease in color from sample to sample as the time of raying increased. The sample rayed for 10 minutes is practically water-white. The perilla samples rayed 3, 5, and 10 minutes are also practically water-white.

More work is in progress to confirm and amplify these observations.

Acknowledgment

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Action of Heat and Blowing on Linseed and Perilla Oils and Glycerides Derived from Them

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IN PREVIOUS work designed to establish fundamental data regarding the behavior of drying oils when heated, blown, or thickened by ultra-violet light, variations were observed which seemed to be traceable to variations in the constituents of the oil. Thus the presence of only a small percentage of mucilaginous matter and phosphatides derived from the seed was shown to exert a relatively large influence on the rate of thickening of linseed oil when heated.[3]

In extending the work it was decided to use less complicated mixtures and to attempt to synthesize some of the constituents of the oil. A glyceride of linolenic acid was synthesized[4] and the rate of molecular weight increase determined when this glyceride was heated. Since perilla oil is richer in linolenic compounds than linseed oil, it was used as a starting point. Linseed and perilla oils also contain different proportions of alpha and beta isomers of linolenic acid. The glyceride is synthesized from the crystalline hexabromide. This should eliminate the beta form if the hexabromide is not a mixture. However, in order to see whether there is any difference in the glycerides synthesized in this way from the two oils, both linseed and perilla oils were used.

This paper contains data showing the rate of change of certain analytical figures when the synthesized glycerides are heated, as well as similar data for the natural linseed and perilla oils for comparison.

It was previously stated[4] that the synthesized glyceride dried to a smooth, elastic film. Data on a few films are given and a new method of making films for study is described.

Materials

Perilla oil of suitable purity for research work was kindly furnished by Maximilian Toch. It had the following characteristics when used in this work:

Specific gravity at 15.5°/15.5° C.	0.9358
Refractive index at 25° C.	1.4804
Iodine number (Wijs, 30 minutes)	205
Hexabromide number	47.8
Acid value	3.08
Molecular weight	765

Linseed oil derived from selected northwest seed was treated to remove the break, chilled to 6.6° C. to separate part of the saturated glycerides, and filtered cold. This oil showed the following characteristics when used in this work:

Specific gravity at 15.5°/15.5° C.	0.9355
Refractive index at 25° C.	1.4776
Iodine number (Wijs, 30 minutes)	187.6
Hexabromide number	37.6
Acid value	4.38
Molecular weight	760

Linolenic glyceride was synthesized by essentially the same method as previously described,[4] with the following modifications in order to give a purer product and to facilitate the preparation:

> Three hundred grams of the fatty acids are dissolved in 900 cc. of ethyl ether containing 10 per cent of glacial acetic acid and 3 per cent of absolute ethyl alcohol. The mixture is then brominated in the usual way. The resulting hexabromide is crystalline and is easily purified. The crystalline hexabromide is carefully washed with ethyl ether and finally removed from the ethereal solution by centrifuging. The product is recrystallized from hot xylene until it shows a melting point of 178–179° C. Since the purity and texture of the hexabromide greatly affect the rate of formation of the glycerol ester, the recrystallization from xylene is practically essential.
>
> The esterification is greatly aided if the glycerol is kept saturated with hydrochloric acid by passing the dry gas along with the carbon dioxide into the reaction chamber, the tube leading below the surface of the reactants. Usually carbon dioxide containing 5 to 10 per cent of dry hydrogen chloride is sufficient. In this way the reaction time is reduced to about 8 hours.

The glycerides thus prepared have the following characteristics:

	PERILLA	LINSEED	THEORETICAL FOR LINOLENIC MONOGLYCERIDE
Refractive index at 25° C.	1.4864	1.4832	
Iodine number (Wijs, 30 minutes)	211.2	212.2	217.7
Molecular weight (F. P. benzene)	708	677	352
Hexabromide number	28.8	28.5	

Ultimate Analysis

(Figures in per cent)

	GLYCERIDE SYNTHESIZED FROM:				THEORETICAL FOR LINOLENIC:	
	Perilla Oil		Linseed Oil		Mono-glyceride	Diglyceride
SAMPLE	1	2	3	4		
Carbon	71.85	71.97	71.68	71.77	71.53	76.40
Hydrogen	10.06	10.27	10.19	10.12	10.28	10.54
Oxygen	18.09	17.76	18.13	18.11	18.17	13.06

The figures for iodine number and ultimate analysis indicate that the product is linolenic monoglyceride and that it is fairly pure. The molecular weight is about double the theoretical value. It is possible that this dihydroxy body shows association in benzene. Work is now in progress to determine what types of compounds give abnormal molecular weights in benzene and other solvents.

Experimental

EFFECT OF HEATING—In runs 65, 66, 67, and 68, 500 grams of perilla oil were heated in a 1000-cc. three-neck Pyrex

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[3] Long and Wentz, THIS JOURNAL, 18, 1247 (1926).

[4] Long, Knauss, and Smull, *Ibid.*, 19, 62 (1927).

flask. The oil was mechanically stirred at 200 r. p. m. In runs 65 and 66 air carrying water vapor equivalent to a relative humidity of 62.6 per cent at 25° C. was passed over the surface at the rate of 3.53 liters per minute. In run 67 carbon dioxide was substituted for air. In run 68 the air was bubbled through the oil by means of a glass bubbler tube with fine holes, thus combining the effects of heating and mild blowing. Thirty minutes were required to bring the oil up to 293° C., the temperature (±2° C.) maintained in these four runs.

Table I—Perilla Oil

After Heating	Refractive Index (25° C.)	Molecular Weight	After Heating	Refractive Index (25° C.)	Molecular Weight
Minutes			*Minutes*		
RUN 65—FREE FLAME			RUN 66—METAL BATH		
[a]	1.4807	793		1.4806	790
30	1.4828	892		1.4834	874
60	1.4855	1084		1.4859	990
75	1.4873	1288		1.4869	1123
90	1.4891	1439		1.4887	1277
105	1.4901	1592		1.4900	1382
120				1.4910	1622
125	1.4910				
135	1.4922	1895		1.4917	1719
144	Gelled				
150				1.4924	1910
165				Gelled	
RUN 67—CARBON DIOXIDE			RUN 68—AIR BLOWN THROUGH OIL		
Hours					
[a]	1.4806	780	[a]	1.4804	785
1.0	1.4820	918	15	1.4834	914
2	1.4845	1070	30	1.4850	1078
3	1.4867	1253	45	1.4875	1262
4	1.4882	1458	60	1.4895	1608
5	1.4894	1586	75	1.4906	2010
6	1.4900	1835	85	1.4916	Gelled
7	1.4878	1430			
7.5	Gelled				

[a] Time required to raise oil to 293° C.

In runs 69, 70, 71, and 72, 125 grams of monoglyceride were heated in a 500-cc. three-neck Pyrex flask. Dry nitrogen was passed over the surface of the oil at the rate of 1.27 liters per minute. The vapors escaping from the flask were passed through a tower of glass beads and two sets of calcium chloride tubes as previously described[4] in order to catch and weigh the water evolved at the time each sample was taken. Wash bottles containing an acetic acid solution of phenylhydrazine were inserted at the end of the train to observe liberation of acrolein. A small, steady evolution of acrolein was observed in runs 69, 71, and 72. In run 70, where the temperature was 293° C. instead of 250° C., decomposition was observed in the flask and the evolution of acrolein was very much greater—five times as great, judging from the volume of phenylhydrazone precipitate.

The oil was stirred at 200 r. p. m. Escape of vapors around the stirrer was prevented by fitting the stirrer with a 2-cm. mercury seal.

The calcium chloride was treated with hydrogen chloride gas to remove calcium oxide and the excess hydrogen chloride swept out with carbon dioxide. The air was dried before passing into the flask containing the glyceride by passing through two tubes of the same calcium chloride. In this way any error due to the vapor pressure of the calcium chloride system was eliminated.

In run 73, 125 grams of perilla oil were heated at 293° C. in the same apparatus with the same air rate.

The refractive index, molecular weight, iodine number, and hexabromide number (method of Bailey and Baldsiefen)[5] were determined on samples withdrawn at specified intervals. Results are given in Tables I to IV.

Table II—Linolenic Monoglyceride from Linseed Oil

After Heating	H_2O Evolved	Refractive Index (25° C.)	Molecular Weight	Iodine Number (Wijs, 30 Min.)	Hexabromide Number
Minutes	*Gram*				
		RUN 69—250° C.			
[a]		1.4882	712	211.7	28.5
15	0.4799	1.4914	767	193.8	22.7
35	0.2923	1.4930	819	190.6	17.3
65	0.2786	1.4994	1213	168.2	14.8
75	0.1620	1.5034	1379	153.1	3.3
84	0.1104	1.5056	1733	144.5	1.9
	1.3232				
		RUN 70—293° C.[b]			
[b]		1.4892	755	207.1	24.9
25	0.6303	1.5096	1668	146.7	
35	0.4507	1.5192	1694	83.0	
45	0.2780				
	1.3590				

[a] Time required to raise oil to temperature of run.
[b] Active decomposition observed; more acrolein evolved.

Table III—Linolenic Monoglyceride from Perilla Oil

After Heating	H_2O Evolved	Refractive Index (25° C.)	Molecular Weight	Iodine Number (Wijs, 30 Min.)	Hexabromide Number
Minutes	*Gram*				
		RUN 71—250° C.			
[a]		1.4888	745	210.1	28.72
15	0.5436	1.4916	853	208.8	26.27
35	0.2816	1.4939	992	204.5	17.2
65	0.2494	1.4996	1324	188.8	13.2
75	0.1590	1.5028	1510	178.0	6.24
84	0.1062	1.5047	1777	165.6	4.3
87	Gelled				
	1.3398				
		RUN 72—225° AND 250° C.			
[a]		1.4882	737	209.9	28.2
70	0.5305	1.4912	844	208.9	24.1
120	0.3526	1.4933	896	208.2	19.2
	0.3471	1.4949	971	206.2	15.6
180[b]	0.0967	1.4965	1083	196.4	9.8
210	0.1013	1.5015	1461	182.7	4.7
230	0.0967	1.5032	1692	171.5	2.6
240			Gelled		
246					
	1.5249				

[a] Time required to raise oil to temperature of run.
[b] Temperature maintained at 225° C. for 3 hours then raised to 250° C. in 5 minutes.

Table IV—Run 73, Perilla Oil at 293° C.[b]

After Heating	H_2O Evolved	Refractive Index	Molecular Weight	Iodine Number (Wijs, 30 Min.)
Hours	*Gram*			
[a]		1.4807	795	201.6
1.5	0.2366	1.4848	912	170.9
2.5	0.1087	1.4864	1138	144.3
3.5	0.1089	1.4887	1554	143.2
4.5	0.0940	1.4903	1871	141.4
5.5	0.0961		Gelled	
	0.6443			

[a] Time required to heat oil to 293° C.
[b] Not much acrolein evolved.

Table V—Blown Linseed Oil

After Blowing	Specific Gravity (15.5° C.)	Refractive Index (25° C.)	Molecular Weight	Iodine Number (Wijs, 30 Min.)	Hexabromide Number
Hours					
		RUN 74—138° C.			
1	0.9431	1.4819	860	166.9	21.9
2	0.9613	1.4824	967	156.4	18.7
3	0.9694	1.4846	1040	144.6	16.0
4	0.9747	1.4849	1185	138.6	13.7
5	0.9816	1.4857	1293	135.0	13.0
		RUN 75—121° C.			
0.5	0.9457	1.4794	844	170.7	
2.0	0.9588	1.4815	947		
3.5	0.9729	1.4838	1057	150.5	
5.0	0.9793	1.4848	1168	138.2	
6.5	0.9822	1.4866	1285	137.0	
8			1373		

Effect of Blowing—In runs 74 and 75, 1530 grams of linseed oil were heated by Bunsen flames in a vessel made from wrought-iron pipe 122 cm. long. A copper tube admitted through a hole in the top cap extended to the bottom, where it was bent into a ring of 3.92 cm. inside diameter provided with sixteen holes of 0.5-mm. diameter. The pipe was tapped and fitted with three cups for thermometers. Air saturated with moisture at 25° C. was blown through the oil at the rate of 6.5 liters per minute.

Samples were tested at regular intervals to determine

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[5] This Journal, 12, 1189 (1920).

the rate of change of specific gravity, refractive index, molecular weight, iodine number, and hexabromide number. Results are given in Table V for two blows, one at 138° C. and the other at 121° C.

More work is in progress to get data showing the effect of variation of humidity of the air stream, further effect of temperature, and the effect of traces of driers.

New Method of Making Films—In previous work with oil and varnish films the following difficulties had been encountered when using plates of amalgamated tinned iron:

1—Unless the plates were leveled with great care, thickened oils and varnishes thinned with solvents to insure proper flow and produce uniform films, flowed toward the low corner during drying, making one end of the film thicker than the other. Elaborate attempts to level the metal plates were only partially successful.

2—It was difficult to get films of the same thickness from different samples of brushing. Weighing the oil and covering a measured area of plate met with indifferent success with samples of varying specific gravity and viscosity.

3—That surface of the film next to the plate acquired the grain pattern of the plate, which, aside from imperfections, is sufficiently rough that the impression is appreciable compared with the usual film thickness of 0.1 mm. Brushing also often left marks and at times areas which were not comparable with the rest of the film.

These difficulties were practically eliminated by flowing the thickened oils and varnishes, thinned with solvents, on the surface of clean liquid mercury in shallow pans. Shallow pans 22 by 22 cm. and 1 cm. deep were built from heavy tinned iron, with the corners soldered. The pans were amalgamated by rubbing with mercury and then filled with enough mercury to cover the bottom completely to a depth of several millimeters. Glass trays were tried, but much of the oil collected in the groove around the edge caused by the meniscus, whereas with amalgamated pans this is absent.

Method. A weighed quantity of oil is thinned with 5 to 10 cc. of V. M. P. naphtha or other solvent, warmed and filtered through cheesecloth, and the beaker and filter washed with 30 cc. more naphtha. (Five grams of oil were used as a start, but change in specific gravity from 0.935 to 0.99 required correction of this weight to the extent of 6 per cent as a maximum.) The thinned oil is poured on the surface of the mercury in the shallow pans in the oven. Vibration of the mercury surface at critical times during the setting and drying of the oil produced wrinkled films. This vibration may be prevented by not opening the oven door for 8 hours after flowing the films, and locating the oven to avoid vibration from walking in the room.

If a number of pans are placed above one another in the same oven the pans should be separated by a distance of at least 2 to 3 cm.; otherwise, the solvent is liable to condense at the sides of the pans, giving thick portions at the sides and corners.

The practice in this laboratory is to allow the film to set in the air stream for 4 hours with the oven at 25° C., then raise the temperature to 65.5° C., and dry for 32 hours at 65.5° C. in an air stream carrying a relative humidity of 62.5 per cent.

Typical results from studies now in progress on the effects of various driers are given in Table VI. They indicate the limitations of accuracy of film data obtained by this method for various thicknesses of film.

Table VI—Linseed Oil Films with Driers

Thickness	Ultimate Tensile Strength	Elongation
Mm.	*Grams/sq. cm.*	*Per cent*
0.078	5130	20
0.071	4930	21.25
0.083	7350	20
0.072	7360	20
0.062	12900	27.5
0.065	15380	27.5
0.056	18930	27.5
0.051	19800	25.0
	MONOGLYCERIDE (NO DRIERS)	
0.121	4130	16.25

Discussion of Results

The number of possible reactions has been reduced and the case consequently simplified by studying the behavior of a single glyceride rather than a mixture.

At 293° C. decomposition of the synthesized linolenic monoglyceride is rapid and the expected products—acrolein, carbon dioxide, and water—have all been detected. At 225° C. the reactions coincident with thickening are taking place to only a small extent. The hexabromide number, however, decreases rapidly—after 180 minutes it had fallen from 28.2 to 15.6. The total unsaturation, which seems to be measured to a fairly complete extent in this substance, by the Wijs iodine number had, however, decreased only 3.7 points.

A decrease of 12.6 in hexabromide number is equivalent to 0.367 × 0.126 = 0.0462 gram of that linolenic acid which forms a solid hexabromide. If even only one of the ethylene linkages were saturated, the corresponding decrease in iodine absorption would be $0.0462 \times \frac{2 \times 126.93}{278.24} = 0.0422$ gram of iodine per gram of oil. The decrease in iodine number corresponds, however, to only 0.037 gram of iodine per gram of oil. The decrease in hexabromide number is therefore greater than the decrease in unsaturation. This indicates that the heating at 225° C. is causing a change to an isomer which does not form a solid hexabromide.

Further, the glyceride itself, as synthesized from a crystalline hexabromide, has an iodine number which indicates unsaturation agreeing closely with three ethylene linkages per molecule. The hexabromide number, however, is only 28.8, which corresponds to only 0.367 × 28.8 = 10.57 per cent of that linolenic acid which yields a solid hexabromide.

At 250° C. the isomeric change would be expected to be more rapid. However, the iodine number decreases rapidly and the molecular weight increases rapidly, indicating other changes which mask any isomeric change.

The monoglyceride solidifies to a gel in each case at a molecular weight between 1700 and 1800.

The linolenic monoglyceride synthesized from the crystalline hexabromide obtained from perilla oil is very similar to that synthesized by the same method from linseed oil, although a difference is observed in the iodine number of the products obtained after heating for 84 minutes. Since perilla oil has a much higher hexabromide number, it is a better starting point for the synthesis of glycerides of that linolenic acid which forms the crystalline hexabromide.

The behavior of linseed and perilla oils on heating and blowing is given for comparison. Perilla oil gives off less water up to the point of gelation than does the same weight of monoglyceride. This would be expected. The coincident molecular weight changes, however, indicate that in the early part of the run this water is formed by elimination of OH groups in the molecules rather than by condensations between molecules.

The hexabromide number decreases steadily and reaches a small value by the time the oil has changed completely to a gel. This required 84 minutes at 250° C. In the case of the natural oils, which required a much longer time, the hexabromide number had decreased to practically zero long before the oil as a whole had set to a gel. It is possible that tiny particles of gel have formed which are invisible in the remaining portion of the liquid oil and which gradually grow until the gel is the predominant phase. In natural oils the inactive or less reactive constituents of the oil will accumulate in this liquid phase. There is already good evidence that the gel is a di- or higher polymer. If the dipolymer is a solid, then coupling of molecules to form the solid phase produces bodies of higher molecular weight in a liquid which will have practically the same molecular weight as the original oil but which will be progressively depleted of its more reactive constituents. This liquid may finally be absorbed by the gel particles. Disappearance of the liquid gives the phenomenon of setting.

To test this theory of the final step in the setting of perilla or linseed oil to a product usually spoken of as a gel, linseed and perilla oils were heated until this gelation occurred. The resultant gels were extracted with acetone in Soxhlet extractors for 6 weeks. The extracted gels when thoroughly evacuated at 100° C. did not adsorb carbon dioxide at 20° or 100° C., but when dropped into acetone solutions of the liquid oil extracted from them by acetone, the gel took up the oil completely within the proportions contained by the original gel.

It is conceivable that no coupling occurs and that the change when glycerides are heated in an inert gas or exposed to radiations is simply a transformation to an isomer which happens to be a solid and which takes up oxygen and dries more readily than the isomers in the original oil. It may further be argued that the isomer which takes up oxygen most readily is the least receptive to halogen and that the decrease in iodine number can be explained on this basis. There are many features of the process not explained by this mechanism, however.

In run 74 both the hexabromide and iodine numbers decrease steadily. The total decrease in hexabromide number during this run corresponds to $0.089 \times 0.367 = 0.0326$ gram of that linolenic acid which forms a solid hexabromide. If two of the ethylene linkages in each molecule have been saturated or rendered inactive by isomeric change, the decrease in iodine absorption would amount to $0.0326 \times \frac{4 \times 126.93}{278.24} = 0.0594$ gram of iodine per gram of oil. The actual decrease observed amounts to 0.319 gram of iodine per gram of oil which is five times as great. This shows that in the blowing of oil at 138° C. the decrease in unsaturation cannot be ascribed merely to isomeric change. Further, the decrease in iodine number for a given molecular weight increase is much greater than the corresponding decrease for an equal molecular weight change in the case of linseed oil heated at 293° C.; also the curve for rate of molecular weight increase has a smaller slope than the corresponding curve when oil is heated. These data seem to indicate that when oil is heated at 293° C. coupling and condensation reactions are favored, whereas when blown at lower temperatures reactions occur which involve addition of oxygen with smaller molecular weight increase and greater reduction of the number of ethylene linkages.

Both in the runs with the single glyceride and those with natural oils, the decrease in iodine number corresponding to, say, a doubling of the molecular weight does not seem to bear any fixed ratio to the total. Thus, for a doubling of the molecular weight the decrease in iodine number is approximately 27 in both runs 71 and 72, but is 60 in run 69.

In run 70 at the higher temperature decomposition of the glyceride, with consequent small gain in molecular weight, was accompanied by a large decrease in iodine number.

When the linolenic monoglyceride is heated the weight of water evolved corresponds to 1 mol for each 2 mols of original glyceride. This suggests coupling of 2 molecules of monoglyceride with elimination of 1 molecule of water. The action does not seem to be so simple as this, for the water evolved in individual periods shows a sharp decrease from period to period in the case of this hydroxy body. It is suggestive that the weight of water evolved in run 73 is approximately the same in each hour period.

In runs 73 and 74 the curves showing rate of change in molecular weight indicate steady coupling of the molecules to form dipolymers. It would seem that part of the water evolved must come from two OH groups within a molecule and only part by condensations of two or more molecules.

Summary

Relatively pure linolenic glyceride was prepared from perilla and linseed oils.

When heated at 225° C. this glyceride seems to undergo an isomeric change. At 250° C. coupling and condensation reactions occur. At 293° C. this glyceride is rapidly decomposed.

Blowing favors reactions which decrease the unsaturation with relatively small attendant increase in molecular weight. Heating favors coupling and condensation reactions.

The use of liquid mercury surfaces in shallow pans of amalgamated tinned iron has many advantages in making oil films for study. The method is described.

Acknowledgment

The authors gratefully acknowledge the help of J. G. Smull, C. A. Knauss, D. V. Ransom, J. D. Ridsdale, and R. M. Roderick in obtaining these data.

Cereals and Rickets[1]

By Harry Steenbock, Archie Black, and Byron H. Thomas

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With calcium the fifth most abundant element in the earth's crust, it seems curious that animals should experience difficulty in finding a sufficiency of it for the construction and maintenance of normal skeleton. That such is the case is borne out by the general occurrence of rickets and of diseases comparable with rickets in man and in many domestic animals, such as pigs and chickens. Not only are the young seriously deformed, hampered in their growth and made susceptible to other diseases by this affliction, but adults show increased fragility of bone and poor tooth construction, and often experience abnormal reproduction.

It is now generally accepted that rickets and its analogs are caused by dietary deficiencies. These may consist of a deficiency of lime, a deficiency of phosphorus, a disproportionality between calcium and phosphorus, or a deficiency of vitamin D, a highly active compound owing its physiological properties to ultra-violet radiation.

It should be emphasized that the dietary requirements for calcium and phosphorus are not absolute. The amount required by an animal varies with the relative proportion of calcium to phosphorus and the presence of vitamin D. It is, indeed, highly probable that with suitable relation of calcium and phosphorus vitamin D may actually become well-nigh, if not entirely, dispensable.

There is no question but that one of the causes of rickets

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[1] Abstract of a paper presented at the 7th Midwest Regional Meeting of the American Chemical Society, Chicago, Ill., May 27 and 28, 1927.

in animals is the widespread deficiency of calcium and the less prevalent or only occasional deficiency of phosphorus in food materials. Under ordinary conditions none of our cereal grains, for example, contain a sufficiency of calcium for adult man when consumed as the sole article of food. Only a liberal consumption of milk, eggs, or vegetables corrects this difficulty. Polished rice, pearl barley, wheat farina, and patent wheat flour are notoriously deficient, and of these polished rice and patent flour are deficient in phosphorus as well.

That cereal grains and their starchy products will produce rickets is generally admitted, but the time has arrived when nutritionists are no longer content with pointing out the novelties of special edible materials, such as yeast, cod-liver oil, and orange juice. They are now concerning themselves with the determination of small marginal differences in the nutritive value of those materials which go to make up the major portion of the food of various peoples.

In 1925 Mellanby, of Sheffield, England, reported that of different cereal products—namely, barley, oatmeal, rice, white flour, wheat, and maize—oatmeal is the worst offender in the production of rickets in puppies, and white flour the least. To explain these findings, so at variance with the personal experience of the Scotchman and with what is to be expected from mineral analyses, Mellanby assumed that in oatmeal there is present a certain toxic factor which he speaks of as a toxamine.

At the time of the appearance of Mellanby's report experiments with rats carried out in the author's laboratory did not support Mellanby's contentions. Since then many hundreds of rats and eighty-three dogs have been used to study these relations in greater detail. With careful attention paid to litter mate controls, and food consumption—using general appearance of animals, growth, x-ray examination, chemical analysis of blood, ash analysis of bone, and histological examination of costochondral junctions as the criteria, it has been impossible to demonstrate that rolled oats is especially rickets-producing. In fact, rolled oats has shown itself to be on the average somewhat less rickets-producing than maize in both dog and rat experiments, but somewhat more so than wheat in the trials with rats. All the tests carried out with dogs, which are exceedingly susceptible to rickets, show that all cereals are so decidedly rickets-producing that a large number of trials with very carefully executed controls are necessary to demonstrate which is the worst.

In any case the defect of the cereals can be remedied by the judicious supplemental use of foods high in calcium—and also high in phosphorus in special instances—and by the treatment of the cereal with ultra-violet radiations. By the latter means vitamin D can be produced in abundance so that even without mineral additions a rachitic condition can be much improved.

Knowledge of these facts makes it possible to use cereal grains and their products for human and animal nutrition to the greatest advantage.

A Critical Analysis of Equations for the Design of Fractionating Columns[1,2]

By Loren H. Shirk and Ralph E. Montonna

School of Chemistry, University of Minnesota, Minneapolis, Minn.

The various proposed rectification equations have been subjected to critical analysis.

The method of McCabe and Thiele has been found to be the most practical and accurate for use in column design.

An apparatus has been designed to secure the data necessary for a comparison of the methods of calculation of the number of plates required for a given separation.

Data showing the over-all efficiency of a bubbler-cap plate column with alcohol-water mixtures under various conditions have been obtained.

A method of determining the percentage of alcohol in extremely dilute waste liquors has been devised.

The criticism of mathematical methods which assume continuous instead of stepwise conditions has been shown to be justified.

DURING the past five years the rapidly increasing literature in the field of chemical engineering has contained numerous articles dealing with the theory of fractionation and various equations have been developed by different investigators for the calculation of the theoretical number of plates or length of column required for a given separation. Most of these equations have been based upon a very limited amount of experimental data, and there is little evidence to show the engineer seeking to use them for the practical design of stills how well they actually represent the conditions of plant practice. Furthermore, the multiplicity of methods leaves the designer in doubt as to which one would give the best approximation of plant conditions and at the same time be the easiest and most rapid to apply to the desired problem. It seemed desirable, therefore, to secure experimental data on a scale approaching plant conditions and to apply the most promising equations to these data for the purpose of finding out which ones most nearly approximated the results and how close an agreement was to be expected for the particular system chosen.

The system water–ethyl alcohol was chosen for study, for several reasons. It is a common commercial mixture and data might be of practical use; results would be more comparable with those of other investigators, most of whom have worked with this system; reliable liquid-vapor equilibrium data[3] are available for the range covered by this investigation; and finally, simple, accurate, and reliable analytical methods are known. A suitable still was designed and the column constants for different ethyl alcohol–water mixtures were determined with varying and carefully controlled rates of distillation and reflux ratios. Using these constants, the theoretical number of plates required for the

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 72nd Meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926.

[2] Abstracted from a thesis submitted by Loren H. Shirk to the faculty of the Graduate School of the University of Minnesota in June, 1926, in partial fulfilment of the requirements for the degree of master of science in chemical engineering.

[3] This Journal, **12**, 496 (1920); **13**, 168 (1921).

separation of the various mixtures was calculated by each of the chosen methods. A comparison of the methods is thus secured on the same set of data both as regards ease of calculation and accuracy of prediction.

The basic equations upon which the theory of fractional distillation of binary mixtures is built have been derived by three different lines of reasoning, all leading to practically the same result. Sorel,[4] who did the pioneer work in this field, derived his equations from material balances. A second method which was essentially the same in theory and gave similar results, was that of Gay,[5] which was based entirely on heat balances. The latest procedure, which has a somewhat different foundation but gives the same type of equations, is Murphree's method[6] based on the gas absorption equations of Lewis and Whitman.[7]

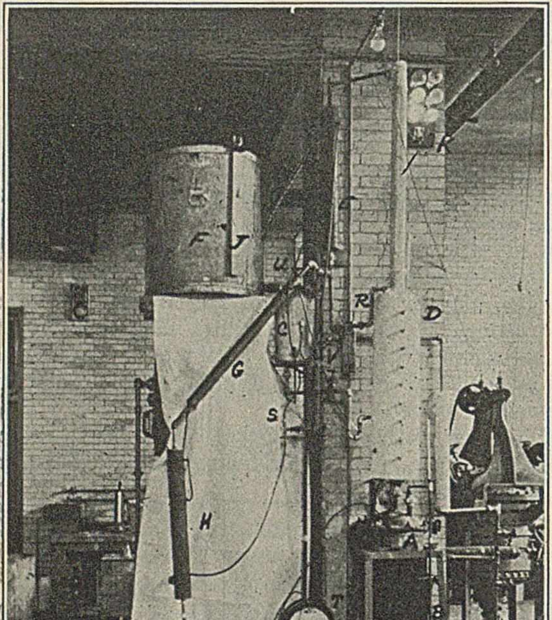

Figure 1—Apparatus for Comparison of Methods of Calculation of Number of Plates Required for a Given Separation

These fundamental equations have been applied to the calculation and design of fractionating columns in four different ways. These methods are (1) the algebraic stepwise procedure, which was used by Sorel,[4] Gay,[5] and Murphree,[6] (2) the graphical stepwise method, used by Rodebush,[8] McCabe and Thiele,[9] Murphree,[10] Ponchon,[11] and Savarit,[12] (3) the use of graphical integration as employed by Lewis[13] and Leslie;[14] and (4) Peters' method,[15] which consisted in combining the liquid-vapor equilibrium equation with the basic equations of distillation and mathematically integrating the combined equation so obtained. None of the methods representing the first class was applied to the data because, although mathematically exact, they are obviously too long and involved to warrant their use in engineering practice. The graphical methods of the second class appeared rapid and easy to apply and three of these were applied to the data—viz., those of Rodebush, McCabe and Thiele, and Murphree. Both representatives of the third class, the methods of Lewis and of Leslie, were used because of the variation in their method of integration, and finally Peters' method was tried as representing the fourth procedure.

The work of Van Nuys[16] consisted of a lengthy mathematical presentation of the principles of rectification, which serves excellently as a study of the factors involved but is unnecessarily complicated for practical use. The best experimental work has been that of Peters,[17] who used Lewis' method[13] of calculation, and that of Calingaert and Huggins[18] on packed columns using Peters' modification[15] of Lewis' formula. Peters does not give sufficient data to make his experimental work available for calculation by other methods, while that of Calingaert and Huggins applies only to packed columns. Clark S. Robinson[19] attempted a test of the efficiency of a plate column, but his results are less valuable except as a method of conducting tests, because he did not determine the percentage of alcohol in the waste liquor.

Apparatus

The apparatus (Figure 1) was especially designed with the view to securing the necessary data easily. It consisted of an iron pot still, *A*, heated by a paraffin bath over a gas plate, *I*, and carrying a nine-plate cast-aluminum column, *D*. The reflux condenser, *E*, was provided with a take-off to the product condenser, *G* and *H*, while the refluxed liquor returned to the top plate of the column through the trap, *R*, where it was measured by an orifice meter. The column and vapor pipes were lagged with one-inch magnesia covering and the latter was wound with a chromel-wire heating element as an additional precaution against condensation.

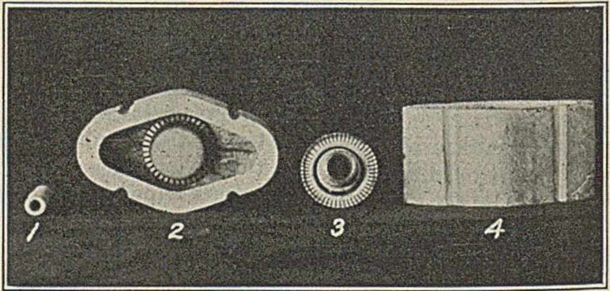

Figure 2—Details of Plates

The feed tank, *F*, was equipped with a float gage and level indicator, *J*, for determining the rate of feed flow, and delivered into a constant-head tank, *C*, where it was preheated to the boiling point by means of a steam coil. The heated feed passed through the regulator valve, *V*, into a trap leading into the third plate from the bottom of the column. A sight glass in the constant-level tank enabled the operator to keep the feed under constant head. The waste liquor was removed through the siphon, *B*, and flowed through a cooler condenser, *W*. A record of still temperature was kept by

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[4] *Compt. rend.*, **108**, 1128, 1204, 1317 (1889); **118**, 1213 (1894); see also "La Rectification de l'Alcool," Paris, 1893.

[5] *Chimie & industrie*, **3**, 157; **4**, 178, 735 (1920); **6**, 567 (1921); **10**, 811, 1026 (1923).

[6] This Journal, **17**, 747 (1925).

[7] *Ibid.*, **16**, 1215 (1924).

[8] *Ibid.*, **14**, 1036 (1922).

[9] *Ibid.*, **17**, 605 (1925).

[10] *Ibid.*, **17**, 960 (1925).

[11] *Tech. moderne*, **13**, 20, 55 (1921).

[12] *Chimie & industrie*, **9**, Special No., May, 1923, p. 737.

[13] This Journal, **14**, 492 (1922).

[14] "Motor Fuels," p. 70, Chemical Catalog Co., Inc., New York, 1923.

[15] This Journal, **15**, 402 (1923).

[16] *Chem. Met. Eng.*, **28**, 207, 255, 311, 359, 408 (1923).

[17] This Journal, **14**, 476 (1922).

[18] *Ibid.*, **16**, 585 (1924).

[19] *Ibid.*, **14**, 480 (1922).

the recording thermometer, *T*, and readings were periodically taken of the temperatures in the constant head tank, the top plate of the column, the top of the vapor line, and the waste liquor siphon to record operating conditions during the run.

Details of the plates are shown in Figure 2. They were of the bubble-cap type with slotted bell caps, one cap on each plate. Vapor pipes were one inch in diameter. An average depth of $1^5/_8$ inches of liquid was kept on each plate by the overflow tubes, which were $^1/_2$ inch in diameter. The caps averaged thirty-seven slots, $^1/_{16}$ inch wide and $^1/_4$ inch long. There were $1^1/_8$ inches of liquid over the top of the slots. The plates were 9 by 5 inches by $4^1/_2$ inches high outside and were $^7/_{16}$ inch thick.

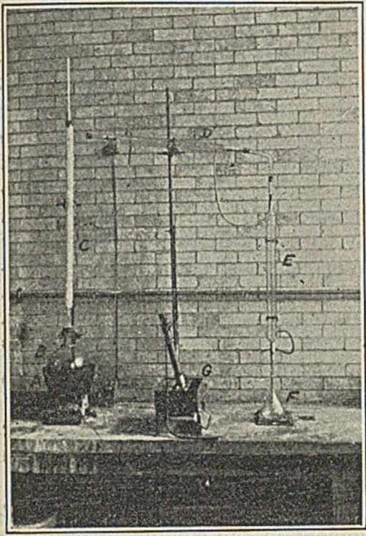


Figure 3—Apparatus for Accurate Analysis of Extremely Dilute Waste Liquors

Operation of Still

The still was run for about 3 hours before any readings were taken to insure the establishment of uniform conditions. Data were then collected over a period of 2 hours. All runs used in the calculations were made in duplicate. The feed was regulated by setting the valve *V* and the waste liquor by the siphon valve, *B*, so that input and output (product plus waste liquor) were approximately equal. The regulation of the flow of waste liquor by means of a siphon was difficult, so that there was some accumulation in the still. Also, the float gage and level indicator, *J*, did not prove a very satisfactory way of measuring rate of feed input. A material balance between the measured and calculated quantities of feed, waste, and product showed, however, that the actual output of the still was within less than one per cent of the liquor fed. Better methods of measuring feed and waste liquor flow will be devised for further work with this apparatus. The rate of distillation was controlled by the rate of heating with the gas burner, *I*. The reflux condenser was entirely separate from the product condensers to allow of more accurate control. The rate of reflux was kept constant by controlling the flow of cooling water with the valve *S* so that the differential reading across the flowmeter gage, *R*, remained constant. The flowmeter was calibrated after each run to determine the flow at that reading of the gage. The chromel heating unit was regulated by means of the lamp-bank resistance, *K*, to keep the temperature of the vapor pipe slightly above that of the top plate. The feed was kept constant by setting the valve *V* so that the desired rate of feed was obtained and maintaining a constant level in the sight glass of the tank *C* by regulating the flow through the valve *V* from the feed storage, *F*. At the end of the run the distillate and waste liquors were analyzed.

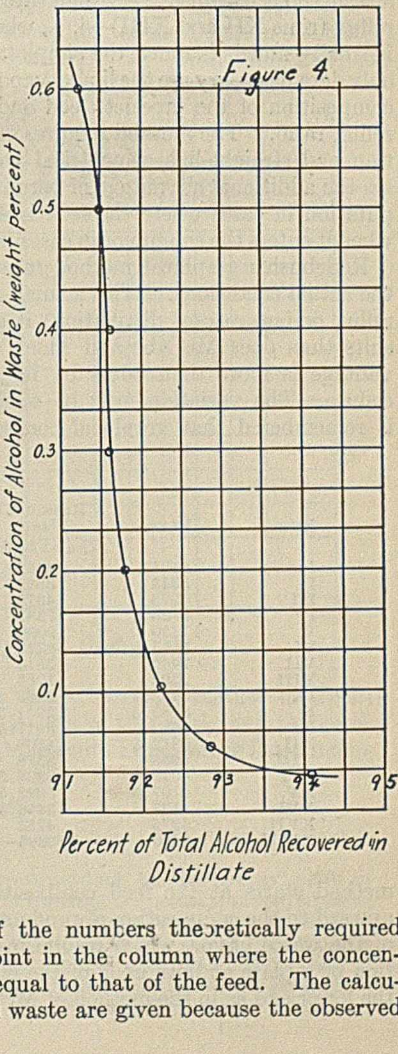
Analytical Methods

The alcohol used in the runs was c. p. 95 per cent ethyl alcohol. All percentages down to 0.5 per cent were determined directly by means of the Zeiss immersion refractometer. Below 0.5 per cent accurate analysis was impossible and a method had to be devised to analyze the extremely dilute waste liquors with accuracy. The apparatus (Figure 3) consisted of a 5-liter flask, *B*, heated by an oil bath, *A*, and carrying a 30-inch (76-cm.) modified Hempel column, $1^1/_4$ inches (3.2 cm.) in diameter, filled with pieces of glass tubing $^1/_4$ inch (6 mm.) long. The column delivered through two 24-inch (61-cm.) Liebig condensers into a graduated flask.

Four liters of the liquid to be analyzed were placed in the flask and 500 cc. distilled off. The heat was regulated so that this distillation required 90 minutes. The alcohol in the distillate was determined by the refractometer and reference to the calibration curve (Figure 4) showed what percentage of that present in the original waste liquor this amount represented. The calibration curve was secured by accurately weighing out varying concentrations between the limits of 0.6 and 0.02 per cent alcohol. Three or four determinations were made at each concentration and the percentage recovery was averaged. The results were plotted (Figure 4) and gave a smooth curve showing the percentage recovery to be expected by distilling over a 500-cc. portion. The method was checked by analyzing unknown solutions and gave a variation of less than one per cent. Below the limit of 0.02 per cent the concentration of alcohol in the distilled sample was too low for accurate determination with the refractometer, but the waste liquor in these experiments was always above that figure. The use of this method eliminated a criticism of the work of other investigators where this value was only roughly estimated or not determined at all.

Discussion of Results

The observed data are recorded in Table I and the results of the calculations in Table II. The column efficiency (Table II) is the total number of theoretical plates calculated by McCabe and Thiele's method divided by the actual number of plates used and expressed as per cent. This represents the over-all efficiency of the column and, although accurate as a criterion of the different methods of calculation, it unfortunately throws no light on the possible variation in plate efficiency throughout the column. Since no determination of the actual feed-plate concentration was made in most of the experiments, the calculated number of plates represents the sum of the numbers theoretically required above and below a point in the column where the concentration of liquid was equal to that of the feed. The calculated rates of feed and waste are given because the observed



rates, owing to accumulation in the still, are not directly applicable and the calculated rates have been found to check the actual feed and waste within less than one per cent.

The results of calculating over-all column efficiencies by five different methods are summarized in Table III. Those experiments were chosen for calculation which were conducted under widely varying conditions of reflux and rate of distillation and on which most reliable data were available. Table III reveals at once that the graphical methods give results which more nearly approximate the actual conditions than do the mathematical methods.

Table I—Observed Data

Run	Removal of Product	Proportion of Alcohol by Weight			Ratio Reflux to Product	Temperature	
		Feed	Product	Waste		Top of column	Still
	Grams per hour	%	%	%		°C.	°C.
I	1733	25.00	73.00	6.360	1.32	80.5	87.5
II	1686	26.64	75.00	4.180	1.20	80.5	91.5
III	1609	21.42	73.00	3.470	1.41	79.8	94.0
IV	2348	18.83	67.00	3.530	1.49	81.0	94.5
V	2240	17.50	76.00	3.100	1.54	79.0	96.0
VI	1237	17.75	75.50	1.250	3.02	79.0	99.0
VII	1647	12.95	58.50	0.047	0.87	82.5	100.0
VIII	430	12.95	72.00	0.050	1.66	81.5	100.0
IX	809.5	17.21	74.00	0.100	2.71	91.0	99.5
X	831	14.75	67.00	0.036	2.03	91.5	100.0
XI	1095	16.20	68.17	0.035	3.82	92.0	99.8
XII	1504.5	19.22	73.25	2.350	2.13	81.0	100.0
XIII	1107	16.23	72.75	0.080	1.98	91.0	99.8
XIV	694	14.88	86.00	0.054	4.60	79.8	99.8
XV	1015	14.36	86.00	0.100	4.60	87.7	100.5
XVI	711	14.85	86.00	0.055	4.60	80.0	100.0
XVII	1493	19.22	73.20	2.400	2.13	81.0	100.0
XVIII	824	17.21	73.25	0.100	2.71	90.7	99.8

Of all the methods thus far advanced, the graphical method of McCabe and Thiele has been found to be the best adapted to practical use. It is equally accurate as the other graphical methods except at very high rates of distillation and low reflux (runs XII and XIII)—i. e., where the number of plates is small—and it is much the simplest and most rapid. The only data necessary are the liquid-vapor equilibrium curve, the composition of the product, feed and waste liquor, and the reflux ratio. The method requires only one simple substitution and straight-line geometrical construction. It possesses the additional advantage of permitting correction in computation in cases where the feed is not at the boiling point when it enters the column or in cases where two feeds are used.

Rodebush's graphical method most closely approximated the actual conditions. With a small number of plates (small reflux or fast rate of distillation) it gives slightly better results than does McCabe and Thiele's method, but this advantage is more than offset by its more complicated procedure. The variation may be easily understood when it is remembered that graphical computation by Rodebush's method starts at the feed composition and proceeds both upward to the composition of product and downward to that of the waste liquor, which results in overlapping by a fraction of a plate at both ends of the curve, instead of only at the lower end as in the method of McCabe and Thiele. This overlapping may result in one plate more in the column total, which means a noticeable percentage difference if the number of plates is small. Rodebush's method requires the same data as that of McCabe and Thiele, but more mathematical transformations must be made and the geometrical construction is more difficult so that it is more time-consuming. In general, however, graphical methods are preferable to mathematical methods, both for accuracy and for ease of use.

Table II—Calculated Data

Run	Feed	Removal of Waste	Vapor up Column	Mol Fraction Alcohol in:			Molal Ratio Feed to Unit Product	Theoretical Minimum Reflux Ratio	Column Efficiency (*K*)
				Feed	Product	Waste			
		Grams per hour							%
I	6195	4462	4025	0.1158	0.515	0.02480	5.39	0.067	30
II	5315	3619	3712	0.1250	0.542	0.01640	4.84	0.133	30
III	6225	4616	3880	0.0965	0.515	0.01380	6.05	0.151	30
IV	9735	7387	5850	0.0834	0.443	0.01420	6.18	0.0034	30
V	11330	9090	5695	0.0768	0.555	0.01220	8.41	0.345	40
VI	5565	4328	4970	0.0780	0.548	0.00500	7.44	0.318	40
VII	7460	5813	3080	0.0530	0.355	0.00018	6.75	0.000	80
VIII	2395	1965	1145	0.0530	0.502	0.00020	9.54	0.349	90
IX	3497.5	2688	3005	0.0744	0.529	0.00039	7.15	0.287	60
X	3782.5	2951.5	2518	0.0620	0.443	0.00014	7.16	0.104	70
XI	4612.5	3517.5	5280	0.0700	0.456	0.00014	6.43	0.100	70
XII	6312.5	4808	4710	0.0850	0.518	0.00940	5.95	0.191	30
XIII	4985	3878	3300	0.0710	0.512	0.00031	7.25	0.245	50
XIV	4022.5	3328.5	3890	0.0640	0.706	0.00020	11.54	0.876	90
XV	6107.5	5092.5	5690	0.0613	0.706	0.00039	11.60	0.896	80
XVI	4127.5	3416.5	3980	0.0640	0.704	0.00020	11.10	0.868	90
XVII	6275	4782	4675	0.0850	0.518	0.00950	5.95	0.195	30
XVIII	3520	2696	3058	0.0744	0.526	0.00039	7.15	0.267	60

The two previous methods are developed from the equations of W. K. Lewis. The method of Murphree differs in that its basis is the gas absorption equations. The mathematical method was not applied, but the graphical solution was found to check exactly with the method of McCabe and Thiele. However, it involved a needless tabulation of values for a result that can be obtained by a much less complicated procedure by the other method. It is extremely useful for calculations when two or three volatile components are distilled, but is needlessly complicated for use with binary mixtures. The fact that mathematical development upon an entirely different basis leads to the same results, however, increases the confidence in the correctness of the assumptions upon which the theory of fractionation is founded.

Lewis' mathematical method of calculation assumes an infinitesimal rate of enrichment in the column instead of a stepwise process such as is assumed in the above graphical methods. That Lewis recognized this assumption as an approximation is shown by his use of the words "substantially identical"[20] in deriving his differential equation. For this reason the method gives low values of *K* (runs VI and VII) when a small number of plates are used—i. e., high rate of distillation or low reflux. This substantiates the criticism of McCabe and Thiele[9] that "the larger the number of plates, the more accurate is this (Lewis) method, but for columns of but a few plates the error introduced by assuming continuous for stepwise conditions is appreciable." Lewis' method has been used extensively and his equations serve as a basis for several other methods of calculation. It is very much simpler than Sorel's method, but requires considerable time to apply so that it is not recommended over the graphical methods discussed above.

The equations derived by E. H. Leslie, using a stepwise balance of heat and material and adopting weight instead of mol fraction basis, are rather more lengthy than Lewis' method but give results more nearly like the graphical methods. This is probably due to the stepwise method of plotting the enrichment curve for graphical integration. Leslie's method of plotting, however, required more time to apply to a given set of conditions than any of the other methods, and the results expressed as fractions of a plate are not more useful than the whole number of plates given by the graphical methods, since practical use requires the addition of one more

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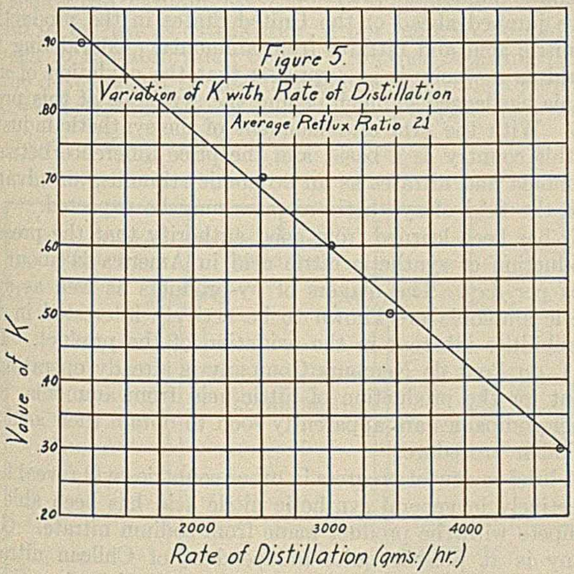
[20] This Journal, **14**, 494 (1922).

whole plate. The nomenclature employed is extremely simple and this method might be used to check the graphical results when extreme accuracy is desired. In ordinary practice, however, the time required for its use is not justified by its final accuracy.

Table III—Over-All Column Efficiencies by Five Methods

Run	Withdrawal of Product	Vapor up Column	Reflux Ratio	Column Efficiency McCabe and Thiele	Lewis	Leslie	Rodebush	Murphree
	Grams per hour			%	%	%	%	%
VI	1237	4970	3.02	40	10.76	30.61	40	40
IX	809.5	3005	2.71	60	27.86	54.43	60	60
XI	1095	5280	3.82	70	22.20	65.37	70	70
XII	1504.5	4710	2.13	30	8.32	21.14	40	30
XIII	1107	3300	1.98	50	31.40	44.10	60	50
XIV	694	3890	4.60	90	75.50	90.06	90	90

The equations derived by Peters[15] from the Clausius-Clapeyron equation contain a number of errors which yield expressions incapable of solution when the required values are substituted. His derivations have been carefully followed and corrections made where errors were found. The corrected equations give values which check those obtained by the use of Leslie's method very closely for the number of plates in the rectifying column. For the exhausting column, however, even when the necessary corrections are made, the equations give an absurd result or in some cases an expression incapable of solution. This probably means that the fundamental assumptions upon which they are based are wrong. However, no attempt was made to check the derivation of these equations as the method presents no appreciable simplification of calculations over other purely mathematical procedures. Its greatest value would lie in its application to systems in which vapor pressure data were lacking but thermal data were available.



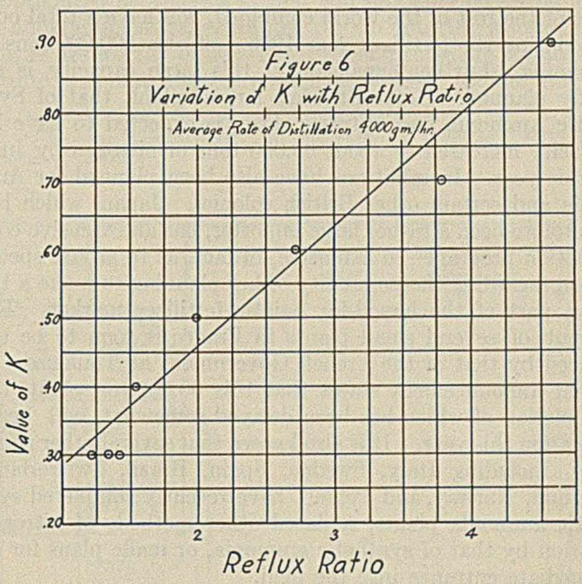
The use of ethyl alcohol and water gives values for plate column efficiencies which (Table II) vary from 30 per cent when the rate of distillation is high and the reflux is low to 90 per cent with a low rate of distillation and higher reflux. The effect of variation of rate of distillation, reflux ratio, and composition of feed on column efficiency can be studied from these experiments. However, the primary purpose of this investigation was the comparison of the various theoretical equations under widely varying conditions. For this reason no definite conclusions can be drawn concerning the effect of the above variables on column efficiencies because all of them were varied simultaneously. A further study of these variables under carefully controlled conditions will be made by one of us.

The values of K for five experiments with approximately similar reflux ratios were plotted as ordinates versus the rate of distillation as abscissas (Figure 5). The resulting curve indicates that the value of K varies inversely as some function of the rate of distillation, as would be expected since a more rapid rate of distillation gives less time for approach to the condition of true liquid-vapor equilibrium on the plates such as is assumed by the theory. The values of K for eight experiments having approximately equal rates of distillation were plotted as ordinates versus reflux ratios as abscissas (Figure 6). This curve indicates that the efficiency varies directly with the reflux ratio, as would be expected since a greater amount of reflux per unit product allows greater contact of liquid and vapor phases giving more efficient rectification.

Both of these findings indicate an agreement with the conclusions of Calingaert and Huggins[18] from their study of packed columns. However, these conclusions have recently been questioned in a paper by Leslie and Geniesse[21] which has appeared since this investigation was completed. Definite conclusions between these two points of view should not be drawn from the experimental data presented here because of the simultaneous variation of several conditions. The authors present this inconclusive evidence to indicate that this is an open question which can only be settled by further experimental investigation. One of them proposes to carry on an investigation of these points in this laboratory.

Acknowledgment

The authors wish to express their gratitude to Charles A. Mann and George H. Montillon, of the Division of Chemical Engineering of the University of Minnesota, and to W. H. McAdams, of the Massachusetts Institute of Technology, for advice and criticism of this work, and to Lester L. Johnson, fellow of the Minnesota Engineering Experiment Station, for aid.



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[21] This Journal, 18, 590 (1926).

Cement to Resist Acid—According to the Department of Commerce, a British firm is utilizing a specially prepared hard pitch to produce an acid-resisting plastic cement for use in constructing chimneys, sewer pipes, culverts, storage tanks, etc. The process is patented in the United States and the erection of a factory is contemplated. Literature descriptive of "Prodorite" will be loaned on request to the Chemical Division.

Outlets for Ammonia—Present and Prospective[1]

By V. N. Morris

Fixed Nitrogen Research Laboratory, Bureau of Soils, Washington, D. C.

LESS than six years ago the first successful synthetic ammonia plant in America started operation. Since then our progress along the line of nitrogen fixation has been commendable. At the end of 1926 eight plants in the United States were either producing or were ready to produce synthetic ammonia. Notwithstanding the possibility of supply surpassing demand, expansion and construction are continuing without sign of abatement. The Allied Chemical and Dye Corporation, for instance, has recently announced plans for a large plant to be erected at Hopewell, Va. It is understood that the output of this plant will go into fertilizers. It is also believed that a considerable expansion of the Lazote plant at Belle, W. Va., is soon to be undertaken. It is known that part of the output of this plant will eventually be marketed in the form of fertilizers. The recent investigation of American conditions by German interests has made apparent another possible addition to the list of manufacturers of synthetic ammonia in this country. It is also worthy of mention that the plants of the Commercial Solvents Corporation and of the Great Western Electrochemical Company were scheduled to be completed and to start operation about the first of the present year.

In other countries the developments have been just as noteworthy as in the United States. According to the director of the Stickstoff-Syndikat,[2] Germany, whose present production of synthetic nitrogen compounds is much greater than that of the rest of the world combined, will have a total output during the fertilizer year 1926–7 of over 500,000 tons of ammonia. Further expansion of this large capacity is already planned. Great Britain's largest plant, that of Synthetic Ammonia and Nitrates, Ltd., is expected to have its capacity increased to about 65,000 tons of nitrogen by June of this year. Installations have also been planned for Australia and certain other British colonies. Japan, which has heretofore been a rather large importer, has an extensive construction program—so extensive, in fact, as to arouse speculation regarding the possibility of her planning to make a bid for a part of the hoped-for Asiatic fertilizer market. The output of several small plants in France is soon to be enhanced by that of the French Government at Toulouse. A recent announcement states that this 60,000-ton plant, the completion of which has been delayed somewhat, will begin operation this year. It is also known that several other countries, including Italy, Sweden, Spain, Brazil, Switzerland, Belgium, Norway, and Poland, have recently completed synthetic ammonia plants, replaced other methods of nitrogen fixation by that of synthetic ammonia, or made plans for an immediate entrance into the field.

What disposition is to be made of this rapidly increasing output of ammonia? No single statement can answer this question in full. The solution of the problem depends chiefly, however, on the development of new outlets for ammonia—new not only in the sense of the development of products differing from those into which it has heretofore been converted, but new also from the point of view of the fields of utilization of all such products, whether new or old. This last mentioned extension must depend to a considerable extent upon a campaign of education. In the discussion which follows, stress is laid upon these newer outlets, faith in which is largely the basis for the rapid expansion of the synthetic ammonia industry. The discussion should not be considered as being limited to synthetic ammonia. The fact remains, however, that the synthetic product has not only cut into the market for by-product ammonia and brought about a steady decline in the production of Chilean nitrate, but is even beginning to replace the arc process of nitrogen fixation, which has been in operation for so many years in Norway.

The accompanying chart gives a picture of the various outlets for ammonia. It shows certain potential ones as well as those actually developed. It should be borne in mind that nearly all the salts shown can, if marketed in a suitable physical condition, be used as fertilizers. The various uses of a given compound are not shown except in cases where omitting them would give the impression that the compound served only as an intermediate for the production of some other substance. Fertilizer mixtures containing two nitrogenous salts are also shown. The chart indicates the ingredients of the various mixtures. Such mixtures as are commonly marketed under given trade names are indicated by their trade names.

Oxidation to Nitric Acid

Outstanding among the prospective developments, particularly from the American point of view, is that of the oxidation of ammonia. Germany and other European countries have jumped ahead of the United States in the production of nitric acid and nitrates from ammonia. Considering the world as a whole, it is surprising that the oxidation of ammonia has lagged so much behind the synthesis of this product. With the firm establishment of the synthetic industry in this country as a basis, and the price difference between ammonia and nitrates as an economic stimulus, an advance into the field of synthetic nitrates may be expected.

It has been learned from good authority that the present production of synthetic nitric acid in America is about 25 tons per day. The makers of by-products as well as synthetic ammonia are known to be actively interested in the possibilities inherent in the oxidation of the product. The E. I. du Pont de Nemours Company is already operating a plant for the production of nitric acid from ammonia, and other companies are apparently soon to obtain their acid by a similar procedure.

A brief review of progress in other countries will reveal how effectively in general synthetic nitric acid has been able to compete with the product made from sodium nitrate. Germany is at present quite independent of Chilean nitrate. Her exports attest to the fact that the production of synthetic nitrates is a firmly established industry. In Great Britain the output of the United Alkali Company's ammonia plant is being oxidized to nitric acid, and some of the larger gas companies are reported to be interested in the possibility of obtaining a profitable outlet for their ammonia via the oxidation route. The recent Swedish plans call for the production of 1500 tons of concentrated nitric acid per year, with a possible maximum of 6000 tons. Italy and France are also known to have oxidation installations in operation. The plans of Russia, Poland, and Czechoslovakia are stated to call for at least a partial oxidation of the output of their synthetic ammonia plants. The outlook for Chilean nitrate

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[1] Received March 23, 1927.

[2] Bueb, *Chem. Age (London)*, **14**, 494 (1926).

in the nitric acid industry of Europe is certainly not very bright.

Improvements in the technology of manufacture cannot fail to have a beneficial influence on the output of synthetic nitric acid and nitrates. Among the possible improvements which may be expected are those which would result from absorption in a refrigerated system, catalysis of the re-oxidation of the nitric oxide liberated during absorption, operation under pressure, and oxidation with oxygen or oxygen-enriched air.

Since a large part of the cost of the installation of an ammonia oxidation plant can be charged to the absorption towers, any process tending to lessen the tower requirements is much to be desired. In the towers part of the nitrogen tetroxide absorbed is released again as nitric oxide. The slow re-oxidation of this nitric oxide is generally stated to determine the rate of absorption in the ordinary systems. The effective catalysis of this reaction, the possibilities of which are now being investigated in this laboratory, would obviously result in a considerable saving. It has long been known that good absorption and rapid oxidation result from the use of lower temperatures. It is claimed that sufficient cooling will do away with the necessity of absorbing the end gases in a soda solution. The advantages to be expected from such a process have recently been discussed by Toniolo.[3]

Increasing the oxygen content of the air mixed with ammonia is another process having promising possibilities for certain cases. Although it appears that absorption should be benefited by such a modification, since dilution by nitrogen adds to the difficulty of the absorption of the oxides, the fact remains that the air has not been enriched at certain plants where oxygen is readily available. A decided disadvantage resulting from the use of a mixture containing a higher percentage of oxygen arises from the detrimental effect of excess oxygen on the platinum catalyst. In such plants it has been found to be just as satisfactory, if not more so, to add the oxygen to the absorption towers. Another deterring factor in the development in this direction has been the knowledge that explosive mixtures of ammonia and oxygen may easily be obtained. According to the claims of patents recently granted to Cederburg,[4] means of avoiding this explosibility have been discovered. By making use of oxygen in place of air, it is possible to obtain nitrogen oxides in a more concentrated form. Since the possibility of having available much cheaper oxygen in the future does not appear at all remote, much may be expected of such a process.

Of the possible ways of disposing of ammonia via the nitrogen oxides, that having to do with the chamber process of sulfuric acid manufacture appears at present to be the most important. The fact that the sulfuric acid industry is capable of providing an all-year market for nitrogen oxides should be an added incentive towards ammonia oxidation, since the demand for ammonia as such is somewhat seasonal. Work along this line is being actively promoted in the United States at the present time, and a number of installations are already in successful operation. In Europe this practice is now almost universal.

Outlets for Nitric Acid and Nitrates

The explosive and fertilizer industries are the largest consumers of nitric acid and nitrates. Barring an unforeseen national emergency, no very rapid expansion of the explosive industry is anticipated. As soon as production and economic conditions permit, however, we may expect American synthetic nitrates to enter the fertilizer market. It seems, in fact, that any further considerable expansion of the atmospheric nitrogen industry in this country must inevitably lead to a fertilizer outlet. Since "nitrate" nitrogen is more readily available than other forms of nitrogen, a certain minimum of this form is desirable for mixed fertilizers. Curtis[5] has recently discussed the problem from this point of view.

Although the major portion of the synthetic fertilizers to be produced in America at first will probably be in the form of ammonium salts, there are certain nitrates whose possibilities are worthy of mention. Among these are ammonium nitrate, calcium nitrate, potassium nitrate, sodium nitrate,

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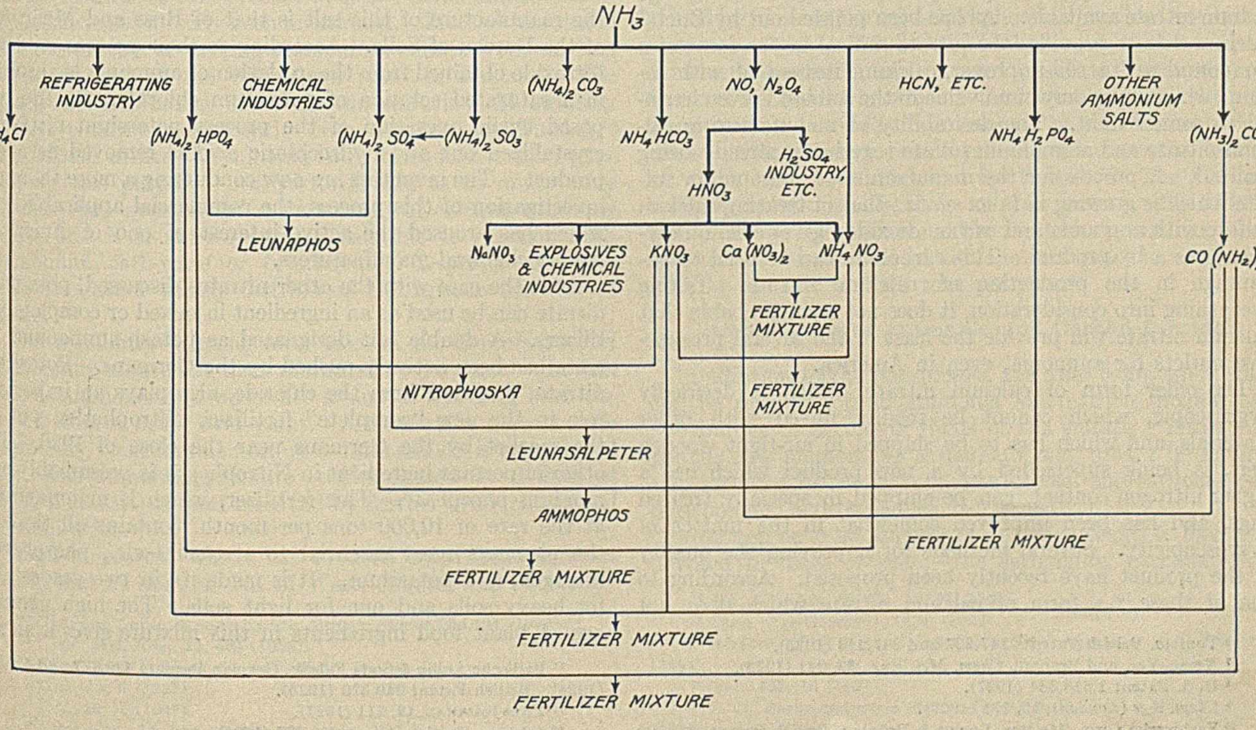
[3] *Chem. Met. Eng.*, **34**, 92 (1927).

[4] British Patents 244,134 and 246,889 (1926).

[5] "Mineral Raw Materials for the Fertilizer Industry," Natl. Fert. Assocn., p. 45 (1926).



THE OUTLETS FOR AMMONIA

and various mixtures containing one or more of these compounds as ingredients.

Ammonium Nitrate

Ammonium nitrate, with its high content in both ammonia and "nitrate" nitrogen, would be a highly prized fertilizer were it not for its explosibility and hygroscopicity. It was one of the first synthetic fertilizers put out by the Germans and has been on the market for several years, usually in the form of mixtures with other salts such as ammonium sulfate, potassium chloride and nitrate, calcium sulfate, and calcium nitrate. A method for producing a fine-grained crystalline form of ammonium nitrate has recently been developed in Europe. In this process the hot liquors, containing 90 to 95 per cent of ammonium nitrate, are run into a sort of dough-mixer, in which a blast of cold air is passed continuously over the crystallizing mass. According to another proposal,[6] the heat of reaction of ammonia and nitric acid is utilized for the evaporation of at least a portion of the water present. Considerable work has been done both in this country and abroad on the graining and coating of ammonium nitrate.[7] Symmes[8] has recently patented a process for obtaining a granular product by spraying into a gaseous cooling medium. That interest in ammonium nitrate is not confined to the United States and Germany is manifested by recent reports from Italy, England, Norway, and Sweden. The plans of Sweden call for the production of 3000 tons annually, whereas the Norwegians are reported[9] to be ready to begin the manufacture of this salt from synthetic ammonia.

Calcium Nitrate

Although the high hygroscopicity of calcium nitrate makes its use less attractive to American than to European farmers, this salt has been placed on the American market by German interests. Germany has within the last year or two taken the lead away from the Scandinavian countries in the production of calcium nitrate for agricultural purposes. Necessity has led to a technology in manufacture which has provided a product as acceptable in many respects as is the average sodium nitrate available. As has been pointed out by Bueb,[2] calcium nitrate provides the nitrate radical in the form of a compound with a soil-improver, calcium, instead of with sodium, which is not only of no value in the soil but is even harmful to some extent. The desirability of manufacturing calcium nitrate and ammonium sulfate together is already being realized. A process for the manufacture of ammonium sulfate which is growing in favor —viz., that of treating calcium sulfate with ammonia and carbon dioxide—gives calcium carbonate as a by-product. This carbonate can be used to advantage in the production of calcium nitrate. Taking everything into consideration, it does not seem probable that calcium nitrate will provide the least of the several prospective outlets for ammonia, even in America.

The older form of calcium nitrate, which is decidedly hygroscopic, which cannot be readily mixed with other materials, and which has to be shipped in air-tight wooden kegs, is being superseded by a new product which has a higher nitrogen content, can be shipped in specially treated bags, and has been improved somewhat in the matter of hygroscopicity. Several methods for improving the quality of the product have recently been proposed. According to one of these,[10] a form of calcium nitrate which does not readily become moist may be obtained by the intimate mixing of a small proportion of the hydrate of calcium nitrate with the product resulting from the almost complete dehydration of a solution of the salt. In another proposed manufacturing improvement the highly concentrated solution is brought in contact with rollers heated to 250° C., the solid salt being removed by scrapers. Another process[11] for which advantages are claimed is that of adding a small percentage of ammonium nitrate to the saturated solution of the calcium salt. Crystallization is stated to occur much more readily after such an addition. Spraying the concentrated solution through a nozzle is one method proposed for obtaining a granular product and one having improved properties. It has been claimed that certain of these new forms of calcium nitrate are less hygroscopic than the ordinary product. This claim has recently been disputed by Ross, Mehring, and Merz.[12] These authors do point out that the recent German product has a greater capacity for moisture since it is marketed in a form having only about two molecules of hydrated water.

Mixtures of calcium nitrate with other substances have been proposed as fertilizers. The mixture of this salt with urea in varying proportions has been the subject of a recent patent.[13] Other possibilities include mixtures of calcium nitrate with certain of the calcium phosphates. This laboratory now has under investigation a process in which the nitric oxides from ammonia oxidation are absorbed in a suspension of phosphate rock, the initial products desired being monocalcium phosphate and calcium nitrate. No decision regarding the possibility of making industrial application of this process can be made until certain additional phases of the problem have been investigated.

Potassium Nitrate

The conversion of ammonia to potassium nitrate offers still another means of disposing of the former substance. Since potassium nitrate possesses very satisfactory physical properties and contains two of the major nutrient elements desired for fertilizers, the problem of its utilization in agriculture is largely an economic one. The most recent American contribution to the development of a satisfactory method for the manufacture of this salt is that of Ross and Mehring,[14] of the Bureau of Soils. According to their process, nitrogen tetroxide obtained from the oxidation of ammonia is absorbed in a saturated solution of potassium chloride. In the proposed cyclic operation of the process potassium nitrate is crystallized out and hydrochloric acid is removed as a by-product. The inventors are now conducting a more thorough investigation of this process, the commercial applicability of which has aroused the active interest of one of America's largest chemical manufacturers.

As is the case with the other nitrates discussed, potassium nitrate can be used as an ingredient in mixed or complete fertilizers. A double salt designated as potash-ammonium nitrate has been actively pushed by the Germans. Potassium nitrate, prepared from the chloride, also plays an important role in the new "complete" fertilizer, Nitrophoska, put on the market by the Germans near the close of 1926. The other important ingredient in Nitrophoska is presumably ammonium phosphate. This fertilizer, which is manufactured at the rate of 10,000 tons per month, contains all three of the elements most essential to the soil—viz., phosphorus, nitrogen, and potassium. It is made up in two grades, one for heavy soils and one for light soils. The high percentage of plant food ingredients in this mixture gives it an ad-

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[6] Toniolo, British Patents 247,227 and 247,228 (1925).

[7] Krase, Yee, and Braham, *Chem. Met. Eng.*, **32**, 241 (1925).

[8] U. S. Patent 1,613,334 (1927).

[9] *Chem. Age* (*London*), **16**, 171 (1927).

[10] Farbwerke vorm. Meister, Lucius & Brüning, British Patent 242,990 (1924).

[11] Badische Anilin & Soda Fabrik, German Patents 429,477 and 429,478 (1924); British Patent 249,370 (1925).

[12] THIS JOURNAL, **19**, 211 (1927).

[13] Johnson, British Patent 246,377 (1925).

[14] U. S. Patent 1,604,660 (1926).

vantage over many others. According to another proposal[15] of the Germans, urea may also be added to potassium nitrate and ammonium phosphate to produce a fertilizer mixture.

Ammonium Sulfate

As has been previously mentioned, it is probable that in America the fertilizer manufacturers will continue for some time to give more attention to ammonium salts than to synthetic nitrates. One ammonium salt, the nitrate, has already been discussed, and others have been mentioned in connection with various fertilizer mixtures.

The most common nitrogenous fertilizer, with the exception of Chilean nitrate, is ammonium sulfate. In America and most other countries ammonium sulfate has been manufactured in large quantities from by-product ammonia and sulfuric acid. Since 1923 the Germans have been sending ever increasing quantities of the synthetic salt into the world market. The effect has been to reduce the high prices prevailing prior to that date. A double salt, ammonium sulfate-nitrate, sold under the name of Leunasalpeter, is another widely exported German product.

The fact that an exportable surplus of ammonium sulfate is already being made from by-product ammonia in America has been used as an argument against the possibility of synthetic ammonia's being utilized for this purpose. The uniformity and improved appearance of the synthetic product, however, may yet allow it to compete, particularly if a cheaper source of the sulfate radical can be developed. In connection with such a cheaper source the process recently discussed by Jackman[16] before the Michigan Gas Association is worthy of mention. This process involves the interaction of gypsum and ammonium carbonate, and is claimed to be more economical than other methods. A plant has been constructed to make use of the process in connection with a gas works at Battle Creek, Mich. For the full development of such a process it has been pointed out by British critics[17] that there are certain difficulties which will have to be overcome. In Germany, where a cheap source of sulfur is lacking, ammonium sulfate is made from gypsum, carbon dioxide, and ammonia. The correlation of this process with the manufacture of calcium nitrate has already been mentioned. Freeth[18] has stated that the process of making ammonium sulfate from calcium sulfate is used at the Billingham plant in England. The consequent depressing effect on the sulfuric acid industry of that country has recently been discussed by Parrish.[19] The British utilize the mineral, anhydrite, rather than gypsum for this purpose. Anhydrite is said to be much more suitable than gypsum, since its content of calcium sulfate is higher and it is more readily susceptible to reaction with ammonium carbonate or bicarbonate. Deposits of anhydrite are rather widely distributed throughout the United States.

The possibility of using niter cake in the manufacture of ammonium sulfate has been discussed by Moliter.[20] In this process ammonia and water are added to the niter cake obtained from a nitric acid plant. After certain intermediate operations, considerable normal sodium sulfate is crystallized out. The ammonium sulfate (contaminated by a little of the sodium salt) is later removed by further evaporation and crystallization.

Another process which has aroused some little interest in England at least is that of West, Jaques, and Morgan.[21] Although the ultimate objective is ammonium sulfate, the primary product is the sulfite. The process consists in allowing ammonia to react with dilute sulfur dioxide, such as weak burner gases, in presence of water vapor. Under easily regulated conditions solid ammonium sulfite is produced in a form stated to be very sensitive to oxidation by the air. Certain drawbacks to the method have been mentioned by Parrish.[19]

Ammonium Phosphates

The problem of the selection of an ammonium product which can be manufactured cheaply enough to compete with ammonium sulfate has been the subject of discussions by Curtis,[22] Maxted,[23] and others. The phosphates appear quite attractive in this connection, since they provide phosphorus as well as nitrogen in a readily available form. Both the mono- and diammonium phosphates can be used as fertilizers. The latter salt has been favored by the Germans, but the former, being less hygroscopic and having a higher ratio of phosphorus to nitrogen, is more suited to American conditions.

It has been found possible in general to mix the ammonium phosphates with other fertilizer materials. A mixture with potassium nitrate, Nitrophoska, has already been discussed. One of the grades of Ammophos, a product manufactured in America, consists of a mixture of ammonium sulfate and monoammonium phosphate,[24] while the Leunaphos of the Germans is similar except for the substitution of the di- for the mono-salt. According to Daugherty,[25] the manufacture of Leunaphos on a large scale will not begin until after the completion of the phosphoric acid plant at Piesteritz in the late spring of this year. Other German products consist of the phosphate mixed with ammonium nitrate[26] in one case, and with potassium chloride[12] in another.

It is quite generally recognized that a rapid increase in the output of ammonium phosphates awaits only a cheaper phosphoric acid. In this connection the possible utilization of the Liljenroth[27] process has aroused considerable interest. In the operation of this process, yellow phosphorus is first produced in an electric furnace. Phosphoric acid is then obtained by blowing the vaporized phosphorus mixed with steam over a catalyst at 1000° C. The hydrogen, which is simultaneously generated, can be used to advantage in the synthesis of the ammonia, which is then combined with the phosphoric acid. Possible improvements of this last step have been outlined in two recent patents, the essential features of which have been discussed by Parrish.[19] The Germans are already taking advantage of this process. By utilizing part of the power available at the Piesteritz cyanamide plant, they will by the middle of 1927 be in a position to produce P_2O_5 at the rate of 6000 tons per year.[25]

Compounds of Ammonia and Carbon Dioxide

In addition to the phosphates, the solid compounds which can be produced from ammonia and carbon dioxide have possibilities of becoming rivals of the sulfate. These compounds are ammonium carbamate and urea. If water is also included in the system, two others, the carbonate and bicarbonate, may be added to the list.

Although no great amount of attention seems to have been devoted to three of these—the carbamate, carbonate, and

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[15] Badische Anilin & Soda Fabrik, British Patent 236,494 (1925).

[16] *Chem. Met. Eng.*, **33**, 484 (1926).

[17] *Chem. Age (London)*, **15**, 267 (1926).

[18] *Ibid.*, **16**, 9 (1927).

[19] *Ibid.*, **16**, 10 (1927).

[20] *Chem.-Ztg.*, **50**, 485 (1926).

[21] *Chem. Age (London)*, **14**, 201 (1926).

[22] *Am. Fertilizer*, **64**, No. 13, 67 (1926).

[23] *Chem. Age (London)*, **16**, 6 (1927).

[24] Braham, *U. S. Dept. Commerce, Trade Information Bull.* **240**, p. 36 (1924).

[25] *Ibid.*, **451**, 16 (1927).

[26] I. G. Farbenindustrie Aktien-Gesellschaft, British Patent 256,972 (1925).

[27] U. S. Patents 1,594,372 and 1,605,960 (1926).

bicarbonate—it has been reported that one of the largest manufacturers of synthetic ammonia in America converts part of its product into the last-named salt. The possibilities of these three compounds have recently been reviewed by Maxted.[23] Since carbon dioxide is available in large quantities whenever the hydrogen for the synthesis of ammonia is obtained by the water-gas catalytic process, the lack of materials should never be a source of difficulty in the manufacture of such compounds. On account of the instability of both carbonate and carbamate, most of the investigation has been concerned with the production of urea, a more stable compound. A recent Badische patent[28] states that the instability of ammonium bicarbonate can be attributed to the presence of small quantities of the carbonate and carbamate. When the salt is prepared free from these impurities, the loss of ammonia on storage is said to be very slight. That the carbamate can also be prepared in stable form is indicated by the claims of a patent recently granted to British investigators.[29]

Although Germany seems to have been the only country which has produced urea on a commercial scale, others have been actively investigating the project. According to Bueb[2] the problems connected with the successful manufacture of urea were solved by the Germans in 1924. It now seems doubtful whether their solution was as successful as reported, although German urea is at present on the American market. The exact details of the German process are not available. The synthesis of urea in general has, however, been thoroughly discussed by Matignon and Frejacques.[30] The results of certain phases of the investigation which is being conducted in this country have recently been published by Clark and Krase[31] and by Krase and Hetherington.[32] Casale[33] has recently patented a process for manufacturing urea. According to his method, carbon dioxide is brought into contact with synthetic ammonia just as the latter leaves the catalyst chamber, the purpose of this procedure being to make use of the thermal and volume energy contained in the gas. The urea formed is cooled in the lower part of the reaction chamber.

Fertilizer mixtures consisting of urea and calcium nitrate, and of urea, potassium nitrate, and ammonium phosphate, have already been discussed. Urea and ammonium chloride are the ingredients of a mixture, the process for the manufacture of which has been protected. According to this process[34] carbon monoxide and chlorine are first combined to form phosgene, and ammonia is then injected in the ratio of four volumes to one of phosgene. The equation representing the reaction is:

$$COCl_2 + 4NH_3 \rightleftharpoons CO(NH_2)_2 + 2NH_4Cl$$

MacDowell[35] has stated that urea cannot be mixed with soluble phosphates, since gummy masses result. In Switzerland, however, there has been developed a process for the manufacture of Phosphazote, a mixture of urea and acid phosphate. The properties of various salts of urea, including the phosphate, have been studied in this laboratory.

Both advantages and disadvantages may be listed for urea. Its tendency to take up moisture, although strong, is less than that of Chilean nitrate. According to MacDowell, field tests have indicated that urea is not superior to ammonium sulfate as a general fertilizer. Bueb[2] states, however, that its application is destined to be very successful with such crops as tobacco and hops, and with vines, in gardens, and on pasture lands. Since its nitrogen content is nearly 47 per cent, its use in America, where freight charges are important, should increase rapidly, provided the necessary propaganda is forthcoming. Alexander[36] has recently directed attention to the fact that its use in fertilizers is not the only outlet for synthetic urea. It can also be utilized in the manufacture of synthetic resins and artificial (non-breakable) glass. In summary, it can apparently be safely stated that the outlook for synthetic urea is bright.

Ammonium Chloride

Ammonium chloride is another salt which can be readily prepared from ammonia. Its production has not been pushed probably because the presence of the chloride radical is known to be detrimental to certain crops. The manufacture of this salt in conjunction with the Solvay soda process seems to offer attractive possibilities. It has been reported that some of the American output of synthetic ammonia is being marketed in the form of ammonium chloride.

Other Compounds

Although most of the recent developments have been in the fertilizer field, there have been certain others that cannot be so classified. Conversion to ammonium dichromate, for instance, has been suggested as offering an additional outlet for ammonia. A patent issued to the Badische Anilin und Soda Fabrik[37] discusses the production of hydrocyanic acid, ammonium cyanide, and formamide from ammonia and an alkyl formate. To produce hydrocyanic acid, the demand for which is increasing, the patent specifies that ammonia and methyl formate be sent over an alumina catalyst at 260° C. There has always been a certain demand for ammonia in various chemical industries. The rayon industry has been a recent addition to the list. Quinn[38] states that the development of those rayon processes which use ammonia offers an additional outlet of probably increasing importance.

Propaganda

According to Bueb,[2] agriculture has always been the center of the German propaganda efforts. The first step was a widespread series of ocular demonstrations of the effect of nitrogen in promoting the growth of plants. Then followed accurate determinations of the increases in the yields of various crops, and demonstrations by means of model farms of the profits to be gained from utilization of the most modern scientific experience. Although certain projects of a propaganda nature which the Germans had contemplated for China may have been somewhat fantastic, there is no doubt but that the methods they used at home were quite successful.

While Speyer[39] has stated that low price and adaptable variety of form have made the major contributions towards creating a demand for nitrogen in England, certain efforts along the line of additional propaganda have been carried out. On December 1, 1926, the newly created Nitram, Ltd., took over the selling and propaganda functions of both Synthetic Ammonia and Nitrates, Ltd., and the British Sulfate of Ammonia Federation. A recent report[40] states, furthermore, that both the British Government and the new big chemical merger, Imperial Chemical Industries, Ltd., are concentrating upon research from an agricultural point of view, the object being to assist and educate the farmer.

There has even been a rumor of the possible establishment

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[28] British Patent 244,645 (1925).

[29] Synthetic Ammonia and Nitrates, Ltd., British Patent 258,048(1925).

[30] *Bull. soc. chim.*, **31**, 307 (1922).

[31] This Journal, **19**, 205 (1927).

[32] *Ibid.*, **19**, 208 (1927).

[33] British Patent 241,123 (1925).

[34] Siemens and Haske, Aktien-Gesellschaft, British Patent 245,768 (1925).

[35] *Chem. Met. Eng.*, **33**, 9 (1926).

[36] *Chem. Age (London)*, **16**, 4 (1927).

[37] British Patent 254,787 (1925).

[38] *Chem. Met. Eng.*, **34**, 48 (1927).

[39] *Chem. Age (London)*, **14**, 496 (1926).

[40] *Ibid.*, **16**, 137 (1927).

of a nitrogen institute in the United States. One of the functions of such an institute would undoubtedly have to do with propaganda. Just what forms this propaganda should take in America is a question outside the scope of this paper. The fact remains, however, that the per capita consumption of nitrogen in this country is low. Education of the prospective user of nitrogen cannot fail to have a beneficial influence upon the demand for this substance.

Trade in Synthetic Resins and Their Raw Materials[1]

By Otto Wilson

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In studying the remarkable expansion in the use of synthetic resins, an expansion which has doubled their output in four years, we are impressed once more with the interdependence of modern industries. The radio, springing up overnight, found ready at hand these most useful of plastics and profited greatly by them, and they have played an appreciable part in the 100 per cent increase in automobile output since the war and in the steady growth of the electrical industry. Demands from these and a great variety of other industries have in turn raised the manufacture of resins to a position of commercial prominence from which they look forward to a far greater growth in the years ahead.

Because of the centralized manufacture of the resins in this country the Government for the most part has been unable to publish figures showing the annual production. Sales and production figures are available only for the years 1920, 1921, and 1922. Since 1922 they have been incorporated with the returns for synthetic tanning materials. The total for these two classes of manufactures combined shows a rapid rise, registering a gain in the three years preceding 1926 of nearly 60 per cent. Most of this gain may be attributed to the resins.

Table I—Production and Sales of Synthetic Phenolic Resins and Synthetic Tanning Materials

	Manufacturers	Production		Sales	
		Pounds	Value	Pounds	Value
1918:					
Resins	5	4,233,400	$2,642,100	[a]	[a]
Tanning materials	1				
1919:					
Resins	5	3,794,500	2,381,400	[a]	[a]
Tanning materials	1				
1920:					
Resins	4	4,659,700	3,410,200	[a]	[a]
Tanning materials	4	3,142,900	233,700	[a]	[a]
1921:					
Resins	3	1,643,800	[a]	1,674,500	$1,352,200
Tanning materials	4	1,902,600	[a]	1,721,400	141,000
1922:					
Resins	5	5,944,100	[a]	6,415,900	4,315,200
Tanning materials	4	1,910,500	[a]	1,981,600	103,600
1923:					
Resins	2	9,763,700	[a]	10,068,400	5,816,600
Tanning materials	3				
1924:					
Resins	2	12,778,100	[a]	12,745,500	8,818,000
Tanning materials	3				
1925:					
Resins	2	14,687,100	[a]	13,896,600	8,698,800
Tanning materials	1				
1926:					
Resins	2	14,107,000[b]	[a]	14,325,000[b]	7,647,000[b]
Tanning materials	2				

[a] Not stated.
[b] Preliminary.

Recently announced preliminary returns for 1926 show a slight falling off in total production of these commodities as compared with the previous year, and a decrease in total value of sales but a gain in quantity of sales. But that, of course, does not necessarily imply a decrease in resin production.

The figures in Table I, gathered and published by the United States Tariff Commission, show the output and sales of these resins and of synthetic tanning materials for the last nine years.

Of the various forms in which these resins are marketed, the molding powders and laminated blocks, tubes, etc., make up by far the larger part of the totals given in Table I. No figures have been made available to the public which would indicate the proportions of the total represented by these classes or by the resins in the forms of varnishes, cements, or the hard transparent article, except that the one large manufacturing company gave as its total output of the last-named product in 1925 about 178,000 pounds, only a small fraction of the whole manufacture of resins.

Foreign Competition

Born in America, the synthetic resin industry was early established on both sides of the Atlantic. But its development here has been a response to domestic demands, and except in the importation of raw materials it has figured little in foreign trade. Synthetic resins are not listed separately among the country's exports, but sales to foreign countries are of no great consequence. The only recent year for which statistics of the trade were published was 1922, when 128,000 pounds valued at $13,000 were exported, nearly all to Canada. The principal channel through which they find their way abroad is in the form of the great variety of manufactures into which they enter, and these are not distinguished statistically from similar articles made from other materials.

In the import trade the resins of foreign manufacturers are effectually held back at the border by the high duties, particularly by the provision in the 1922 Tariff Act for American valuation as a basis for computing ad valorem duties. The present rate is 7 cents per pound and 45 per cent. Even at this rate there is a certain small trade (Table II).

Table II—Imports of Synthetic Resins[a]

Year	Pounds	Value
1919	1114	$ 2860
1920	2479	2681
1921	1420	2366
1922	2518	3498
1923	3183	10512
1924	8756	4183
1925	1537	889
1926	1649	1298

[a] Figures since 1922 are for "resin-like products" prepared from coal-tar derivatives.

The tariff, however, does not cover articles made from the hard, amber-like form of these resins, and in these lines competition from abroad has been keenly felt. After the war the manufacture of beads and smokers' articles, such as cigar and cigaret holders, from synthetic resin for awhile achieved encouraging results. But presently similar imported goods began to displace them, and salesmen for the American articles were met everywhere by the statement that the foreign goods could be had at far lower prices than they could quote. American manufacturers in these lines were practically driven from the market.

On the ground of unfair competition a number of firms

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[1] Received April 8, 1927.

requested the President to bar these goods from entry into the United States, asserting that they were identical in composition with those made from materials and processes covered by United States patents, and in many cases were represented to be of a material covered by a United States trademark. On the recommendation of the U. S. Tariff Commission a temporary order was issued prohibiting the entry of these goods, and in May and June, 1926, extended hearings were held to determine whether this order should continue in force. In December an order was issued permitting the entry of these articles after December 6, the date when the first two synthetic resin patents, taken out seventeen years before, expired, but making an exception of multicolored articles, on which further hearings were held early in 1927.

The final decision of the commission, dated May 25, 1927, upheld the claims of the complainants. It recommended that synthetic phenolic resins and articles made wholly or in part from them, as covered by two specified basic patents, should be excluded from entry into the United States, as well as articles made from any kind of synthetic phenolic resins unless they were marked so as to distinguish them clearly from articles made of such resins produced by the Bakelite Corporation. The decision was not unanimous, two of the five commissioners dissenting wholly or partly on the grounds that the patents concerned were in dispute and that the commission's right to assume their validity, under the circumstances, was doubtful.

As disclosed in the hearings, European costs of producing these goods are one-half to two-thirds lower than the American cost. The reasons for this large difference have not been officially ascertained, but very apparently they lie chiefly in lower manufacturing costs, which make up the larger part of the total production cost. Processes in Europe involve greater use of hand labor than those in this country, and in the chief competing countries, including Czechoslovakia, Austria, and Germany, labor costs are much less than here.

RAW MATERIALS

The sources of supply of the chief raw materials used in resin manufacture—formaldehyde, phenol, and cresylic acid—are adequate to meet the demand, and the principal concern with regard to them has related to prices. Formaldehyde and phenol are produced increasingly as the result of synthetic processes, and there is no shortage of the material which yields cresylic acid.

Formaldehyde

Domestic production of formaldehyde has been adequate, and there has been no necessity for calling on foreign sources. The mounting demand for the synthetic resins has pushed formaldehyde production up sharply in the last two or three years. The total annual output is now three or four times the pre-war average. In 1925 the gain in output over the previous year was 20 per cent, and the preliminary figures for 1926 show that the increase still continued in that year. Table III shows how rapidly the manufacture has been advancing.

Table III—Production and Sales of Formaldehyde in the United States

YEAR	PRODUCTION	SALES	
	Pounds	Pounds	Value
1914[a]	[b]	8,426,200	$ 655,000
1919[a]	25,006,800	19,663,800	3,938,300
1921[a]	9,657,400	6,056,500	651,700
1922	23,958,000	16,140,000	1,676,400
1923	24,081,200	18,854,500	2,474,500
1924	26,155,200	20,542,400	1,971,100
1925	31,455,700	23,391,600	1,895,900
1926	31,953,200[c]	22,552,200[c]	2,050,900[c]

[a] Census Bureau figures; all others from U. S. Tariff Commission.
[b] Not available.
[c] Preliminary.

Although formaldehyde has many other uses, the synthetic resins now constitute probably its most important outlet and the growth in output is to be attributed in large degree to the demands from that source and from the manufacture of indigo.

A new factor which is likely to affect permanently the course of formaldehyde prices appeared in 1925. This was the entry into the markets of synthetic methanol from Germany. While fluctuations in prices of methanol and formaldehyde do not closely parallel each other, there is naturally a relationship between the two. With methanol selling at $2.00 to $2.50 per gallon immediately after the war, formaldehyde sales showed an average valuation of about 20 cents. Methanol in the last two or three years has been much reduced in price and formaldehyde sales have had an average value of 8 to 10 cents. Synthetic methanol manufacture has been begun in this country, and its influence and that of the imported article will undoubtedly be in evidence in the future course of formaldehyde prices.

Phenol

In the production of phenol in this country the synthetic article now very much holds the center of the stage. It is estimated that in 1925 more than three-fourths of the total manufacture was produced by the synthetic process. This development has been due very largely to the advance of the synthetic resins. Their rise rapidly used up the large surplus left over from the war, and when it had vanished manufacturers were faced with a possible shortage, since the output from the distillation plants was insufficient for their growing needs. The Tariff Act of 1922 put a heavy increase of duty on phenol, and the next year the manufacture of the synthetic article, which in 1918 had turned out more than 100 million pounds but had been suspended since the war, was resumed. So rapid was the increase in output that a total of more than 10 million pounds was recorded for 1924 and of nearly 15 million pounds for 1925. But this apparently was an overproduction, and the preliminary returns for 1926, recently announced, show a decided falling off.

The course of production and sales since the war as compared with our two war years is shown in Table IV.

Table IV—Production and Sales of Phenol in the United States[a]

YEAR	PRODUCTION		SALES		
	Pounds	Value	Pounds	Value	Unit value
1917	64,146,500	$23,715,800	[b]	[b]	$0.37
1918	106,794,300	37,270,300	[b]	[b]	0.35
1919	1,543,700	155,600	[b]	[b]	0.10
1920	...	...	...	...	...
1921	...	...	292,600	$ 41,600	0.14
1922	1,286,000	[b]	1,266,600	268,300	0.21
1923	3,310,900	[b]	2,180,200	589,800	0.27
1924	10,521,900	[b]	8,273,600	2,505,500	0.30
1925	14,734,100	[b]	8,524,200	1,771,300	0.21
1926	8,691,000[c]	[b]	5,480,000[c]	987,000[c]	0.18

[a] U. S. Tariff Commission, "Census of Dyes and Other Synthetic Chemicals."
[b] Not stated.
[c] Preliminary.

A development that is being watched with much interest is the prospective manufacture of phenol by a new synthetic process. It is more direct than the one now in use and promises to reduce the cost of production. The process has been patented, but has not yet been made the basis of commercial manufacture.

The resumption of phenol manufacture in this country and the charging of a high rate of duty have kept imports comparatively low. Formerly most of our supplies came from abroad. Until 1916 phenol was admitted free and in pre-war days 80 or 90 per cent of our requirements came from abroad, mostly from England and Germany. The existing rate of 40 per cent and 7 cents has more than reversed this proportion, although there is still a trade of some importance (Table V).

Table V—Imports of Phenol into the United States

Year	Crystal Pounds	Liquid Pounds
1917	30,700	314,600
1918	148,300	134,400
1919	...	2,100
1920	...	1,000
1921	250	...
1922	349,500	147,100
1923	126,600	2,800
1924	176,100	441,600
1925	256,100	98,700
1926	218,400	25,900

Since the war phenol imports have come very largely from England. The raw material from which it is obtained in that country is derived from coke ovens, gas houses, and blast furnaces. The coke ovens, operated in connection with coal mines or steel mills, have been undergoing the same change as in this country, and a recent official statement gave the proportion of by-product ovens in 1924, as disclosed by a census survey, as about 75 per cent of the total. In the gas houses the coal gas process largely prevails, in contrast to the practice in this country where water gas has for the most part taken the place of coal gas. Tar from coal gas is much richer in the tar acids than that from water gas, and England can produce much more of them than she needs. The 1924 census showed an output of coke-oven and blast-furnace tar of some 500,000 tons, from which more than 3 million pounds of carbolic acid were obtained. No figures are to be had which would show what proportion of the total output in England is represented by these amounts.

British raw-material costs in making phenol are somewhat lower than in this country, and labor and other costs are very much lower. An investigation made in 1923 showed that the American cost of production, including that of both natural and synthetic phenol, was 142.5 per cent of that of the largest producer of refined phenol in England.

Cresylic Acid

Although in synthetic resin manufacture cresylic acid is practically interchangeable with phenol, conditions of production and trade are materially different. It is not made synthetically, the whole supply coming from tar distillation. As commercial production in this country is in the hands of a single large concern, with twenty or twenty-five plants, annual figures of output cannot be given. There has, however, been a marked increase within the last two or three years.

Prior to the passage of the Tariff Act of 1922 all cresylic acid entered free. The normal importation was heavy, averaging some 8 or 9 million pounds a year. In 1920 the trade reached its peak with a total of 10,600,000 pounds, including cresol and distillates of tar containing a considerable proportion of cresol, the whole being valued at $957,000. The use of war-time phenol greatly reduced the import trade. The 1922 Tariff Act put a heavy duty on refined cresylic acid but pemitted the crude still to come in free. The line was drawn by assuming that crude cresylic acid would fall in that class of tar products distilling less than 5 per cent tar acids below 190° C. Foreign manufacturers apparently have been able to control their processes so that grades of cresylic acid can be produced which will fall in that class but which can be easily refined to higher grades.

Although domestic production has considerably increased since 1922, imports have continued to come in to the extent of some 2 million pounds a year, nearly all free of duty. Within the last year cresylic acid imports have shown a big gain, the 1926 trade being nearly three times that of the year before.

Imports of cresylic acid were not separately classified under that name before 1924. For the last three years crude cresylic acid imports and those of distillates yielding less than 5 per cent tar acids under 190° C., all of which are admitted free, have been as shown in Table VI.

Table VI—Imports of Crude Cresylic Acid, Etc.

Year	Cresylic Acid		Tar Distillates Yielding Less than 5 Per Cent Tar Acids under 190° C.	
	Pounds	Value	Pounds	Value
1924	2,327,500	$157,600	2,440,400	$151,900
1925	2,163,600	122,700	5,994,800	367,700
1926	5,802,900	331,600	3,136,800	197,000

Refined cresylic acids subject to duty are classified as tar distillates yielding 75 per cent or more of tar acids below 215° C. Imports for the three years have been as follows:

Year	Pounds	Value
1924	378,400	$38,800
1925	135,800	29,000
1926	7,200	4,200

Cresylic acid can be produced in England at much lower cost than in this country. A recent inquiry revealed an average cost about one-half that of American manufacture.

Estimation of Organic Matter in Sewage and Effluent[1]

Modification of Adeney's Acid Dichromate Method

By W. E. Abbott

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ORGANIC substances can be oxidized rapidly and almost completely to carbon dioxide by a mixture of potassium dichromate and sulfuric acid at a high temperature. Several methods have been described for estimating the carbon in organic substances by the use of this oxidizing mixture, the carbon dioxide evolved being absorbed and weighed. Small amounts of carbon monoxide are produced, however, and must be oxidized either by passing the mixed gases with air over heated platinized asbestos or by some other means.

Several years ago Adeney found that many organic substances were completely oxidized by prolonged digestion with a concentrated mixture of sulfuric acid and potassium dichromate at the temperature of the water bath. Moreover, at this temperature there was no appreciable spontaneous loss of oxygen from the dichromate such as occurred at higher temperatures. It was thus possible to use a measured amount of potassium dichromate and to titrate the excess at the conclusion of the digestion. The loss represented the oxygen required to oxidize the organic matter to carbon dioxide and water. In other words, the method promised to be the means of estimating the oxygen which a polluted liquid would consume during the complete conversion of its organic matter to carbon dioxide, water, and ammonia. Unfortunately, this reaction could not be

[1] Received March 28, 1927.

directly applied to polluted liquids, owing to the chloride which they contained in solution. The chloride reacted with the dichromate to form chromyl chloride and chlorine, thereby causing a very large error. It was necessary either to find some means of correcting for this chloride error or to displace the chloride before performing the test. The second method was found most feasible, evaporation with sulfuric acid being adopted to drive off hydrochloric acid.

These facts were disclosed by Adeney to the writer several years ago. Three years ago the test was adapted for use in this laboratory, a very large number of tests being performed from time to time to investigate possible limitations. The results obtained in these tests and the experience gained in the use of the method as a routine determination are discussed in this paper.

Conditions for Successful Chloride Removal

A modification of Adeney's acid dichromate method for the determination of organic matter in sewage and effluent is described, together with the principal reasons for its adoption.

Experimental evidence is summarized to show that the oxygen absorption in the method is of the same magnitude as the oxygen absorption which would occur during the complete conversion of the organic matter to carbon dioxide, water, and ammonia.

The new method is shown to possess very marked advantages over the permanganate absorption test.

Many series of tests were carried out both with chloride solutions and effluent samples to determine the most satisfactory procedure. It was invariably found necessary to evaporate until the sulfuric acid became concentrated to about 50 per cent by volume before there was much chloride loss. The addition of 3 cc. of 10 per cent sulfuric acid to 25–100 cc. of a liquid containing 100 to 200 p. p. m. of chlorine gave the most satisfactory results.

In every case there was some darkening of the liquid during this evaporation, and considerable charring was observed in certain cases when the liquid had reached a low bulk. Observations were therefore carried out to determine the minimum time for which the liquid must be maintained at low bulk with the certainty of chloride removal. It was found that occasional stirring during 3 minutes after the liquid had attained a bulk of about 0.7 cc. left in the worst case only an insignificant trace of chloride. Maintenance on the water bath for 10 minutes after the attainment of this bulk gave a loss of from 0 to 5 per cent of the total oxidizability. Use of the test as a routine determination has shown that some trials are necessary before the point at which chloride removal is complete can be judged satisfactorily. Until this skill is attained it is best to allow an excessive contact with acid, as the loss of oxidizability is not great, whereas the presence of residual chloride would produce a large error.

Relation between Acid-Dichromate Concentration and Oxidation Effected

Working with pure substances, it was found that the amount of oxidation depended primarily on the concentration of sulfuric acid in the solution. The percentage oxidation increased rapidly at first and then more slowly with increase in the concentration of acid. The maximum oxidation was always obtained when solid dichromate, dry organic matter, and concentrated sulfuric acid interacted. The dichromate concentration in solution was of comparative unimportance.

Method Adopted

Twenty-five cubic centimeters of a raw sewage or an equivalent volume of other liquid are placed in a small evaporating basin, and 0.3 cc. concentrated sulfuric acid or 3 cc. of 10 per cent sulfuric acid added. The top of the basin is covered with a filter paper laid between two solid-glass triangles to ward off smuts and dust. Evaporation on the water bath is continued with occasional stirring until about 0.7 cc. of liquid remains, when the sample is vigorously stirred at intervals during 3 or 4 minutes to remove the chloride. Twenty-five cubic centimeters of 0.125 *N* dichromate solution are added and evaporation is resumed until about 1 cc. remains. Five to ten cubic centimeters of concentrated sulfuric acid are added, and the basin is left on the water bath for 2 hours. The liquid is then diluted with distilled water, and the residual dichromate is titrated with ferrous sulfate, using potassium ferricyanide as external indicator. The greatest care failed to eliminate the necessity for blank determinations. The liquid in the basins undergoing digestion must be maintained above 94° C.

Application to Known Organic Substances

In the procedure finally adopted the conditions for maximum oxidation are not maintained throughout. The oxygen absorbed from dichromate by various organic substances when subjected to the modified dichromate test was therefore determined. The oxygen actually absorbed was expressed as a percentage of the oxygen calculated as necessary to convert the substance into carbon dioxide, water, and ammonia. This percentage usually varied slightly from day to day. The results are summarized in Table I. These figures are all lower than they would have been had not the procedure for chloride removal been necessary.

Table I—Percentage Oxidation

	Digestion with Excess Sulfuric Acid			
Substance	None	1 hour	2 hours	3 hours
Rochelle salt			90	
Lactose			89 to 93	
Sodium oxalate	98		98	
Succinic acid		93	99	99
Asparagine			90 to 95	
Sulfanilic acid			78 to 80	80
Cellulose (filter paper)	83 to 84	84	85 to 90	
Peptone (Difco)			60	65 to 70
Peptone (Witte)				66
Egg albumin				61
Gelatin		62	66	
Stearic acid	44	73		74

This causes losses due to the decomposition by the acid during the evaporation to drive off chloride and also because for some time after the addition of dichromate solution a weak acid and dichromate solution is acting on the organic matter. The last-mentioned loss can be eliminated by neutralizing the acid with sodium carbonate before adding the dichromate. With certain substances the percentage oxidation was increased—e. g., with sulfanilic acid from 80 to 99 per cent. In actual practice with raw sewage samples the increase in oxidizability was slight. Apart from direct losses, the low values recorded may in certain cases be due either to the formation of stable compounds which resist further oxidation under the given conditions or to the evolution of volatile compounds such as carbon monoxide which escape further oxidation.

Comparison of Acid-Dichromate Absorption and Oxygen Absorbed during Carbonaceous Fermentation

A sample of raw sewage previously freed from suspended matter by centrifugation was diluted suitably with water and incubated at 21° C. The dissolved-oxygen absorption and the various nitrogen compounds were estimated daily until nitrification commenced. The dissolved oxygen absorbed by the sample during the purely carbonaceous fermentation was obtained from these figures after making the appropriate corrections for the dissolved-oxygen absorption of the diluting water.

Table II shows the results obtained during three such series of tests. The dissolved-oxygen absorption is on the average 80 per cent of the dichromate absorption in these experiments.

Table II

Acid-Dichromate Absorption	Dissolved Oxygen Absorbed before Nitrification Starts
P. p. m.	*P. p. m.*
120	100
101	88
107	74

Since Adeney has shown that 70 to 80 per cent of the organic matter is oxidized to carbon dioxide, water, and ammonia before nitrification commences, it would appear that in the examples given the dichromate absorption figure approximates the oxygen required to convert all the organic matter into carbon dioxide, water, and ammonia.

Relation between Acid-Dichromate Absorption and 5 Days' Dissolved-Oxygen Absorption

The relation for any class of liquid varies considerably, no doubt mainly because of the sensitiveness of the dissolved oxygen test to the quantity and quality of the suspended matter in the sample.

Table III shows the variation of ratio between these two tests with time as a raw sewage is changed by aeration with activated sludge. To avoid the fluctuations in the dissolved-oxygen absorption due to suspended matter, the analyses were performed after the liquids had been centrifuged and decanted from the suspended matter.

Table III

Aeration	Oxygen Absorption: Acid dichromate	Oxygen Absorption: 5 Days dissolved oxygen	Ratio $\frac{\text{Acid dichromate}}{\text{5 Days dissolved oxygen}}$
Hours	*P. p. m.*	*P. p. m.*	
	TEST 1		
Raw sewage	206	130	1.58
1	106	80	1.32
2	86	55	1.56
4	...	...	...
5	63.5	39	1.63
6	57.5	40	1.44
7	48	31	1.55
8	45.5	25	1.82
22	28.0	7	4.00
	TEST 2		
Raw sewage	158	112	1.41
1	78.5	53.6	1.46
2	65	39.7	1.63
4	50	28.2	1.77
5	42.8	21.1	2.02
6	44.3	22.0	2.01
7	37.2	17.5	2.12
8	33.6	17.3	1.94
22	20.7	3.2	6.46

Relation between Acid-Dichromate Absorption and Oxygen Absorption from Permanganate

This varies with each sample, but for any class of liquids the ratio does not vary much from a constant average value. The ratios depend on the type of permanganate absorption test used. The modification employed in these determinations, and which gives results which are on the average only 66 per cent of the absorption when using the A.P.H.A. 1923 procedure, is performed as follows: 100 cc. of an effluent (or a smaller volume of a stronger liquid diluted to 100 cc. with distilled water) are mixed with 50 cc. of 0.0125 *N* potassium permanganate and 10 cc. of 30 per cent sulfuric acid, and placed in a 37° C. incubator for 4 hours. The residual permanganate is then titrated. Nitrite is destroyed with urea before permanganate addition.

With crude sewage the dichromate absorption is on the average 5.1 times greater than the permanganate absorption. The individual ratios vary between 4.6 and 6.3. For raw sewage from which the suspended solids have been removed by centrifuging and decanting, the average ratio is 4.5. For well-purified activated-sludge effluents the average ratio is 2.5. Again the individual ratios vary within narrow limits—namely, 2.2 and 3.0. The variation of the ratio as the liquid changes from crude sewage to purified effluent is shown in Table IV, which records the changes in a sewage sample on aerating with 21 per cent activated sludge. All samples were separated from suspended matter by centrifuging and decanting before analysis.

Table IV

Aeration	Oxygen Absorption from: Acid dichromate	Oxygen Absorption from: Permanganate	Ratio $\frac{\text{Dichromate}}{\text{Permanganate}}$
Hours	*P. p. m.*	*P. p. m.*	
Raw sewage	206	39.0	5.3
1	106	23.6	4.5
2	86	20.6	4.2
5	63	16.2	3.9
6	57.5	16.6	3.5
7	48	15.7	3.0
22	28	12.6	2.2

It is apparent that the dichromate absorption test affords a more sensitive index of the course of purification than the permanganate absorption test. For instance, as a result of aeration from the sixth to seventh hour the dichromate method records in the example 16.5 per cent purification while the permanganate absorption only records 5.4 per cent. Likewise, the percentage purification measured in terms of acid-dichromate absorption is always greater than in terms of the 4 hours' permanganate absorption—e. g., after 22 hours' aeration 86.4 per cent against 67.7 per cent.

The two alternative modifications published by Adeney[2] last year give in actual practice results of the same magnitude as the local modification, the hot-plate procedure giving rather higher and the water-bath procedure rather lower percentage oxidation. The resulting scientific advantage of the hot-plate procedure appeared to be offset for routine purposes by the extra attention required for careful temperature regulation on the hot plate. As a result the procedure has not been changed for the present.

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[2] Adeney and Dawson, *Sci. Proc. Roy. Dublin Soc.*, **18** (N. S.), 199 (1926).

Contamination of Soil Source of Oil "Discoveries"

The Geological Survey has announced that contamination of the soils from filling stations or other sources of refinery products is probably responsible for most of the reports regarding the finding of gasoline or kerosene-like material in wells, springs, basements, and other excavations. The reports come from various parts of the United States, said George Otis Smith, the director, and often lead to local excitement. His further comments upon the situation follow:

> In a large number of cases, these reports lead to local excitement and the hope that the material indicates natural occurrences of crude oil which can be developed commercially. These reports come from all sorts of geologically impossible locations. They may be in regions where the underlying rocks are Archean or granites as well as in regions where the underlying rocks are sediments not intrinsically hopeless as sources of oils.
>
> We believe that in practically all such cases the reported occurrences are due to contamination of the soils from filling stations or other sources of refinery products. Of course, there are a few occurrences of particularly high-grade natural petroleums which contain as much as 80 or even 85 per cent gasoline, but even these highest grade crudes do not possess "the chemical and physical properties of gasoline." They are likely to have a notable difference in distillation range. No cases have come to our attention in which the laboratory technician is not able to determine whether the material submitted is a fugitive distilled product or a mixture of products, on the one hand, or a natural product on the other.

Ammonia Content of Cold-Storage Eggs

An Investigation of Cold-Storage Eggs Sold at Retail in Massachusetts[1]

By Hermann C. Lythgoe

Department of Public Health, State House, Boston, Mass.

THE cold storage of eggs is a purely commercial proposition and benefits the producer, the dealer, and the consumer. The producer gets a market for his surplus spring eggs. The dealer is able to store this surplus and sell it later in the season, usually at a profit, but sometimes at a loss. The consumer is able to obtain eggs throughout the year at less variance in price than would be possible otherwise.

Only about 10 per cent of the eggs produced are placed in cold storage. Of these about 5 per cent are stored by April 1, about 40 per cent by May 1, and about 83 per cent by June 1, so that all are in storage by July 1. On August 1 about 2 per cent have been removed; on September 1, about 10 per cent; on October 1, about 22 per cent; on November 1, about 60 per cent; on December 1, about 63 per cent; on January 1, about 82 per cent; on February 1, about 95 per cent. These figures represent five-year average holdings, 1920 to 1924. In Massachusetts 18,214,980 dozen eggs were placed in storage during 1926, and the maximum holdings were 11,103,120 dozen on August 1. The maximum holdings in the United States during 1926 were 295,350,000 dozen on August 1.

The Massachusetts cold-storage egg law provides that whenever eggs that have been in cold storage are sold, at wholesale or retail, the container shall be plainly and conspicuously marked with the words, "Cold-Storage Eggs," or there shall be attached to such container a sign having upon it the said words. The law further provides that when such eggs are sold at retail or are offered or exposed for sale without a container, or are placed upon the counter, a sign bearing the words "Cold-Storage Eggs" shall be displayed among, upon, or immediately above the eggs. The element of time in storage is not mentioned in this law, but similar legislation in other states requires a thirty-day period of refrigeration to elapse before the eggs are considered to be cold-storage eggs.

In cases involving prosecution for violation of this law, it is necessary to prove that the eggs in question have actually been in cold storage, and this proof cannot be shown by any known methods of analysis. Examinations of any sort which will indicate to some extent the probable age of the egg, and its relative decomposition, are of great value to the field man, who, when armed with the information that the eggs are somewhat old but are free from extensive decomposition, can frequently gather the necessary evidence to show that cold storage was responsible for their condition. Chemical and physical examinations that will indicate the condition of the eggs also furnish valuable circumstantial evidence to supplement such direct evidence as may be available.

As an egg becomes old the contents go through the forms of decomposition usual in this class of foods, such as reduction of the dextrose and increase in acidity of the fat, as well as ammonia production. The rate of decomposition is influenced by the temperature at which the egg is kept. The ammonia production is confined practically to the yolk of the egg and, consequently, when dealing with broken-out eggs, the fat determination is essential for a correct interpretation of the analysis.

The determination of ammonia in eggs for ordinary inspectional purposes was first applied to broken-out eggs as a means of detecting any admixture of decomposed eggs. For this purpose it has been very successful. For many years the Massachusetts Department of Public Health has used the ammonia content as a means of differentiating between fresh and old edible eggs.

Eggs Used

The cold-storage eggs used in this study were either sold as such properly labeled by the vendor, or were ascertained to have been such by the inspector either at the time of sale or subsequently. They all represented retail sales obtained during the past five years as delivered to the consumer. Some of the eggs were sold practically as soon as received from the wholesaler; many had been in the retailer's possession for from three days to a week; and a few had been in the retailer's possession for two weeks.

Method

The ammonia was determined by the well-known aerometric method of Folin,[2] using Nessler solution as the reagent.

The cylinders were $1^3/_8$ inches (3.5 cm.) internal diameter and $11^1/_2$ inches (29.2 cm.) high. Twenty grams of egg were used. The air pressure was sufficient to measure 2 inches (5 cm.) of mercury in a manometer attached to the outlet pipe. Two hours' aeration was sufficient to recover all the ammonia.

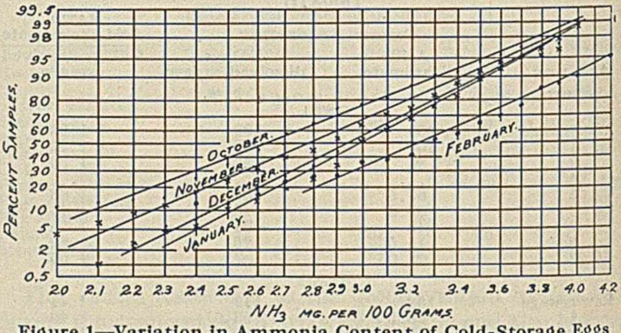

Figure 1—Variation in Ammonia Content of Cold-Storage Eggs

Results

The ammonia figures, segregated by months, were compiled as summation series, expressed as percentage of samples containing up to and including the quantity of ammonia indicated in Table I.

Table I—Ammonia Content of Eggs Examined

	Oct.	Nov.	Dec.	Jan.	Feb.
Number of samples	82	405	374	187	40
	Milligrams ammonia per 100 grams				
Lowest	1.8	1.4	1.9	2.1	2.2
Lower quartile	2.46	2.52	2.69	2.85	2.80
Median	2.65	2.86	2.97	2.99	3.28
Geometric mean	2.68	2.86	3.00	3.05	3.24
Arithmetic mean	2.73	2.90	3.03	3.08	3.29
Upper quartile	2.92	3.20	3.24	3.29	3.66
Highest	3.8	4.3	4.2	4.3	4.3

The median of each series is lower than the arithmetic mean thereby suggesting that the series is of a logarithmic char-

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[1] Received March 22, 1927.

[2] *Z. physiol. Chem.*, **37**, 161 (1902); *J. Biol. Chem.*, **11**, 532 (1912).

acter. These figures plotted upon logarithmic-probability scales[3] are shown in Figure 1. Each series is approximately a logarithmic-probability series.

There appears to be a close relationship between the October, November, and December series, but the February series has a much lower percentage of samples relatively low in ammonia. During January fewer samples were collected than in December, because most of the violations of the law had been checked before the latter part of January. The analyses of the January eggs do not represent an average as of January 15, but as of an earlier date. Consequently, the curve falls nearer to the December curve than it would had collections of samples followed the rule of the other months. The eggs collected in February were practically all purchased as cold-storage eggs and were collected with a view of finding decomposed eggs rather than of ascertaining the existence of violations of the cold-storage egg law.

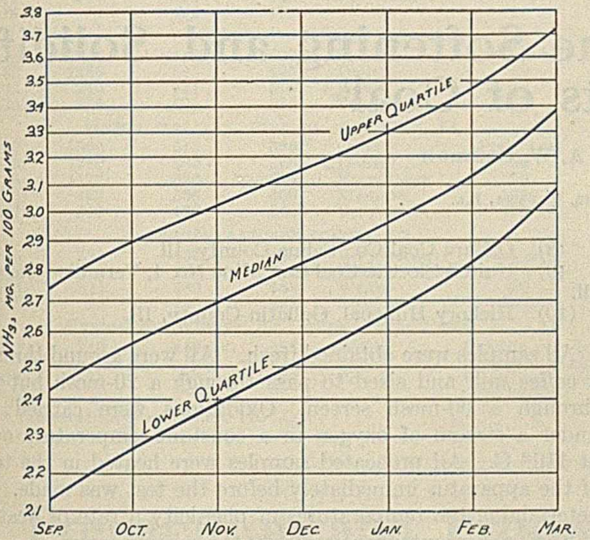

Figure 2—Estimated Seasonal Variance in Ammonia Content of Cold-Storage Eggs

Assuming that the difference in ammonia content between cold-storage eggs sold in September and in October would be relatively the same as exists between those sold in October and November, as well as between those sold in November and December the estimated September line was drawn on the chart from which the lower quartile, the median, and the upper quartile were taken, and similiar values were taken from the other lines. These values are given in Table II.

Table II—Average Ammonia Content as of Fifteenth of Month

(Figures in milligrams ammonia per 100 grams)

	Lower Quartile	Median	Upper Quartile
September	2.1	2.4	2.8
October	2.3	2.6	2.9
November	2.5	2.9	3.1
December	2.6	2.9	3.2
January	2.7	2.9	3.2
February	2.8	3.2	3.5

These figures have been plotted using logarithmic-probability scales, the months being plotted on the probability scale as percentages of nine months, the usual time elapsing from the maximum to the minimum holding of eggs in cold storage. With the exception of the January figures, for reasons already explained, each series plotted approximately in a straight line, and from this line was determined the figures employed in preparing Figure 2 upon arithmetic-logarithmic scales, which shows the expected seasonal variance in the ammonia content of commercial cold-storage eggs when sold at retail. The figures from September 1 to October 15, as well as those from February 15 to March 1, are extrapolated.

The zone between the upper and lower quartile represents the estimated content of half the storage eggs on the market. It is to be expected that 25 per cent of commercial cold-storage eggs will be above the upper quartile, and 25 per cent will be below the lower quartile, in ammonia content. The actual market conditions indicate that cold-storage eggs of low ammonia content soon disappear, and during February they are practically all gone. This is the result of commercial conditions. During the early part of the season it is of financial advantage to the unscrupulous dealer to sell the better grade of cold-storage eggs as fresh eggs at fresh-egg prices. The better grades of cold-storage eggs are therefore removed from storage prior to the middle of January, after which there is no particular advantage in violating the cold-storage egg law because of the usual seasonal decrease in the price of all eggs.

A compilation of eleven hundred analyses of cold-storage eggs collected during the entire season for a period of five years, and plotted upon logarithmic-probability scales, is shown in Figure 3. The points form a straight line between 2.1 and 4.3 mg. of ammonia content and represent about 95 per cent of the total samples. It is therefore reasonable to assume that it is improbable but not impossible to market cold-storage eggs with an ammonia content below 2.1 mg. per 100 grams.

Although the ammonia content of some of these eggs was above 4 mg. per 100 grams and they were not perceptibly rotten as judged by the odor, this fact cannot be construed as showing that broken-out eggs containing such amounts of ammonia are not decomposed, because considerable of the excess of ammonia in such "shell eggs" is caused by evaporation, which increases the fat as well as the ammonia.

Jenkins and Pennington[4] in 1919 studied the commercial preservation of eggs by cold storage. They showed the changes in ammonia content of sixty lots of eggs stored at different times during the season. The geometric means of all these figures representative as of the first of each month were calculated by the writer and were found to be slightly above those of the median line in Figure 2, and for the months

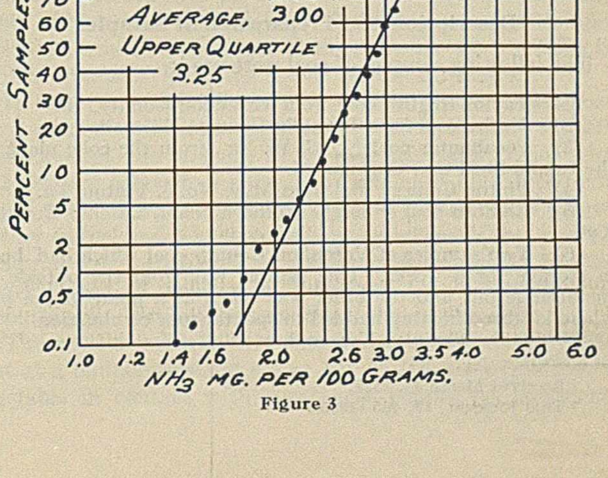

Figure 3

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[3] For a description of this type of plotting see Whipple, *J. Franklin Inst.*, **182**, 37, 205 (1916); "Vital Statistics," p. 392, John Wiley & Sons, Inc.

[4] *U. S. Dept. Agr., Bull.* **775**.

covered by the chart the ammonia content is as follows: September, 2.50; October, 2.72; November, 2.83; December, 2.86; January, 2.94; February, 3.26; and March 3.35 mg. per 100 grams.

Conclusion

It is an axiom in the egg business that with an advance in price deliveries should be delayed in anticipation of further advances, and as prices decline the goods should be rushed to market in order to avoid losses by continued declining prices. The consumer can take advantage of this trade custom by watching the wholesale quotations published each day in the newspapers. He should purchase the best grade of cold-storage eggs in the early part of the season when the price of the non-storage eggs is high and advancing, but when the prices begin to drop he should buy the non-storage variety.

Effect of Weathering on the Softening and Solidification Points of Coal[1]

By T. E. Layng and A. W. Coffman

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MANY methods have been used for the storage of coal, but none have been perfect, so that it is necessary to furnish a control test for storage which will enable the consumer to move his coal at such a time as will conserve to the best advantage the heating and coking properties of the fuel. It was with the hope of establishing such a control test that this study of the effect of weathering on the softening and solidification points of coal was undertaken.

Apparatus and Method

The apparatus and manipulation used for the determination of the softening and solidification points of coal are described in detail by Layng and Hathorne[2] in their work on the determination of the temperature of plasticity. In brief, this method consists of passing nitrogen through a small mass of 20- to 60-mesh coal, simultaneously heating the coal mass in a combustion tube surrounded by an electric furnace. As the temperature increases the coal softens and offers resistance to the flow of the nitrogen, setting up a back pressure which is measured by means of a manometer. The pressure and temperature are noted at regular intervals.

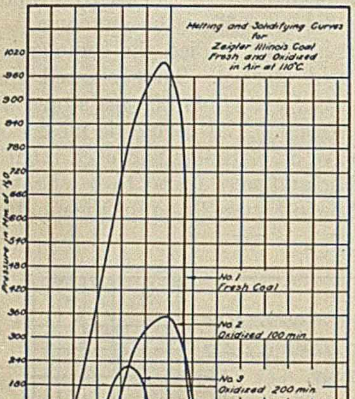

Figure 1

Description and Preparation of Samples

The following samples of coal were used:

(1) Taylor-English coal from Vermilion County, Ill.
(2) Ziegler coal from Franklin County, Ill.
(3) Pocahontas coal No. 3, W. Va., from the coke plant of the Inland Steel Co., Chicago, Ill.
(4) Vinton Colliery coal from Mine No. 6, Vinton, Pa.
(5) Elkhorn coal from the Elkhorn Seam, Latcher County, Ky.
(6) Two samples of Vermilion County coal which had been in storage for 6 weeks. One sample was from the outside of the storage pile and the other was taken at a point in the pile where localized heating had led to spontaneous combustion.
(7) Jellico County, Ky., coal.
(8) O'Gara Coal Co., Saline County, Ill.
(9) United Electric Coal Co., Mine No. 4, Vermilion County, Ill.
(10) Hickory Hill coal, Gallatin County, Ill.

All samples were obtained fresh. All were ground through a coffee mill and sized to pass through a 20-mesh but not through a 60-mesh screen. Oxidations were carried out under a stream of oxygen in a constant-temperature oven at 110° C. All preheated samples were heated in the tube of the apparatus immediately before the test was made. In determining the temperatures of plasticity a rate of heating of 2° C. per minute was used over the critical range.

Interpretation of Results

Table I lists the results obtained on five different coals that had been weathered by accelerated oxidation at 110° C. for various periods of time. It should be noted that such a weathering increases the temperature of initial plasticity, decreases the maximum pressure, and decreases the temperature of solid coke formation; furthermore, that such an oxidation progressively decreases the quality of the coke formed. Figures 1 and 2 show typical sets of data plotted graphically. Table I also shows similar data for a coal taken from storage. In this case also the changes took place in the portion of coal which had undergone excessive weathering. This shows that the changes of a coal upon oxidation are of such a nature that it should be possible to use the softening and solidification points as an indication of the extent of weathering. Coals that are plastic over a greater range of temperature are more difficult to oxidize and may consequently be stored with less difficulty.

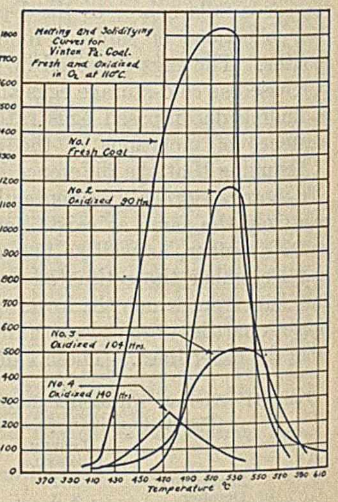

Figure 2

Table II shows results obtained upon preheating coals to various temperatures in both air and nitrogen and then cooling in the same atmosphere before determining their range of plasticity. A temperature of 150° C. in air seems to be the maximum to which a coal can be heated without being

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[1] Received March 31, 1927.

[2] This Journal, 17, 165 (1925).

Table I—Temperatures of Initial Plasticity, Maximum Pressure, and Coke Formation for Fresh and Oxidized Coals

Initial Plasticity °C.	Max. Pressure Mm.	Temp. Max. Pressure °C.	Coke Formation °C.	Coke Quality	Time of Oxidation[a] Hours
		TAYLOR-ENGLISH, VERMILION COUNTY, ILL.			
375	504	390	445	Poor	Fresh coal
382	430	432	480	Weak	1.5
383	324	418	470	Very weak	2
395	90	415	470	Powder	3
399	13	414	452	Powder	4
		ZIEGLER, FRANKLIN COUNTY, ILL.			
378	998	465	512	Poor	Fresh coal
404	350	467	512	Weak	1.75
396	230	438	482	Very poor	3.5
376	74	426	477	Powder	7
		POCAHONTAS			
418	1244	518	600	Strong	Fresh coal
432	1385	545	495	Denser	42
438	240	431	576	Weak	56
436	174	495	535	Very poor	90
		VINTON COLLIERY, MINE NO. 6, VINTON, PA.			
403	1800	513	595	Good	Fresh coal
418	1289	535	590	Denser	56
405	1172	530	584	Very dense	90
453	473	556	600	Medium	104
417	246	478	540	Very poor	140
		ELKHORN, LATCHER COUNTY, KY.			
385	755	431	480	Very porous	Fresh coal
388	510	434	490	Denser	15
395	324	438	483	Weak	20
398	23	430	453	Powder	300
		VERMILION COUNTY, ILL., FROM STORAGE PILE			
373	219	413	481	Weak	Outside of pile; storage 6 weeks
375	86	417	469	Powder	Inside of pile; local heating

[a] Temperature of oxidation, 110° C.

detrimental to its coking properties, while preheating may be carried on to higher temperatures in an inert atmosphere without affecting the nature of coke formed. In some cases preheating coal is beneficial to its coking properties. This should be indicative of the extent to which heating should be allowed to progress in storage.

Table II—Temperatures of Initial Plasticity, Maximum Pressure, and Coke Formation for Fresh and Preheated Coals

Initial Plasticity °C.	Max. Pressure Mm.	Temp. Max. Pressure °C.	Coke Formation °C.	Coke Quality	Preheating Treatment Temp. °C.	Preheating Treatment Medium
		JELLICO COUNTY, KY.				
372	754	420	491	Good	Fresh coal	
374	550	424	474	Better than original	150	Air
361	104	410	444	Poor	200	Air
368	94	390	420	Very poor	250	Nitrogen
377	780	439	473	Good	300	Nitrogen
375	480	452	490	Fair	350	Nitrogen
		O'GARA COAL CO., SALINE COUNTY, ILL.				
350	780	480	497	Fair	Fresh coal	
380	560	420	466	Fair	150	Air
380	386	407	470	Weak	200	Air
350	206	402	488	Powder	250	Air
367	12	394	510	Powder	350	Air
383	40	400	445	Fair	250	Nitrogen
396	40	415	458	Powder	350	Nitrogen
		UNITED ELECTRIC COAL CO., VERMILION COUNTY, ILL.				
349	911	442	491	Fair	Fresh coal	
349	530	404	451	Good	250	Nitrogen
390	17	413	434	Powder	350	Nitrogen
		HICKORY HILL, GALLATIN COUNTY, ILL.				
356	504	404	491	Fair	Fresh coal	
350	454	410	434	Fair	300	Nitrogen
345	314	396	435	Poor	350	Nitrogen

Preparation and Properties of Diethyleneglycol Dinitrate[1,2]

By Wm. H. Rinkenbach

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Diethyleneglycol dinitrate may be obtained by the nitration of diethylene glycol with mixtures of nitric and sulfuric acids. Yields, emulsification, and safety of the operation depend upon the type of nitrating mixture used.

The principal properties of the compound have been studied and recorded. Although comparatively insensitive, the compound is explosive when mixed with similar compounds. For this reason it will probably be of some interest in explosives practice, particularly because several of the other properties found add to the value of the compound from this viewpoint.

DIETHYLENEGLYCOL dinitrate, $CH_2(NO_3).CH_2.O.CH_2.CH_2(NO_3)$, not having as yet been described in the literature, a study of its synthesis and properties was undertaken as a part of a program dealing with the glycols and their nitric esters.

Preparation

Wurtz[3] found that nitric acid reacts with diethyleneglycol to yield glycolic, oxalic, and another unnamed acid but did not try the effect of a mixture of nitric and sulfuric acids.

Nitrating mixtures containing varying percentages of water and of nitric and sulfuric acids were made up in the usual way. A measured quantity was cooled, and to this was added a weighed quantity of diethylene glycol, which was purified as described in a previous paper.[4] It was added in small portions with continuous agitation of the mixture, care being taken to maintain the temperature between 5° and 10° C. The time required to complete the nitration was usually 30 minutes.

The results varied considerably with the strength of the acid employed. With the most concentrated acids the dinitrate separated as an oily, upper layer, which decomposed vigorously when allowed to stand in contact with the spent acid at the same temperature for a short time, or when the temperature of the liquid was allowed to rise slightly during the course of separation. With the least concentrated nitrating acids no separation took place or there was formed an emulsion of the oily product in the spent acid which would not separate within 1.5 hours. In this case it was necessary to pour the mixture into ice and water and separate the dinitrate, which then settled out. Nitrating acids of composition intermediate between these extremes gave emulsions which separated into two layers within 1.5 hours.

In either case the volume of the crude product was measured immediately after separation or precipitation. It was then washed one or more times with ice water, twice with a 2 per cent solution of potassium carbonate, and three more times with ice water; each washing was carried out in a separatory funnel and accompanied by agitation. The purified material was then placed in a sulfuric acid desiccator to remove traces of moisture and the weight of pure product determined. Table I summarizes the experiments.

The results indicate that the nitration should be carried out at a temperature not above 10° C., that the product is unstable in contact with spent acid containing free nitric

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[1] Received March 30, 1927.

[2] Published with approval of the Director, U. S. Bureau of Mines.

[3] *Ann. chim.*, [3], **69**, 317 (1863).

[4] Rinkenbach, This Journal, **19**, 474 (1927).

acid, and that the best yields are obtained by using no excess of a nitrating acid containing 25 per cent nitric acid and from 5 to 10 per cent of water. It would appear that the best procedure is to add the glycol to such a nitrating acid, keep the temperature at or below 10° C., pour the resulting emulsion into three times its weight of ice and water and purify the oily precipitate in the manner previously described.

Table I—Preparation of Diethyleneglycol Dinitrate

Nitrating Mixture			HNO_3 Excess over Theoretical	Crude per 100 Grams Glycol	Washed Oil per 100 Grams Glycol	Yield	
H_2O	HNO_3	H_2SO_4				Crude	Washed
%	*%*	*%*	*%*	*Cc.*	*Grams*	*%*	*%*
1.3	38.7	60.0	20	78	[a]	59	
1.3	38.7	60.0	10	[b]	[b]		
8.0	30.0	62.0	0	34+	[c]	26+	
15.5	27.8	56.7	10	90	98.5	68	53
15.5	27.8	56.7	5	93	104	70	56
25.0	25.0	50.0	10	[d]	18		10
10.7	25.0	64.3	0	[e]	113		61
8.0	25.0	67.0	0	[f]	116.5		63
5.0	25.0	70.0	31.5	92[g]	84.6	69	46
5.0	25.0	70.0	0	92[h]	112.6	69	61

[a] During transference to funnel temperature rose slightly and violent decomposition ensued; complete separation had taken place.

[b] Carried out at 22° C.; violent decomposition took place before all the glycol could be added.

[c] Standing at 5° C., decomposition took place 15 minutes after completion of nitration, when some product had separated.

[d] Emulsion formed; poured into ice and water after 2 hours' standing at 5° C.

[e] Emulsion formed; only partial separation; poured into ice and water.

[f] Emulsion formed; no separation; poured into ice and water.

[g] Emulsion formed; no separation; poured into ice and water; volume of oil, 92 cc.

[h] Emulsion formed; no separation; poured into ice and water; volume of oil, 92 cc.

Properties

The diethyleneglycol dinitrate prepared by this method was allowed to stand in a sulfuric acid desiccator for 2 months to remove all trace of moisture or other volatile impurities. During part of this period the pressure was reduced to 1 cm. of mercury. Analysis by means of the nitrometer at the end of this time showed a nitrogen content of 14.12 per cent as compared with a theoretical content of 14.29 per cent. This material was used for the purpose of studying the properties of the compound.

Diethyleneglycol dinitrate is a clear, colorless liquid that has no apparent odor.

SPECIFIC GRAVITY—Nineteen determinations of the specific gravity of diethyleneglycol dinitrate at temperatures ranging from 1.1° to 29.7° C. were made by means of the Westphal balance, using a calibrated thermometer and immersing the container in a water bath. The values obtained, when plotted, gave a straight line, and from this the values in Table II were read off at regular temperature intervals.

Table II—Specific Gravity Determinations

Temperature	Sp. Gr.	Temperature	Sp. Gr.
° C.	*x°/15° C.*	*° C.*	*x°/15° C.*
0.0	1.4092	20.0	1.3846
5.0	1.4030	25.0	1.3785
10.0	1.3969	30.0	1.3724
15.0	1.3908		

FREEZING POINT—By means of a calibrated mercury thermometer, a transparent Dewar flask of 50 cc. capacity and having a long neck, an acetone bath chilled to from −40° to −20° C., and using about 20 grams of material, it was found that when stirred during cooling, diethyleneglycol dinitrate freezes after some supercooling. In one case the liquid supercooled to −35° C. Freezing point values of −11.4°, −11.2°, −11.2°, and −11.4° C. (average −11.3° C.) were obtained in this way. On warming, the crystals melt at about this temperature, but the liquid-solid mixture does not maintain an absolutely constant temperature until all the solid has melted; a slow rise is apparent in spite of vigorous stirring.

Calibration of the thermometer used makes possible a correction of the value given[5] for the freezing point of the homologous compound, ethyleneglycol dinitrate. On applying the necessary correction, this is found to be −22.75° C. instead of the given value (average) of −22.3° C.

VISCOSITY—The viscosities of diethyleneglycol dinitrate and nitroglycerin were determined by means of a viscometer of the pipet type, which was calibrated at definite temperatures by means of liquids having known viscosities. (Table III)

Table III—Viscosity Determinations

Temperature	Diethyleneglycol Dinitrate		Nitroglycerin	
	Time of flow	Viscosity	Time of flow	Viscosity
° C.	*Seconds*	*Poises*	*Seconds*	*Poises*
15.0	50.3	0.099	105.9	0.511
17.5	48.9	0.085	93.0	0.423
20.0	47.8	0.078	84.0	0.355
22.5	46.8	0.073	77.0	0.303
25.0	45.9	0.070	71.8	0.283
27.0	45.1	0.066	68.0	0.258

REFRACTIVE INDEX—The refractive index of diethyleneglycol dinitrate was observed at twenty-one points between 2.55° and 43.2° C. by means of a Zeiss refractometer equipped with a water jacket and a calibrated thermometer and employing sodium light. The values were plotted against temperature readings and found to represent a straight-line function. From this the values in Table IV were read off at regular temperature intervals.

Table IV—Determinations of Refractive Index

Temperature	Refractive Index	Temperature	Refractive Index
° C.		*° C.*	
0.0	1.4593	20.0	1.4517
5.0	1.4574	25.0	1.4498
10.0	1.4555	30.0	1.4479
15.0	1.4536	35.0	1.4460

HEAT OF COMBUSTION—Calorimetric determinations of the heat of combustion of diethyleneglycol dinitrate gave the values in Table V.

Table V—Determinations of Heat of Combustion

Heat of Combustion	At Constant Volume	At Constant Pressure
Calories per gram	2798	2792
Kilogram calories per gram molecule	548.7	547.5

HEAT OF FORMATION—Using the values 94,400 and 67,500 calories per gram molecule as the heats of formation of carbon dioxide and liquid water, respectively, the data (Table V) for heat of combustion gave the values in Table VI.

Table VI—Heat of Formation

Heat of Formation	At Constant Volume	At Constant Pressure
Calories per gram	505.35	510.25
Calories per gram molecule	99,100	100,060

SOLUBILITY EFFECTS—At ordinary temperatures diethyleneglycol dinitrate is completely miscible with nitroglycerin, ethyleneglycol dinitrate, ether, acetone, methanol, chloroform, benzene, toluene, aniline, nitrobenzene, glacial acetic acid, and glycol diacetate. It is immiscible or slightly soluble in ethanol, carbon tetrachloride, and carbon disulfide. Its solubility in water was found to be 4.1 grams per liter of water at 24° C.

HYGROSCOPICITY—Diethyleneglycol dinitrate is slightly hygroscopic. Samples kept in air spaces saturated with water vapor at room temperature (20° to 30° C.) and weighed regularly during periods of from 7 to 15 days showed maximum gains in weight within 48 hours. These were 0.34 and 0.44 per cent of the weight of the samples.

VAPOR PRESSURE—Using the air-bubbling method, in

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[5] Rinkenbach, THIS JOURNAL, 18, 1195 (1926).

which 19 liters of thoroughly dried air were passed through pure material at a fixed temperature and the loss in weight was determined, the vapor pressure of diethyleneglycol dinitrate at 22.4° C. was found to be 0.0098, 0.0079, and 0.0044 (average 0.007) mm. of mercury.

When a drop of the material, contained in a melting point tube, was heated in an oil bath, ebullition began at 161° C. No decomposition was apparent, so this may be taken as the boiling point of the compound.

An effort to determine the boiling point at reduced pressure showed that when a larger quantity was slowly heated to the boiling point the compound underwent a partial decomposition that resulted in variable values and sometimes culminated in the explosion of the material. It was therefore impracticable to derive a vapor-pressure curve for the pure substance.

Inflammability—Diethyleneglycol dinitrate could be ignited only with difficulty; it was necessary to heat it to a point above that of the temperature of the air. When ignited it burned quietly with a yellow, luminous flame.

When small quantities held in the tip of capillary tubes were thrust into a gas flame, no explosion took place in five trials. Some of the material was ejected as a vapor which burned readily and quietly at the mouth of the tube.

Explosibility—The constitution of diethyleneglycol dinitrate would lead to the assumption that, like similar compounds, it is of an explosive nature. Calculation of explosives constants for this substance and for nitroglycerin and glycol dinitrate for purposes of comparison are given in Table VII. For this purpose the equation of decomposition

$$C_4H_8N_2O_7 = N_2 + 0.5474\ CO_2 + 3.4526\ CO + 1.5474\ H_2 + 2.4526\ H_2O$$

was derived by the use of data for the water-gas equilibrium. Extrapolated values of those given by Partington and Shilling[6] for the specific heats of the various products of explosion were used for calculating the heat capacities of the mixture at various temperatures. From these the temperature of explosion was found by the diagrammatic method.

Table VII—Comparison of Explosives Constants

Compound	Temp. of Explosion (t) °C.	Gas Produced from 1 kg. at 760 mm. and: 0° C.	Gas Produced from 1 kg. at 760 mm. and: t	Pressure when 1 kg. Is Exploded in 1 Liter	Energy Developed on Exploding 1 kg. Material
		Liters	*Liters*	*Kg./sq. cm.*	*Meter-kg.*
Diethyleneglycol dinitrate	2810	1,028.58	11,615	11,999	410.7 × 10^6
Glycol dinitrate	4209	736.93	12,099	12,498	695.7 × 10^6
Nitroglycerin	4177	715.53	11,663	12,048	647.8 × 10^6

Table VIII—Sand Bomb Tests

Charge of Mixture	Explosive in Charge	Sand Crushed by 0.300 Gram Mercury Fulminate and: Diethyleneglycol dinitrate	Nitroglycerin	Glycol dinitrate	50% Nitroglycerin, 50% diethyleneglycol dinitrate	50% Glycol dinitrate, 50% diethyleneglycol dinitrate
Gram	*Gram*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*
0.150	0.090	14.6	20.15	20.1	19.6	19.0
0.250	0.150	17.8[a]	26.85	27.7	25.35	26.15
0.333	0.200	2.9[a]	33.9	34.9	31.1	30.8
0.500	0.300	2.2[a]	44.25	47.3	43.0	41.6
0.833	0.500	1.9[a]	68.0	70.3	60.3	62.9

[a] Incomplete detonation.

In order to test the actual explosibility of diethyleneglycol dinitrate and give a direct comparison, the following procedure was carried out:

> Mixtures of exactly 40 per cent of kieselguhr and 60 per cent of liquid explosive by weight were made up, diluted with ether, and stirred until all the ether had been evaporated and an even mixture remained. Weighed charges of each of these mixtures were pressed into No. 8 detonator shells (0.300 gram of mercury fulminate was added in each case), the whole was surmounted by a reënforcing cap, and after being subjected to a pressure of 50 pounds (91,700 grams per sq. cm.) the detonator so constructed was fired in the No. 2 standard sand test bomb.[7] The amount of sand crushed was found by sieving and weighing. Table VIII gives the results.

These results indicate that diethyleneglycol dinitrate is so insensitive that its explosive is not sufficiently strong to produce continuous propagation under conditions which permit nitroglycerin or glycol dinitrate to produce this effect. In admixture with either of these other compounds, however, diethyleneglycol dinitrate can be completely detonated and shows an explosive effect but little less than that of either of the other compounds. From the values given, by taking into account the amount of crushing due to the fulminate, it is possible to calculate the crushing effects of different weights of diethyleneglycol dinitrate when completely detonated, as well as those of the other compounds (Table IX). For purposes of comparison, the values found for mercury fulminate are added.

Table IX—Crushing Effects of Diethyleneglycol Dinitrate

Explosive	Sand Crushed by: Diethyleneglycol dinitrate	Glycol dinitrate	Nitroglycerin	Mercury fulminate
Gram	*Grams*	*Grams*	*Grams*	*Grams*
0.05	5.5	6.7	7.4	
0.10	9.9	13.4	13.3	
0.20	18.7	27.1	25.0	4.0
0.30	27.6	39.5	36.8	7.8
0.50	45.0	62.5	60.2	16.5

These comparative values agree quite well with those calculated from theoretical considerations.

Sensitivity to Impact—From the foregoing facts concerning inflammability and propagation of detonation, it would appear that diethyleneglycol dinitrate is a comparatively insensitive compound. Tests made on the small impact machine[8] on drops of the pure substance showed that it would not detonate when subjected to the blow of a 500-gram weight falling a distance of 110 cm., whereas glycol dinitrate and nitroglycerin detonated when the weight fell distances of 110 cm. and 70 cm., respectively.

Saponification—Diethyleneglycol dinitrate is not easily saponified. No decomposition ensued when dissolved in 3 per cent alcoholic potash; the unchanged ester was recovered on evaporation of the solution at air temperature. This indicates a high degree of stability at ordinary temperatures.

Toxicity and Animal Poisoning—A dilute solution of diethyleneglycol dinitrate in water was injected intramuscularly into guinea pigs. A dosage of 0.0000006 gram of the ester per 100 grams of the animal weight is proportional to the standard dosage prescribed for the injection of nitroglycerin with human beings. Although in some cases double this dosage was used, none of the guinea pigs showed untoward symptoms. It is probable, therefore, that diethyleneglycol dinitrate is no more toxic than nitroglycerin.

In order to determine if diethyleneglycol dinitrate would, when absorbed through the skin, cause increase in the blood pressure and consequent headache, a drop of the pure substance was placed on the forearm of each of three subjects, spread, and allowed to absorb. In one case this was expedited by the addition of several drops of ether. In no case were any unusual symptoms apparent, although each of the three persons was definitely sensitive to nitroglycerin poisoning and similar applications of pure nitroglycerin produced violent headaches. It is to be concluded that if diethyleneglycol dinitrate has any of the effects of nitroglycerin on the human system, these are much less marked than are those of the latter.

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[6] "The Specific Heats of Gases," Ernest Benn, Ltd., 1924.

[7] Storm and Cope, *Bur. Mines, Tech. Paper* **125** (1916).

[8] Hall, Snelling, and Howell, *Bur. Mines, Bull.* **15**, p. 101.

Decomposition of Cellulose in Fresh Sewage Solids[1,2]

By H. Heukelekian

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The decomposition of cellulose in unseeded fresh sewage solids was followed both with and without the addition of lime. Cellulose decomposed rapidly under the conditions of the experiment. About 79 per cent of the cellulose disappeared in the first 3 weeks in the unlimed material; in the limed material 73 per cent disappeared in the first week and 96 per cent in 3 weeks. The reduction of volatile matter in the unlimed material was also lower than in that which was limed.

It is suggested that the acid decomposition products retard the decomposition not only of cellulose but to a greater extent that of non-cellulosic organic matter, thus retarding the general progress of digestion.

FOR several years the digestion of fresh solids has been studied in this laboratory and many questions as to the course of digestion have been elucidated. These studies have indicated that digestion proceeds through certain stages until it is complete; that these different stages are characterized by certain well-marked differences, certain products being formed predominantly at certain stages. It has further been intimated that carbohydrates decompose at the first stage, causing a drop in the pH curve which is characteristic of the first stage of digestion. This low pH level persists for a time, indicating that the production of the acids is proceeding in at least the same rate as their disappearance. At the end of this period the pH curve begins to rise, indicating that the decomposition of the acids is proceeding at a faster rate than their production. As the pH value approaches the neutral point digestion is speeded up until it reaches 7.6, where it can be considered as complete for practical purposes.

All these facts have been deduced from chemical analyses without measuring directly the different components of the fresh solids that are undergoing change. It would seem that, since the digestion of fresh solids is due mainly to the transformation of organic material, the study of the decomposition of each component of this organic matter would help to answer many unsolved questions. It would trace the various changes observed above to the transformation of the different components of the organic matter and establish definitely the causal relationship. Also, by following the transformation of each component, we should be able to complete the picture of the digestion as a whole. Two methods of attack are available in this connection: (1) to follow the course of transformation of each individual component of the organic matter during the digestion of fresh solids; (2) to add these components, at first individually and then combined, to ripe sludge in the percentages as they occur in fresh solids and follow the changes produced. The second method would tend to reproduce the digestion of fresh solids in a synthetic way.

Cellulose is one of the most important components of fresh solids. Toilet paper, vegetable matter, and undigested cellulose in the feces add considerably to the amount of cellulose received in a disposal plant. That it would decompose very readily under the existing condition in Imhoff or separate sludge digestion tanks is to be expected, and yet very little is to be found in sewage disposal literature. That its decomposition would have a profound influence in the course of digestion is also to be expected. How completely cellulose decomposes and to what products it gives rise would be of more than passing interest to know. Whether there are any local or seasonal differences in the cellulose content of sewage and the effect of such variations on the general course of digestion would be of added interest. In short, these studies would open a new vista and add to our conception of the biological processes taking place in the course of digestion.

This paper, which is the first of a series of similar studies as outlined above, will touch only on the decomposition of cellulose in fresh solids and the effect of lime on this decomposition.

Methods

The fresh solids were collected in the way usually employed in this laboratory, put into two bottles one of which was adjusted to a pH of 7.4 by the addition of lime whenever necessary, and kept at 25° C. in an incubator.

For cellulose determinations, 100 cc. of the material were dried and then shaken in a shaking machine with 100 cc. of Schweitzer's reagent. The extract was filtered through Gooch crucibles and an aliquot portion was precipitated with 80 per cent alcohol. The precipitate was filtered through Gooch crucibles, washed consecutively with 1 per cent hydrochloric acid, distilled water, 2 per cent alkali, distilled water, again with dilute acid, and then finally with distilled water until free from chlorides. The difference between the dry and ignited weights of the crucible represents the amount of cellulose in the aliquot portion of the material. Care should be taken to make the Schweitzer's reagent saturated. The method of preparation of the reagent, as well as the procedure of the determination, is more completely described elsewhere.[3]

The other determinations were made according to the regular procedures as described in publications from this laboratory.

Accuracy of Cellulose Determinations

To test the accuracy of the technic of cellulose determinations, 100-cc. portions of ripe sludge (7 per cent solids and diluted 1 to 5) were taken and to some were added weighed amounts of cellulose in the form of finely cut filter paper, and cellulose determinations made on them.

Table I—Extraction of Cellulose from Ripe Sludge and Filter Paper Mixtures

No.	Cellulose Added *Mg.*	Cellulose Recovered *Mg.*	Net Cellulose *Mg.*	Recovered *Per cent*
1	0	4		
2	500	519	515	103
3	0	4		
4	200	204	200	100

The results of these tests (Table I) show that the method is dependable. They further indicate that the amount of cellulose in ripe sludge is very small, almost negligible. This fact in itself would be sufficient to show that cellulose decomposition does take place in fresh solids.

Digestion without Lime

Table II gives the results of the digestion of fresh solids without lime. The pH value drops from pH 5.8 to 5.2 within

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[1] Received April 4, 1927.

[2] Paper 343 of the Journal Series of the New Jersey Agricultural Experiment Station, Department of Sewage Disposal.

[3] Waksman and Heukelekian, *Soil Science*, **17**, 275 (1924).

a week and begins to rise slowly after a month. Cellulose decomposes most rapidly in the first 4 weeks, and the pH value begins to rise only after maximum cellulose decomposition has taken place. It is obvious that the decomposition of cellulose under these conditions gives rise to acids which lower the pH value, and it is only after most of the cellulose is decomposed that the pH value begins to rise. Whether this rise in pH value is due to the destruction of the organic acids produced as a result of cellulose decomposition or to the neutralization of these acids by alkaline products of digestion, or to both, cannot be definitely stated at present. If it is due to the first cause, then obviously the rate of production of these acids when cellulose decomposition is proceeding rapidly is greater then their rate of destruction and this relationship changes when most of the cellulose is decomposed. If it is due to the neutralization of these acids by alkaline products of digestion then it is likewise possible that the rate of production of acid products in the beginning is greater than that of alkaline products.

Table II—Digestion of Cellulose in Fresh Solids without Addition of Lime

TIME	pH	B. O. D.	SOLIDS	VOLATILE MATTER	CELLULOSE ON BASIS VOLATILE MATTER
Days		*P. p. m.*	*Per cent*	*Per cent*	*Per cent*
0	5.8	7400	3.90	78.6	10.4
8	5.2	7760	3.93	76.2	6.6
15	5.2	8530	3.80	74.9	4.5
22	5.2	10570	3.75	74.2	2.2
29	5.3	...	3.58	73.9	2.5
39	5.3	10190	3.61	74.1	1.9
46	5.4	11630	3.48	74.1	2.3
60	5.4	10280	3.44	74.2	2.1
74	5.4	9120	3.47	73.5	...

Table III—Digestion of Cellulose in Fresh Solids Adjusted with Lime

TIME	pH ORIGINAL	LIME ADDED	pH ADJUSTED	B. O. D.	SOLIDS COR. FOR LIME	VOLATILE MATTER	CELLULOSE ON BASIS VOLATILE MATTER
Days		*Grams*		*P. p. m.*	*Per cent*	*Per cent*	*Per cent*
0	5.8	5.1	7.6	7400	3.81	78.6	10.4
8	6.3	4.0	7.4	9020	3.74	70.0	2.8
15	6.9	2.0	7.4	10760	3.80	62.0	1.6
22	6.9	1.0	7.5	13380	3.67	64.9	0.4
29	7.2	0.5	7.5	...	3.50	63.5	0.7
39	7.4	...	....	9500	3.14	59.7	...
46	7.4	...	...	11110	2.73	58.3	1.3
60	7.4	...	...	5430	2.50	58.1	1.1
74	7.2	...	...	3300	2.29	53.4	...

Effect of Lime Addition

According to the data on the limed material, the cellulose decomposition products—e. g., the acids—actually hinder the decomposition of other materials; hence when cellulose decomposition is at its height and for some time thereafter, the decomposition of other materials is retarded and the alkaline products are produced only slowly to neutralize the acids. The reduction of volatile matter in the unlimed materials is lower than in those that are limed (Table IV, also Figures 1 and 2). Further, whereas a greater percentage of the volatile matter reduction can be accounted for by cellulose decomposition in the unlimed material in the first 3 weeks, only a part of the total reduction of volatile matter can be due to cellulose decomposed in the limed material (Table IV), and this in spite of the fact that a greater percentage of cellulose is decomposed in this case. This is brought out clearly by Figures 1 and 2, where the difference between cellulose decomposed and volatile matter reduction is greater in the limed than in the unlimed material. In the unlimed material the curves are more or less identical for 3 weeks, when a slight divergence begins. Hence the acid products of cellulose decomposition retard the decomposition of other constituents—namely, the proteins.

At first it was thought surprising that cellulose decomposition proceeded so rapidly in the unlimed material. However, the organisms decomposing cellulose do not seem to be very much affected by the acid condition. The percentage reduction of cellulose is at first high, and as the amount of cellulose decreases the percentage reduction also decreases until it finally comes to a standstill.

Thus, the first 3 weeks of digestion are predominantly a cellulose decomposition stage. Obviously, the hexoses and the other soluble carbohydrates decompose in the first few days, followed by cellulose decomposition. The third stage would be that of acid regression, due to one or both of the above-named causes.

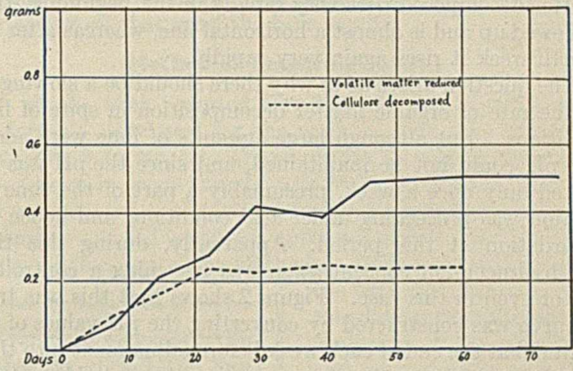

Figure 1—Cellulose Decomposition of Unlimed Material

A week after adjusting the original material of pH 5.8 to pH 7.6 by the addition of 5.1 grams of lime (Table III), the pH value had dropped to 6.3, and 4.0 grams of lime were required to readjust the reaction. From this point on to the fourth week of digestion, the drop in pH value was less and less and the amount of lime required decreased accordingly. At the end of this period the pH value did not drop any more. The rapid change in hydrogen-ion concentration coincided exactly with the rate of cellulose decomposition. Seventy-three per cent of the cellulose decomposed in the first week (Table IV), after which the rate of decomposition dropped, and by the fourth week nearly all the cellulose had disappeared. This correlation between the drop in pH value, the amount of lime added to keep the pH constant, and the rate of cellulose decomposition is a further evidence that organic acids are produced as a result of the decomposition of cellulose.

Although cellulose decomposed rapidly in the unlimed material, it disappeared at a faster rate in the limed material. Within a week 73 per cent of the cellulose disappeared in the limed material and only 36 per cent in the unlimed, while at the end of the third week all the cellulose had disappeared in the limed but only 79 per cent disappeared in the unlimed material. Thus, even though cellulose decomposition can take place in an acid medium, lime stimulates the rate of this decomposition. It also stimulates the decomposition of other materials to a greater extent.

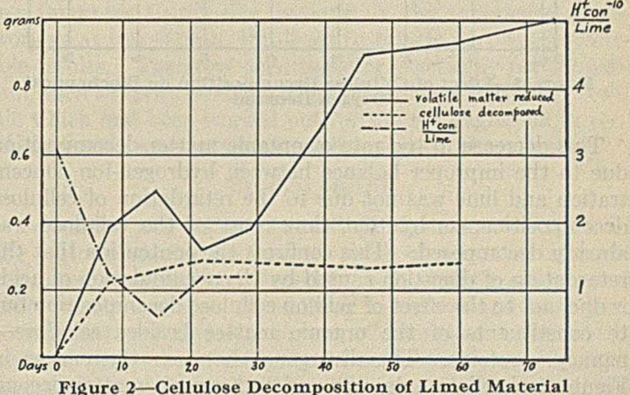

Figure 2—Cellulose Decomposition of Limed Material

The irregularity in the curve for volatile matter reduction (Figure 2) in the first 3 weeks at first seems difficult to explain. The reduction of volatile matter, after proceeding very rapidly for 2 weeks, dropped suddenly during the third. Although a part of this is obviously due to experimental error, since there was according to the determination more volatile matter on the third than on the second, it can be safely said that decomposition of organic matter was at least greatly checked and that the curve should be a horizontal line instead of dropping. Thus the curve for the amount of volatile matter decomposed rises very rapidly in the beginning, then is slowed up and is almost a horizontal line, whereas after the fourth week it rises again very rapidly.

The question arises as to why there should be a slowing up of the rate of organic matter decomposition in spite of lime additions. But although large amounts of lime were added the pH could not be maintained, and since the pH was adjusted only once a week, presumably a part of the time digestion was proceeding under acid conditions and hence the retardation at this period. Apparently, during this time the hydrogen-ion concentration was becoming a controlling factor even in this case. Figure 2 shows that this was true. A curve was constructed by converting the pH values of the material at the end of each week before adjustment into their respective hydrogen-ion concentrations and dividing these by the amount of lime needed to raise the pH values to the optimum of 7.4. It can be readily seen that in the beginning more lime was added in relation to the actual hydrogen-ion concentration, and as the production of acids increased lime was not added in sufficient quantities. The result was depression in the curve instead of a straight line. When the amount of lime added in relation to the hydrogen-ion concentration decreased the rate of volatile matter decomposition decreased; but when the acid production due to cellulose decomposition was reduced, then the relation between the hydrogen-ion concentration and lime required was restored, the curve became a straight line and once more the organic matter decomposition proceeded rapidly.

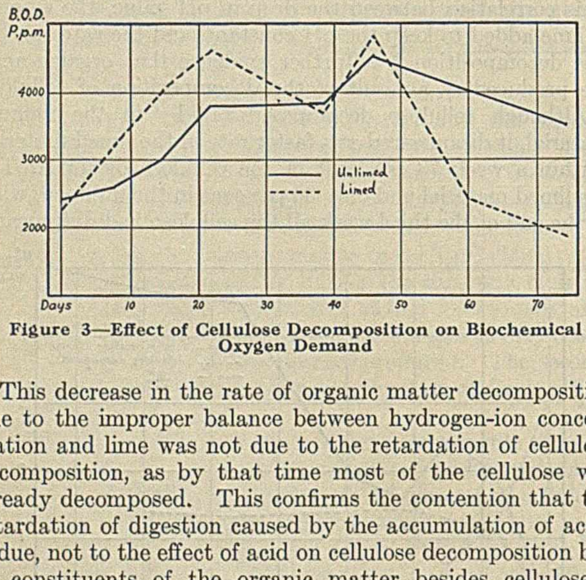

Figure 3—Effect of Cellulose Decomposition on Biochemical Oxygen Demand

This decrease in the rate of organic matter decomposition due to the improper balance between hydrogen-ion concentration and lime was not due to the retardation of cellulose decomposition, as by that time most of the cellulose was already decomposed. This confirms the contention that the retardation of digestion caused by the accumulation of acids is due, not to the effect of acid on cellulose decomposition but to constituents of the organic matter besides cellulose—namely, proteins. The divergence between the curves in Figure 2 of cellulose decomposed and organic matter decomposed becomes greater after the fourth week, when no more lime was necessary to correct the reaction. When corrections are made for the curve of the organic matter decomposed in the limed material, as mentioned above, at no time does the cellulose decomposed account for the total amount of volatile matter that disappeared, and this in spite of the greater rate of cellulose decomposition. In the first place, the initial retardation of non-cellulosic organic matter did not take place in the limed material, and further even after the cellulose decomposition was complete, the organic matter decomposed faster in the limed material than in the unlimed. It should be borne in mind that the unlimed material had still a pH value of 5.4 and, even though the curve for organic matter decomposed is rising, it is not rising at the same rate as it is in the case of the limed material. The figures in Table IV show the same thing in another way. In the beginning only a part of the organic matter decomposed could be accounted for by cellulose decomposition, the percentage rising in the middle as a result of the slowing up of the decomposition of organic matter and falling again because of the greater rate of organic matter decomposition, cellulose decomposed being almost negligible after the first period.

Table IV—Relation between the Reduction of Volatile Matter and Cellulose

	Reduction Volatile Matter		Reduction Cellulose Basis Volatile Matter		Reduction Volatile Matter Accounted for by Cellulose	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
Days	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
0	...	...	...	...	...	...
8	2.3	11.9	36.6	73.0	100.0	60.0
15	7.2	15.4	56.8	84.6	77.3	54.0
22	9.2	10.1	78.9	96.2	85.7	92.0
29	13.7	11.9	76.0	93.2	54.7	75.0
39	12.8	21.0	81.8	...	64.1	...
46	16.0	27.9	77.9	87.5	49.0	31.0
60	16.7	29.2	79.8	89.4	49.0	30.0
74	16.7	43.6	...	...	...	...

Biochemical Oxygen Demand

Biochemical oxygen demand determinations were made on the materials at different intervals to find out whether cellulose decomposition caused a greater instability of the digesting material. Figure 3 represents the results calculated on the basis of volatile matter present at each date of determination. They are rather inconclusive and it cannot be definitely said whether the higher B. O. D. in the limed material is due to the decomposition of cellulose and its products or to that of other substances. But since lime stimulates the decomposition of non-cellulosic materials to a greater extent than cellulose decomposition itself, the high B. O. D. of the limed material would seem to be associated with the former. If the acid decomposition products of cellulose were unstable or caused instability, the curve of B. O. D. of the unlimed material should be higher. This conclusion is, however, difficult to reconcile with the fact that the B. O. D. of the limed material dropped suddenly after the third week, when cellulose decomposition was almost complete but the decomposition of non-cellulosic material was proceeding at a high rate. It is quite possible, however, that this drop of B. O. D., coming right after the disappearance of cellulose, is merely a coincidence and not a causal relationship, and that this drop of B. O. D. is due to the disappearance of some other substance besides cellulose—namely, to protein decomposition products.

Conclusions

1—Cellulose decomposes rapidly when fresh sewage solids are digested.

2—The decomposition of cellulose takes place during the first 3 or 4 weeks of the digestion.

3—Lime accelerates cellulose decomposition.

4—The slow rate of digestion when fresh solids are digested is due to the action of acid decomposition products on the digestion of non-cellulosic organic matter.

5—Lime, by neutralizing these acid decomposition products, accelerates the rate of decomposition of non-cellulosic substances.

Lubricating Oils as Insecticides in Dormant Spraying[1]

By E. L. Green

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A series of lubricating oils, selected to represent the range of available oils, was tested as sprays for San José scale and leaf rollers under set conditions in 1925 and 1926. Their viscosities and boiling ranges were taken and compared with their performance as insecticides. Specifications for oils that may be expected to be successful are indicated and the relation of these properties to the toxicity is pointed out.

CONSIDERING the impunity with which petroleum products are handled by men, it is remarkable that they are quite harmful to insects. This makes them peculiarly useful as insecticides because they involve a minimum of danger to the men who may come into contact with them.

In killing insects oily substances do not enter by way of the mouth and digestive system, but pass into the body directly from the outside either as vapor or liquid.[1,*] Where the effect of the vapor is desired, the "lighter," low-boiling fractions of petroleum are used, and the space in which they are applied should be closed. In orchards, where wind currents prevent a vapor treatment, oils are applied directly as liquid. The oil is dispersed in a relatively large volume of water, which is used to carry it to the insects. The water eventually evaporates, leaving the oil in place. The same amount of oil without a carrying agent would be a tenuous mist, difficult to direct, and larger amounts are expensive and harmful to the trees.

In Washington oil sprays have been used chiefly for the control of insects such as the San José scale (*Aspidiotus perniciosus* Comstock) and fruit-tree leaf roller (*Archips argyrospila* Walk). The studies reported here were a part of an investigation conducted coöperatively by the Divisions of Entomology and Chemistry of the Washington Agricultural Experiment Station during the last three years. The report includes only those uses of oil for sprays applied in the early spring before any foliage is exposed, and is confined to an attempt to discover an oil of maximum toxicity and, by determining its properties, to set up a specification for spray oils that can be expected to be effective in killing insects.

The earlier investigators did not make critical studies of the nature of the oils they used. Beginning about 1910 more attention was paid to this part of the problem, and by 1922 it could be confidently stated that of all the fractions of petroleum the lubricating oils possessed the greatest value in sprays of this kind.[2,3] Crude oil as a whole, and the fractions kerosene, naphthas, burning oils, and gas oils had been tried and rejected in favor of the lubricating oils.

Work in 1924

In 1924, fifteen oils obtained from three oil companies were tried in the field and studied in the laboratory. The type of emulsion was established that was used as a standard treatment on the various oils in all later work. It was also found that a history of the oils, including data from the refinery, was needed in making selections for study. In 1925 and 1926, samples were requested that would conform to certain specifications in order to get definite answers to the questions in mind. In the 1924 studies lubricating oils having very little refining treatment[5] gave as good control of the insects as oils that had been more carefully prepared. Thus it seemed reasonable to neglect, at least for the time, the question of refining and to determine the fraction of the lubricating oil that gave the best results.

Method of Preparing Sprays

In all the work reported here the oils were emulsified by the formula developed for the work in 1924 and called for brevity W. S. C. No. 1.[4] The emulsifier is a solution of potash fish-oil soap in crude cresylic acid.[4,6] This method of emulsion was adopted as a standard treatment in tests where other factors were varied because it appeared to give more uniform emulsions than any other methods. Deliberate variations in the time and manner of stirring did not visibly affect the character of the emulsion, and so it seems reasonable to assume that the diluted sprays were protected from the effects of unintentional variations. The same thing was not found to hold for other types of emulsion. Furthermore, during the three years this prescription has been used at the Washington Station it has consistently yielded the highest rates of kill.

Collection of Field Data on Toxicity

The relative toxicity of the various oils was determined by spraying trials in orchards infested with San José scale and orchard leaf roller. The writer was present at all the field experiments reported and made up the spray solutions. Mr. A. Spuler, of the Division of Entomology, applied the sprays and made the insect studies, particularly the mortality determinations (Table II). The methods used to determine the mortality of both insects have been published.[3,7]

The data obtained show a disappointingly small degree of contrast in many cases. This situation cannot be improved by departing from the optimum conditions and using others less favorable to the oils, because, in the experience of the workers at this station, this leads to erratic and unreproducible results. Therefore conditions for practically perfect control, such as spray strength, type of emulsion, and spray technic which had been worked out for the red engine oil in previous years, were maintained throughout these tests.

Studies on Oils

Petroleum and its commercial products are mixtures of the various members of several series of saturated and unsaturated hydrocarbons, together with varying amounts of other substances that, in addition to carbon and hydrogen, contain nitrogen, sulfur, or oxygen.[8] Isomers are also usually present, making the difficulty of separating the individual components very great.[9,10,11] The most careful fractional distillation produces portions which not only do not show a fixed boiling point, but also overlap the boiling ranges of the adjacent fractions, even when only one series is present.

In all the series, the hydrocarbons of higher molecular weight have the higher boiling points. Hence in any fractionation of petroleum, the later, higher boiling fractions show the higher

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[1] Received March 23, 1927. Published with the approval of the Director of the Washington Agricultural Experiment Station as Scientific Paper 138, College of Agriculture and Experiment Station.

* For numbers in text see bibliography at end of paper.

mean molecular weights. The viscosity and specific gravity are also higher.

The fractions of a single crude oil may perhaps be identified by one of these constants, but with oils prepared from different crude oils this is not true. The representatives of the various homologous series and isomers of the same homologous series of hydrocarbons may then be present in different proportions and where these have not been removed the accessory substances will vary greatly. Consequently two petroleum products from different crudes may have, for instance, similar viscosities and yet in other respects show decided differences. For this reason it may be possible to select commercial oils by tests for definite purposes, but to identify them is often impossible and always extremely difficult.

In any homologous series of hydrocarbons the properties generally change by steps from one member to the next in the series. Crude oils, being made up of a mixture of the members of several homologous series of hydrocarbons besides other substances, are divided by fractional distillation into portions in which, as the boiling range of the fractions rises, the individual members having higher boiling ranges tend to predominate. Therefore, other properties besides boiling range, such as specific gravity, viscosity, and mean molecular weight are found to change gradually from fraction to fraction much as the same properties vary from one individual hydrocarbon to another. If it is assumed that toxicity to insects is a property of the hydrocarbons, it would be reasonable to suppose that this property might also go through gradual changes. It should then be possible to trace a relation between the other properties of an oil and its insecticidal effect and to discover a fraction or portion of a given lubricating oil in which this property is at a maximum. Such a product would be made up largely of the group of hydrocarbons which is the most effective in killing insects. Proof of its existence would in a general way furnish support for the assumptions.

Accordingly, experiments were planned which should disclose this particularly effective fraction. A selected series of oils was tested for insecticidal power by using them as sprays in orchards, and certain constants for each were determined in the laboratory in order to be able to describe them as a basis for specifications. These constants were selected with the purpose of determining and using for a basis of identification such properties as would be likely to influence the killing power.

The following considerations suggested this view: Lubricating oils are very inert chemically and it would appear reasonable to assume that they are not more reactive within the bodies of insects than in the test tube. If this is true and their action is due to their physical properties, perhaps some one of these is intimately concerned with the killing of insects. It was therefore intended to note carefully the variation of insecticidal effect accompanying variations in the properties measured to determine in what cases these were parallel and in what others not parallel.

The physical state of the oil as it travels through the tissues of an insect to the walls of the cells it kills may be vapor, liquid, or emulsion.[12] In the liquid condition the wetting power or oiliness and the viscosity determine the penetration and thus may possibly affect the toxicity. The wetting power measures the tendency of a liquid to spread over solid surfaces only partially in contact with it, displacing films of other fluids. Plane or convex surfaces have been used in studies and in such cases the viscosity should not interfere. But where the surface to be covered is the lining of fine pores the viscosity may be expected to have a decided influence. No suitable methods for determining wetting power[13,14] have been developed, but the viscosity was observed.

VISCOSITY—The determination of viscosity is generally accepted in oil technology as a convenient method for distinguishing lubricating oils. The Saybolt Universal viscometer[15] was used in this work because it is the common instrument of the oil trade. But because of the low temperatures in the field (0–15° C.) at the time of spraying, it was evident that the internal friction of the oils as brought into play under field conditions must be very different from that at the temperatures (37.8° C.) at which the viscosity is usually determined. Therefore viscosity readings were taken at several temperatures from that of the room to 100° C., plotted, and extrapolated in the direction of low temperatures.

SPECIFIC GRAVITY—The specific gravity was taken because by comparing with other constants it is of value in showing the type of crude from which an oil was derived. A set of hydrometers was used and corrections applied to bring the readings to 15° C. (60° F.).

ANALYTICAL DISTILLATION—To study the possibility that the oils attack the tissues of the insects as vapor, the analytical distillation was selected as the third characteristic. It is useful in the detection of blending, closely defines the portion of the crude from which the oil was derived, and the results must have an intimate relation to the vapor tension. In their studies on toxicity Shafer[16,17] used only gasoline, but Moore studied several hydrocarbons and repeatedly[18,19,20] called attention to a relation between vapor pressure and toxicity. It was expected that the present study would disclose such a relation in lubricating oils if it existed. From previous experience in the field and knowledge of the boiling ranges of those oils known to be successful, it did not seem reasonable to expect such a relation.

Apparatus. The apparatus used in the analytical distillation requires some comment. The flasks and condenser were made according to the description in Dean, Hill, Smith, and Jacobs' method.[21] The heating device they recommended could not be made, so this had to be changed. Transite board (1/8 inch or 3 mm.) with a 10-cm. hole was provided for the bottom of the flask. A conical cover of light sheet metal was made which would contain the flask up to the level of the delivery tube. This had a separable seam, which was opened to admit the flask. After it was closed the flask was held inverted and steam-pipe insulating compound was rammed in around it. The transite plate was then attached to the sheet-metal jacket with three stove bolts. The top of the jacket was sealed with plaster of Paris. A small, carefully shielded gas flame was applied to the portion of the flask exposed through the hole in the plate.

During 1925 the vacuum was regulated by hand, a 15-gallon iron tank being placed in the line to prevent rapid fluctuations of pressure. In 1926, however, a regulator patterned after a recent description[22] was made and used. For the sake of comparison with previous results, which had been based upon the recommendations of the Bureau of Mines,[21] a pressure of 40 mm. of mercury was always used. This brought such a stream of air through the regulator that spraying over of the mercury into the pump line became troublesome. This was met by sealing a bulb trap into the line coming out of the regulator, and by filling up the top of the containing tube with pieces of glass tubing to break up the bubbles. No visible fluctuation of the manometer occurred when the regulator was in use. At first a 200-cc. mixing cylinder was used as a receiver; later a device for cutting the 180 cc. of distillate into six 30-cc. portions was substituted, but no work was done upon the separate fractions. The distillate was measured as it collected and its volume plotted against the temperature.

There remains a possibility that the oil has entered the vital tissues of the insects while still a phase of a non-homogeneous system—i. e., an emulsion. Upon the basis of the information available it does not seem reasonable to dismiss this possibility. No studies upon it were found. It does not seem likely that the emulsion state continues through the cell walls, but it may persist to that point.

Oils Studied

1925 TESTS—Lubricating oils (1, 2, 3, and 4) sent by the Standard Oil Company of California were of asphalt-base crude. Except oil 3, none had received more refining treatment than would entitle them to the grade of neutral oils, according to advices from the company. Thus they might be expected to have had the following preparation:[5] The lubricating oil fraction remains in the crude stills after all the burning oils have come off. With paraffin-base oils or asphalt-base oils not containing much tar the entire contents of the crude stills are run to the lubricating-oil stills. Where the amount of asphalt is large, a preliminary run "to tar" may be made, either in the crude-oil stills or some other still, and only the distillate reaches the lubricating-oil division. Here the several fractions of lubricating oil are made by distillation, which is only for separation and not a refining process. This distillation is generally "dry;" several fractions are taken and these are prepared according to the requirements of the market. For the neutral grade the fraction is washed with sulfuric acid, allowed to settle, decanted, and similarly washed with caustic solution and water. The concentration and amount of sulfuric acid used are kept low, so that the result of the treatment is to reduce the acidity of the oil and improve its corrosion tests, but not to improve the color and other characteristics to any considerable extent. Thus the refining losses are kept small, but at the expense of the quality of the finished product. The unsulfonatable residue may be as low as 50 per cent, and is generally not more than 65 per cent.

Oils 5 and 6 were sent by the Texas Company from Port Arthur to represent the lubricating-oil fraction of paraffin-base crude oil. F. W. Hall, chief chemist of the Texas Company, also sent oils 7, 8, and 9. Oil 7 is a special light lubricating oil of asphalt base, oil 8 is a paraffin-base gas oil, the last "cut" below oil 5, and oil 9 is a mixture of red engine oil and enough kerosene (about 25 per cent) to bring its viscosity at 37.8° C. (100° F.) to 70 seconds (Saybolt). This dilution was an attempt to secure greater penetration into the fine pores of the insects by reducing the internal friction of the oil. Similar attempts have been made for other purposes.[23]

1926 Tests—For the third season's work the Standard Oil Company of California was requested to send new supplies as nearly identical as possible with oils 1, 2, 3, and 4 of 1925. They were given the same numbers in 1926. In addition they were asked to send an asphalt-base gas oil (5), a heavy lubricating oil considerably higher in range than red engine oil (6), a typical automobile lubricant of about the middle of the range of those prepared for this purpose (7), which goes by the name "Zerolene 5," and a sample of their technical water-white lubricating oil (8).

The Texas Company was asked to send duplicates of oils 5, 6, 7, and 8 of 1925. These were given the numbers 9, 10, 11, and 12 in 1926. In addition they were asked for a sample of water-white paraffin-base oil (13).

The principal object sought in 1926 was verification of the data obtained in 1925, with reference particularly to the effects on scale. In addition, it was sought to establish the possible place of the water-white (decolorized) oils in dormant spraying and to learn more of the limitations of oils beyond the ranges previously tested.

Results

Studies on Viscosity—Table I gives a description of the oils used, their specific gravities and viscosities. The plots of viscosity against temperature produced curves of similar appearance, differences between curves usually being in displacement along the temperature axis. They approximate a family of hyperbolas with asymptotes parallel to the coördinate axes. This has been noticed by others.[24] From a study of the curves it appears that if the viscosities of lubricating oils are measured only at 37.8° C. (100° F.) or some other temperature near that, this property will be defined as well as though a whole series of tests were made. It should be added that where differences exist at this temperature, they are magnified rapidly below it, while above it they gradually disappear.

Table I—Characteristics of Lubricating Oils

No.	Trade Name	Oil Company	Sp. Gr. (15° C.)	Viscosity
		SEASON OF 1925		
1	Spray stock B	Standard	0.9189	95
2	Spray stock D	Standard	0.9226	97
3	Regular "E" pale paraffin	Standard	0.9173	102
4	Red engine oil stock	Standard	0.9253	260
5	70 viscosity paraffin-base stock	Texas	0.8812	79
6	100 viscosity paraffin-base stock	Texas	0.8880	110
7	70 viscosity asphalt-base stock	Texas	0.9215	69
8	Paraffin-base gas oil	Texas	0.8749	67
9	75 per cent red engine oil, 25 per cent kerosene	Texas	0.8810	76
	Medium red engine oil	Bought locally	0.9280	248
		SEASON OF 1926		
1	Spray stock B	Standard	0.9282	105
2	Spray stock D	Standard	0.9238	100
3	100 pale oil	Standard	0.9225	105
4	Red engine oil stock	Standard	0.9310	237
5	Gas oil from asphalt base	Standard	0.8894	41
6	"W" gear-case oil	Standard	0.952	[a]
7	Zerolene 5 (automobile oil)	Standard	0.9373	460
8	Mineral seal oil (water white)	Standard	0.8638	52
9	70 viscosity paraffin-base stock	Texas	0.8750	73
10	100 viscosity paraffin-base stock	Texas	0.8848	106
11	70 viscosity paraffin-base stock	Texas	0.9214	69
12	Paraffin-base gas oils	Texas	0.8712	65
13	150 viscosity water-white paraffin-base oil	Texas	0.8660	142
	Medium red engine oil	Bought locally	0.9255	230

[a] Not comparable with other oils.

Effects of Variations in Viscosity—On comparing the results of spraying in Table II with Table I, it is apparent that variations of viscosity, other physical properties being constant, do not affect the insect mortality. For example, oils 3 and 5 of 1925, which occur again as 3 and 9 in 1926, have very similar boiling ranges but different viscosities. Their effects on insects are similar. The same is true of oils 4 and 6 of 1925, which are the same as 4 and 10 of 1926. Though differing in viscosity, they gave similar kills of insects.

Table II—Field Tests of Oil Sprays

	Leaf-Roller Eggs at 8 Per Cent			San José Scale at 4 Per Cent[a]		
Oil	Not hatched	Hatched	Per cent hatched	Dead	Alive	Per cent alive
			SEASON OF 1925[b]			
1	10447	50	0.47	5770	1	0.017
2	14857	129	0.9	6200	4	0.064
3	12512	22	0.17	6386	2	0.031
4	13894	13	0.137	9280	0	0.0
5	12815	15	0.117	6460	0	0.0
6	12135	4	0.03	5370	2	0.037
7	10386	1166	10.00	6110	4	0.065
8	11293	68	0.6	3566	0	0.0
9	18254	309	1.66	5410	0	0.0
Check	2866	4763	63.3	3390	362	9.69
			SEASON OF 1926			
1	4935	53	0.94	511	1	0.2
2	4602	110	2.5	901	5	0.6
3	5923	5	0.08	5756	0	0.0
4	4636	0	0.00	814	0	0.0
5	4256	456	9.67	513	10	1.9
6	6922	526	7.6	1450	23	1.6
7	4516	44	0.96	721	0	0.0
8	4711	1	0.02	777	0	0.0
9	4446	5	0.11	856	0	0.0
10	4978	0	0.00	685	0	0.0
11	3856	172	4.22	657	0	0.0
12	5788	84	1.43	873	0	0.0
13	4560	0	0.00	836	0	0.0
R. E. O.	5004	12	0.24	1051	0	0.0
Check	3332	1072	24.2	53	636	77.0

[a] Because of unusually great winter mortality the field results on the San José scale are not so conclusive as desired, although thousands of insects were examined for each test. The experimental orchard at Clarkston showed an average of 90 per cent of winter-kill among the unsprayed scale insects, with individual trees ranging between 83 and 100 per cent of scale mortality. The data on scales in tables or orchard spraying at Clarkston should be interpreted with the understanding that nine-tenths of the dead scales were winter-killed before spraying. This applies only to 1925.

[b] These data have already been published. See reference 6 in bibliography.

Finally, in the case of oil 9 of 1925, which, as has been mentioned, was prepared by diluting an oil like 4 or 6 of 1925

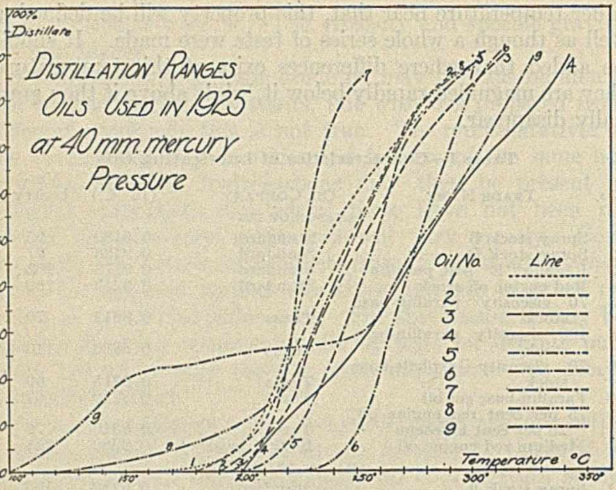

Figure 1

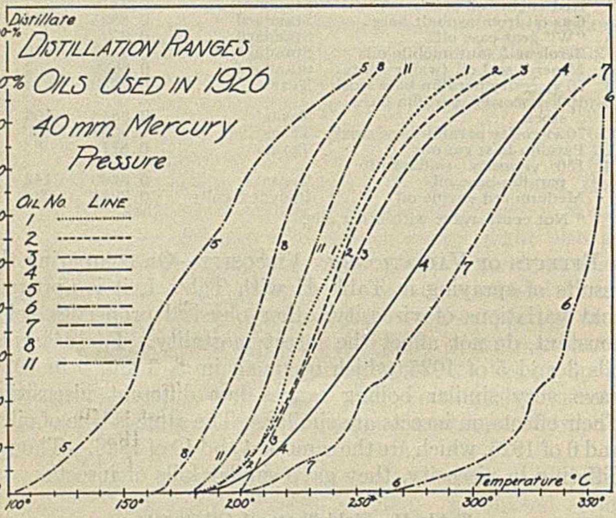

Figure 2

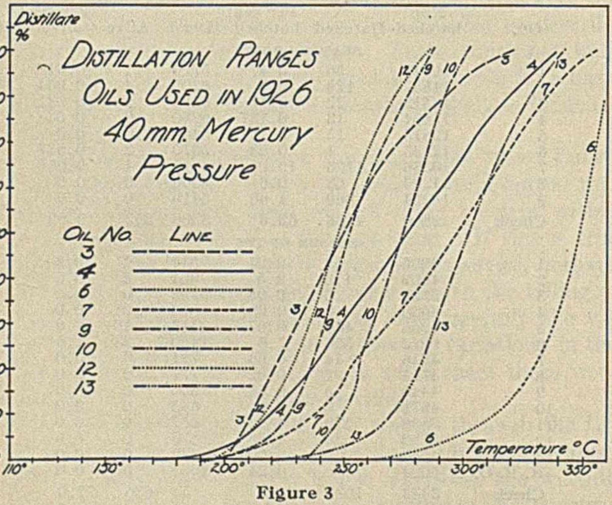

Figure 3

with kerosene, the mortality rate is reduced. If the added kerosene had been water, this spray would have been equivalent in concentration to a 6 per cent spray of red engine oil. In the same year a 6 per cent spray killed all but 7.7 per cent of the leaf-roller eggs and a 7 per cent spray all but 1.03 per cent, while oil 9 killed all but 1.66 per cent.[6] From the tests of the unblended oils it appears that variations in viscosity do not of themselves affect the toxicity of oils, and from the test of oil 9 it appears that the value of an oil as an insecticide is not materially improved by blending to reduce the viscosity. Furthermore, the viscosity of this oil before blending, and that of effective oils like 4 and 6 of 1925, is so very great at the field temperatures that it is evident that viscosity has no important influence on the toxicity.

Effects with Different Boiling Ranges—Figure 1 is a plot of all the boiling ranges of oils used in 1925. They fall into several groups. Oil 7 stands alone, with a lower range than any of the others. 1, 2, and 8 are closely related, and so are 3 and 5, and 4 and 6. Oil 9 is blended. Reference to Table II shows that there are greater differences in effects on insects between the groups than between oils within the same group. Results in 1926 parallel those of 1925 throughout, although exact duplication is impossible.

Because of their greater number, it was necessary to show the boiling range curves of the oils of 1926 in two figures (Figures 2 and 3). The curves of oils 3, 4, 6, and 7 are given on both figures. Reference to these figures and to Table II shows that the duplicates of the oils of 1925 behaved in 1926 as they had in 1925. Therefore, for oils of this type it appears that the greater the fraction distilling between 240° and 300° C. at 40 mm. pressure, the greater will be the toxicity. Oil 7 of 1925 and its duplicate, oil 11 of 1926, contain practically none of this fraction and compared poorly in toxicity with other oils, while oil 6 of 1925 and its duplicate, oil 10 of 1926, contain almost nothing else and gave excellent results throughout. The other oils contain varying amounts of this fraction and their effects on insects varied in proportion.

Other oils tried in 1926 but not in 1925 lead to still other conclusions. The two water-white oils, 8 and 13, both gave excellent controls of insects, yet one is below and the other above the range of the less refined oils found to be effective. The distillation curve of oil 8 of 1926 falls between those of oils 5 and 11, both of which gave poor controls. Oil 13 has a range closely related to that of oil 7, but is quite satisfactory, whereas 7 is not. Only a very small amount of the water-white oils will react with sulfuric acid, and it is believed that they consist almost exclusively of saturated lubricating-oil hydrocarbons.[25] This is at least an indication that it is these hydrocarbons that are effective in killing insects and that the sulfonatable materials may in some cases be detrimental. The refining losses in completely removing the color from lubricating oils are very large, and the identity of the substances so lost is unknown.

Asphalt- versus Paraffin-Base Oils—One of the oils used in 1924 was a lubricating oil of paraffin base. Except for the fact that it deposited a slimy, waxlike material on standing for 3 months, it was very much like several others, but the kill of insects was decidedly poor.[4] This raised the question whether asphalt- and paraffin-base oils could be regarded as interchangeable for spray purposes. It is well established that for a given range of boiling points paraffin-base oils show lower specific gravities and viscosities than asphalt-base oils.[26] A change in the carbon-hydrogen ratio indicates that the proportions of the different series of polynaphthenes are not the same in both. The work done on oils 5, 6, and 8 of 1925, and 9, 10, 12, and 14 of 1926 was intended to demonstrate differences in insecticidal powers of asphalt- and paraffin-base oils. It will be seen that whatever other differences may exist, the effects of these oils upon insects are comparable with those of the oils of asphalt base, 1, 2, 3, and 4 of 1925, and 1, 2, 3, and 4 of 1926. Since none of the oils of 1925 and 1926 used showed any sediment, the burden for the failure mentioned above seems to fall upon the unknown deposit.

Trade Nomenclature—Market conditions in general have a controlling effect on refinery practice. This is well illustrated in the case of the two gas oils. Oil 5 of 1926 was described as an asphalt-base gas oil, and (Figure 2) contained practically nothing of the lubricating oil fraction. Oil 12 of 1926 was described as a paraffin-base gas oil, but it contained a large amount of material ordinarily considered lubricating oil. As a consequence, though similarly named, oil 12 made an effective spray and oil 5 did not.

Conclusions

The property of killing insects under the conditions of this study resides in a considerable range of lubricating oils, but is greatest in the portion that distils over between 240° and 300° C. at 40 mm. pressure.

Toxicity of the kind studied does not appear to be related to the viscosity of the oils.

The presence of significant quantities of vapor or vapor pressure is doubtful, in view of the low field temperatures and the high boiling ranges of effective oils.

Oils for this purpose may be from asphalt- or paraffin-base crude without prejudice to the effects.

Oils that have been subjected to processes for completely removing the color are likely to be more effective than before the decolorizing treatment.

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Crystallization of Paraffin Wax[1]

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A sample of slack wax was sweated and the melting points and the average molecular weights of the individual fractions thus obtained were determined. The fractions were also examined microscopically. During the crystallization of paraffin wax two types of crystals were obtained—needles and plates. The relative amounts of these two types are determined by the conditions under which the crystallization is effected. Comparison of the optical properties shows that the needles obtained in this way are not true single crystals, but are composed of concentric aggregates.

WITHIN recent years a number of investigators have studied the crystallization of paraffin wax from petroleum hydrocarbons and from several other solvents. It has been shown that the solid paraffins may crystallize either in plates or in needles, the crystal habit depending upon the exact conditions under which the crystallization is effected. Similar crystals are obtained when melted paraffin is allowed to cool. The exact relationship between the plates and the needles that may be present in ordinary paraffin wax has not, however, been definitely established, nor has evidence been presented to show that the two types of crystals in the solid wax are distinct crystal entities formed from different chemical compounds or from distinct solid modifications of paraffin.

Preparation of Materials

Several samples of paraffin used were prepared from slack wax from Pennsylvania crude petroleum. The original slack wax was obtained from the Conewango Refining Company. It showed a melting point of 50–51° C. (122–124° F.).

This slack wax was separated into several fractions by sweating. A circle of fine copper screen was fitted to a 15-cm. Büchner funnel, the outlet of the funnel was closed, and cold water was run in until the water level was about 1.25 cm. above the screen. About 550 grams of the melted wax were placed on top of the water, forming a layer about 5 cm. thick. When the paraffin had solidified the water was drained and the funnel and its contents were placed in a large glass cylinder in a thermostat. The temperature was raised very slowly and the oil that sweated from the wax was collected in fractions. The average molecular weight of the material in each fraction was determined by the cryoscopic method, using naphthalene as a solvent.

Fractionation Data

Fraction	Temperature		Weight of Fraction	Melting Point[a]		Av. Mol. Wt.
	° C.	° F.	Grams	° C.	° F.	
1	Below 49.9	Below 120	41	43.3	110.0	415
2	49.9 to 53.9	120 to 129	120	47.2	117.0	403
3	53.9 to 57.2	129 to 135	114	49.9	121.8	417
4	57.2 to 58.3	135 to 137	132	51.7	125.0	432
5	58.3 to 60.0	137 to 140	60	54.0	129.2	443
6 (Res.)	Above 60	Above 140	63	56.7	134.0	445

[a] Am. Soc. Testing Materials, Standard Method D 87–22, Standards, p. 882 (1924).

Beginning with fraction 2, the average molecular weight increases with the melting point. This is to be expected, since the paraffins of lower molecular weight have lower melting points and should concentrate in the more readily fusible fractions. The first fraction, however, has a molecular weight somewhat higher than that of fraction 2. This may be explained by the assumption that the original slack wax contained a small amount of paraffins of higher molecular weights than those of the compounds which constituted the major portion of the crystals. When the wax was sweated these higher hydrocarbons dissolved in the first fraction of the melt, giving an oil of rather high average molecular weight. The

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[1] Received April 7, 1927.

crystals remaining after the removal of the first fraction consisted of a mixture of paraffins of not very widely different molecular weights and on continued sweating gave a series of fractions of oil, each of which was slightly richer in the lower hydrocarbons than was the solid matrix from which it was derived.

From fraction 2 to fraction 5 the molecular weight increased regularly and rather rapidly; while between fractions 5 and 6 there was very little change in molecular weight although the melting points differed by 2.7° C. (4.8° F.). This would appear to indicate that after the removal of the first four fractions of oil the residual crystals consisted largely of a mixture of isomeric paraffins, and that the fifth fraction had a relatively low melting point because it consisted of a eutectic mixture of the various isomers.

Microscopic Studies

The behavior of each fraction on solidification was then studied microscopically. The observations were made at about 100 diameters, using a 16-mm. objective. An iris diaphragm, mounted directly above the objective, made it possible to decrease the aperture and thus to increase the depth of focus and the contrast. The thickness of the needles and the fact that they did not all lie in one plane, together with the very low visibility of the plates, made this accessory exceedingly useful. The sample under examination was contained in a small watch glass or in the depression of a "hanging drop" slide, and was about 1 mm. thick. It was covered but was not in contact with the cover glass.

The specimens were heated and their rates of cooling regulated by means of a hot stage, the temperature of which was indicated by an Anschütz thermometer. For relatively rapid changes of temperature the stage described by Chamot[2] was satisfactory, but for very carefully controlled cooling a more heavily insulated stage with greater lag was preferable. By regulating the current through the heating coil the temperature could be controlled to within 0.1° C. and, with constant line voltage, could be held constant within this limit. These hot stages were used with an ordinary chemical microscope which could be equipped with Nicol prisms for observations with polarized light.

Photomicrographs of the crystals during the various stages of their development were made with the same instrument that was used in the visual examinations. The ordinary eyepiece was replaced by a Leitz "Makam" photomicrographic camera, which permitted continuous observation of the specimen even during the exposure. The observer was thus free to devote his entire attention to the sample and to photograph it at any stage during the cooling. With this equipment it was found that exposures as short as 0.5 second were feasible, so that photomicrographs of growing crystals could be obtained.

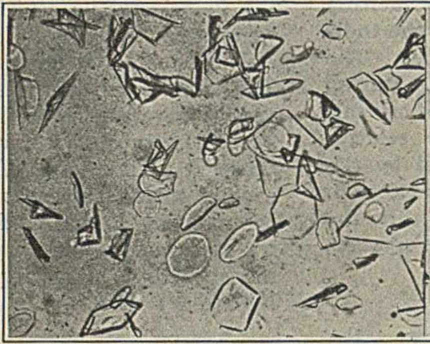

Figure 1—Initial stage of crystallization on slow cooling. Plate crystals beginning to curl at edges

Figure 2—Same field as Figure 1, about one minute later, showing further progress in change to needles

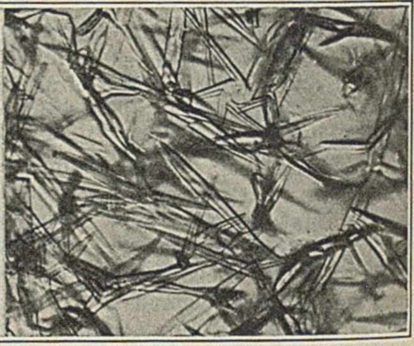

Figure 3—Third stage in crystallization, plates almost completely converted to needles

Under the microscope the several fractions obtained by the sweating of the original slack wax showed essentially the same behavior on solidification, although the exact temperatures and rates at which the various changes took place varied with the individual fraction. In every case the waxes start to solidify as small plates. With rapid cooling (greater than 0.1° C. per minute) these plates almost immediately begin to undergo a change in habit, becoming polygonal in outline, with shaded outlines. (Figure 1) As the change is followed under the microscope it is seen that the edges of the plates are actually rolled up, and that from these rolled edges there develop needles tangent to the original plate. On further cooling this change continues and the needles elongate and become better defined (Figure 2); the larger plates also persist, and both needles and plates grow at the expense of the smaller crystals. Finally, the mass solidifies completely to a coarse-grained mixture of needles and plates, the relative proportions of the two types of crystals being determined by the rate of cooling (Figure 3). With rapid cooling the wax consists chiefly of fine needles mixed with a few small plates. In some cases a single individual crystal is both a needle and a plate; one end may roll and grow into a needle while the opposite end remains a thin plate (Figure 9).

If a sample in which a few coarse crystals have been formed by slow cooling is chilled suddenly, the mother liquor passes through exactly the same cycle as described above. A new crop of small plates is formed, and these plates grow, curl, and change over in part into needles just like the plates formed from the original melt. When a partially solidified sample is held at constant temperature the larger plates and needles increase in size, while the smaller crystals disappear. The effect of this "digestion" is, of course, most marked in the case of fine-grained crystals. With the same rate of cooling the fractions with the higher melting points yield considerably coarser crystals. The temperature range between the initial separation of crystals and the complete solidification of the mass is much shorter with the harder waxes.

When the needles are formed very slowly and are grown to a relatively large size their edges become somewhat serrated and overlapping co-axial layers are evident (Figure 8). Further growth produces a looser structure in which these layers are less distinctly parts of a well-defined needle (Figures 16 and 17). The plates are usually very thin and are more or less rounded. Seen flatwise they are almost invisible, their index of refraction being nearly the same as that of the melt.

Further study of the optical properties of the plates is hindered by the fact that all the crystals tend to lie in the

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[2] "Elementary Chemical Microscopy," p. 222 (1921).

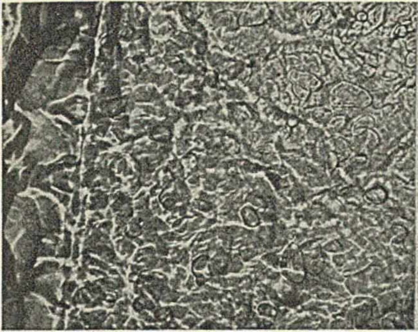

Figure 4—Wax that has been cooled very slowly, almost to complete solidification. Consists almost entirely of plates

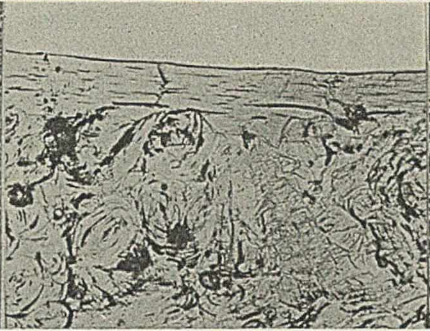

Figure 5—Section of solidified wax, showing layers of plates parallel to surface. Cross section of needles in lower left

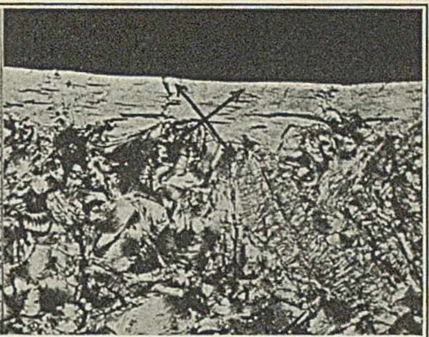

Figure 6—Same field as Figure 5, viewed between crossed Nicols. Black cross indicates planes of vibration of polarized light

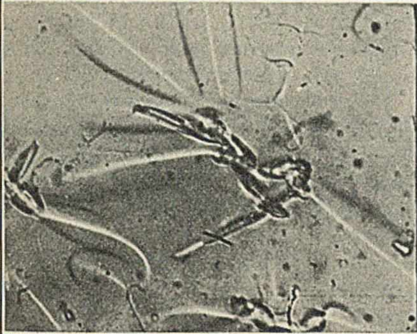

Figure 7—Needles and large plates, showing wrinkling at surface of plates

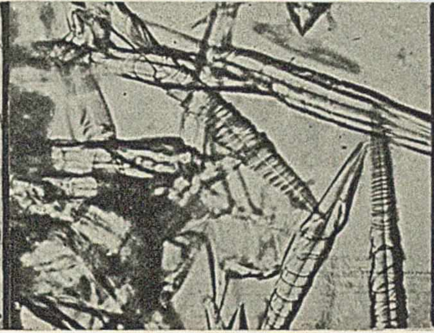

Figure 8—Large needles, showing co-axial layers

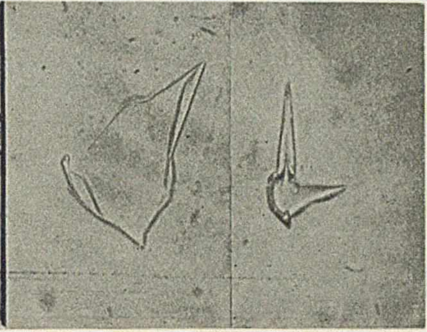

Figure 9—Left: Plate beginning to curl. Right: Needles starting from a plate

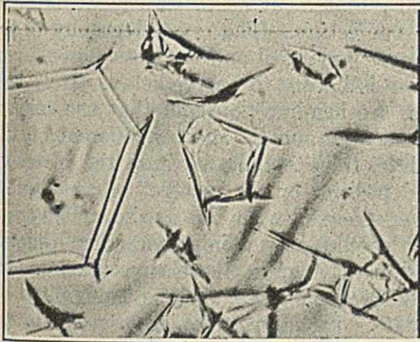

Figure 10—Beginning of several rosettes of needles growing from the curled edges of plates. Surface wrinkles may be observed at the right

Figure 11—Sections of solid wax, showing circular cross sections of several large needles. The striated longitudinal section of a needle is seen in the lower left

Figure 12—Same field as Figure 11, viewed between crossed Nicols. The cross sections of the needles show black crosses, the arms of which are parallel to the planes of vibration of the polarized light

same position, frequently several deep. Crystallization from solvents (kerosene, acetone, xylene) may be more easily controlled, and the product is suitable for detailed study. The index of refraction of the crystals, for vibrations in their principal plane, is approximately 1.44, while for vibrations in the perpendicular plane it is close to 1.54. Seen flatwise the plates are isotropic, but they exhibit fairly strong double refraction when inclined or edgewise, invariably giving parallel extinction and negative "elongation."

By careful search it is possible to find crystals that appear to be separate, and these yield distinct bi-axial interference figures, optically positive, with 2 V about 45 degrees. These observations indicate that the crystals may be ascribed to the orthorhombic system.

By extremely slow and regular cooling (over a period of several hours) the entire mass may be caused to solidify in plates (Figure 4). Usually when a sample of wax is cooled rapidly enough to form needles throughout the main portion of the melt, very large plates developed at the surface of the liquid and approximately parallel to it (Figures 5 and 6). The shrinking during cooling may result in pronounced wrinkling of the surface layer (Figures 7, 10, and 13). It is conceivable that this oriented development of the plates may be initiated by the oriented arrangement of molecules at the surface of the liquid.

In spite of the striking superficial differences between the needles and the plates, there is no indication that these represent two different allotropic modifications of paraffin. They may co-exist at constant temperature in contact with the melt, and there is no line of demarcation between a plate and a needle developed from it and contiguous to it; needle and plate constitute a single solid phase. End views of the needles in the melt show that they are not simply plates seen edgewise. The two types of crystals must be considered as two crystalline habits of the same solid phase.

Microscopic observation of the process of formation of

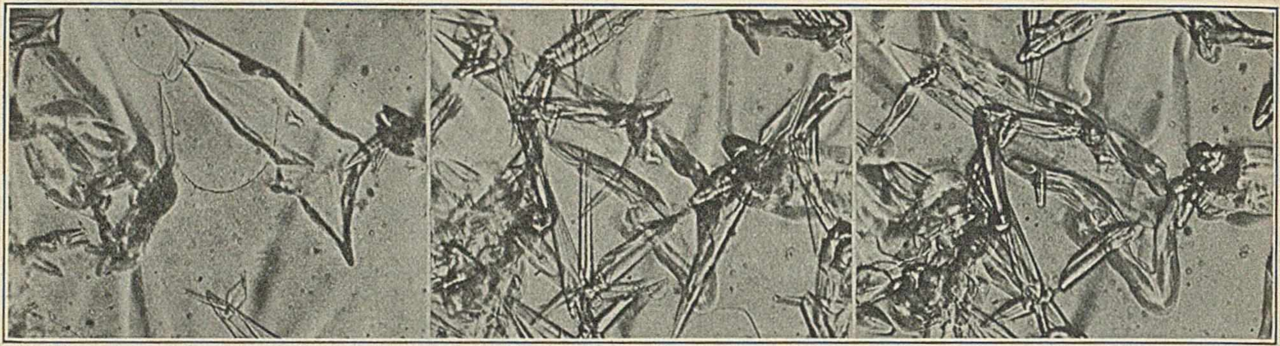

Figure 13 Figure 14 Figure 15

Figure 16 Figure 17

Figures 13 to 17

The photographs show the same field during very slow cooling. In Figure 13 a plate is just beginning to curl. In Figure 14 the curled edges have begun to elongate and develop as needles. Other needles have also appeared. In Figure 15 these needles are becoming thicker and less perfect. In Figures 16 and 17 the progressive coarsening of the needles is shown.

the needles shows definitely that they originate by the curling of the edges of the plates. Although they may lengthen and thicken on digestion in the melt, this fundamental structure persists; the needles are simply plates tightly rolled. Single needles are formed when a plate rolls from one edge only or from two opposite edges; when the original plate begins to roll at several places a polygonal cluster of needles is formed (Figures 9 and 10).

The structure of the needles is consistent with their origin. In cross section they are round or oval and show distinct concentric layers (Figures 5 and 11). That they do not possess the same structure as ordinary needle-like crystals is shown by their appearance between crossed Nicols. Cross sections, instead of being isotropic or extinguishing uniformly as would normal single crystals, show the black cross with arms parallel to the planes of the Nicol prisms, such as is characteristic of radiating or concentric structures (Figures 6 and 12). As in the case of starch granules, spherulites, etc., this effect is much more pronounced when the specimen is rotated.

The birefringence shown by a cross section of a needle is apparently the same as that shown by an equal thickness of solid consisting of plates lying edgewise. Longitudinal sections of the needles show fissures and laminations parallel to the long axis (Figure 11). Between crossed Nicols a longitudinal section of a needle exhibits parallel extinction and negative elongation but does not show a single polarization color or a decrease in the order of the polarization colors at the edges, as would a single normal crystal. Instead, the polarization color at the edge corresponds to that of an equal thickness of a plate crystal seen edgewise, and the "order" of the polarization color decreases toward the center of the needle, finally reaching a value corresponding to that of an equal thickness of plates seen from the flat side. The structural and optical characteristics of the needles, as seen under the microscope, completely agree with and confirm the observations as to their origin.

Crystal behavior such as has been described here is perhaps unique, and any statement as to its causes must be based largely upon conjecture. The crystallography of the pure paraffins is almost unstudied and the possible behavior in a complex mixture is hardly to be predicted. It is possible that the plates are hemimorphic and that the surface tension between the crystal and the melt is different on the two faces of the plate, thus tending to cause the plates to curl. Any further deposition on the "needle" or curled plate might well be in layers co-axial with the needle. The transition from plates to needles is certainly more than a simple alteration of *habitus* or a change in the relative development of the various crystallographic faces, such as is exhibited by many substances. It is probably more or less closely related to the behavior of "plastic" or "liquid" crystals.

In the melting of some of the very soft waxes under the microscope a very novel behavior was observed. When these waxes were allowed to melt rather rapidly, small irregular droplets of a second distinct liquid phase gathered at the surface of the fused mass. On standing for a short time these droplets dissolved in the mother liquor and the liquid became homogeneous.

Synthetic Nitrate Position in Great Britain

The fixation of atmospheric nitrogen seems to have established itself as definitely superior to other methods of fixation, according to Sir Max Muspratt, one of the Directors of Imperial Chemical Industries (Ltd.), recently published in the *Financial Times*. He points out that the natural nitrate of soda from Chile has the greatest difficulty in competing with fixed nitrogen of synthetic origin. Great Britain has made considerable strides in the development of the nitrogen industry, and the output of fixed nitrogen at the nitrogen fixation plant at Billingham-on-Tees is now at the rate of 18,000 tons per annum, and this output will be greatly increased by the end of next year. This plant is owned by Synthetic Ammonia & Nitrates (Ltd.), now associated with Imperial Chemical Industries (Ltd.).

Studies of Chaulmoogra-Group Oils[1]

II—With Special Reference to Refining and the Isolation of Hydnocarpic Acid[2]

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For more than twenty years investigators mixed chaulmoogra oil with various substances to make it suitable for intramuscular or subcutaneous injection. These mixtures have been practically abandoned, as it is now known that chaulmoogra-group oils, if free from rancidity, are very suitable for use without admixture. (The term "mixtures" does not include such preparations as chaulmoogra ethyl esters, which are derived from the oil by chemical changes and have a distinct place in leprosy therapy.) The most important part of the refining process is the removal of free fatty acids. The details of refining are described.

Hydnocarpus wightiana **oil is more economical than chaulmoogra, because obtainable in better quality.** ***H. wightiana*** **oil is also more suitable for the preparation of hydnocarpic acid. By fractionation of the ethyl esters from this oil nearly pure ethyl hydnocarpate can be obtained, whereas the corresponding fraction from chaulmoogra ethyl esters is contaminated with ethyl palmitate. Hydnocarpic acid was obtained in considerably better yields and purer condition than previously reported.**

Analytical characteristics of some chaulmoogra-group oils of minor importance are recorded.

WE ARE frequently informed, in the scientific and semi-scientific press, that the intramuscular and subcutaneous injection of chaulmoogra oil, begun in the nineteenth century as a treatment for leprosy, failed because the oil is "heavy," "slowly absorbed," "very irritating." Nevertheless, intramuscular or subcutaneous injection of chaulmoogra-group oils is at present employed on a large scale for the treatment of lepers in various countries, and the local irritation produced by the treatment is not serious. The comparative failure of the earlier work, in so far as local irritation was involved, is ascribable to the fact that the oil used was of a very low grade. To borrow an expressive phrase from the language of the law courts, it was "decomposed, rancid, putrid, and unfit for human consumption."

At that time, as at present, three chaulmoogra-group oils were used for the treatment of leprosy—*Taraktogenos kurzii* (chaulmoogra), *Hydnocarpus wightiana* (marotti), and *Hydnocarpus anthelmintica* (lukrabo). Unfortunately, chaulmoogra was the only one of these well known to occidental physicians.

Chaulmoogra seeds are obtained from dangerous forests, and their collection is usually deferred until the bears have finished eating the chaulmoogra fruit.[3] The *Taraktogenos* seed does not keep well, and "crude, cold-pressed" commercial chaulmoogra oil contains 13 to 60 per cent of free fatty acid.

It was doubly unfortunate, and indeed surprising, that the refining of this rancid oil, though recommended by Jeanselme,[4] was looked upon with disfavor by practically all the physicians who treated lepers. Brill and Williams[5] were not entirely convinced of the validity of the practitioners' conclusions, but they were nevertheless strongly influenced by such conclusions and by faulty observations purporting that "the compound known as anti-leprol, which is the mixture of the ethyl esters of chaulmoogric and hydnocarpic acids, was without effect." Accordingly, they and other chemists examined crude chaulmoogra oil in search of small amounts of some glucoside, vitamin, or other substance which would account for the activity supposed to be lost on refining. Such searches have been in vain. On the contrary, the effectiveness of chaulmoogric and hydnocarpic acids in the form of ethyl esters or sodium salts has been firmly established.

Although the activity of the above-mentioned ethyl esters and sodium salts is no longer doubted, the pure chaulmoogra-group oils, largely because they are considered less likely to produce untoward effects, have recently been preferred for the treatment of certain types of cases. In 1921 we learned that the Japanese[6] had discovered the value of "chaulmoogra" (probably *Hydnocarpus anthelmintica*) oil of low acidity, and were using it by subcutaneous injection. More recently *Hydnocarpus wightiana* oil of low acidity has come into extensive use in India.[7] This is not refined oil, but cold-pressed oil from seeds of good quality. Seeds or oil of *H. anthelmintica* and *H. wightiana*, in contrast to those of the true chaulmoogra, can be obtained commercially in excellent quality.

Rancidity is now recognized as highly detrimental, but the prejudice against refined oils, as compared with crude oils of fairly good quality, still exists. At Culion, however, refined oils have been used for several years. The physicians here have found that adequately refined chaulmoogra oil is a satisfactory medicinal product (though less active than the ethyl esters). From a medicinal standpoint there appears to be no difference between this and refined *Hydnocarpus wightiana* oil. So little local irritation is produced by these refined oils that the admixture of other ingredients to reduce the irritation has been abandoned as entirely unnecessary.

Crude *H. wightiana* oil is obtainable[8] commercially at less than $1000 per ton with a much lower acidity than commercial chaulmoogra oil of the same or higher prices. For economical reasons, therefore, the *H. wightiana* oil rather than chaulmoogra is now being refined here. The refining loss is considerable in the case of commercial chaulmoogra oil. This loss may be minimized, however, through recovery, by acidification, of the fatty acids and oil present

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[1] Received March 26, 1927. Published with the permission of the Director of Health upon recommendation by the Philippine Leprosy Research Board.

[2] The first paper of this series was by Perkins and Cruz, *Philippine J. Sci.*, **23**, 543 (1923).

[3] Rock, *U. S. Dept. Agr., Bull.* **1057**, 18 (1922).

[4] *Presse med.*, **19**, No. 96, 989 (1911).

[5] *Philippine J. Sci.*, **12A**, 207 (1917).

[6] Mitsuda, III^e Conference Internationale de la Lepre, Paris, 1924, p. 263.

[7] Muir, Leprosy—Diagnosis, Treatment, and Prevention, Cuttack, p. 9 (1925).

[8] The Ernakulam Trading Co., Ernakulam, India, appears to be the only large producer in the areas where this seed is grown.

in the soap solutions drawn off in the refining process. This fatty acid mixture may be utilized in the preparation of ethyl esters.

The refining methods at this laboratory are very simple, and undoubtedly could be improved by an experienced oil refiner. Difficulties have been reported by other workers, however, and as nothing appears to be available on the subject in the literature, these methods are being recorded here.

Refining Technic

In order to remove volatile impurities, steam is passed through the oil for about an hour, either before or after washing with alkali. Sufficient steam is used to give an aqueous distillate of about one-fifth the volume of the oil. The amount of volatile impurities is very small, but the distillate has a strong odor.

The free fatty acids are removed by washing with a solution of caustic alkali, the only difficulty being in the separation of the pure oil from the resulting emulsion. The essential points are believed to be as follows:

1—Heating is required for the separation of the emulsion; in the cold, considerable solid sodium acid chaulmoograte is formed. The better grades of crude oil require only that the water be hot at the start; the lower grades require a temperature of about 90° C. for several hours at each settling.

2—If much soap is present the stirring must be gentle, or a fine, inseparable emulsion will be formed.

3—The original emulsion separates into a fairly clear lower layer and a thick, creamy upper layer, which still contains a considerable portion of the soap.

4—Long heating of this creamy layer with water to remove the soap results in the formation of free fatty acids in the oil. If not much soap is present hot water may be added and the whole allowed to cool and settle. If much soap is present, hot dilute alkali is added and the temperature maintained for several hours. Addition of cold, dilute alkali, with subsequent heating, usually results in much less rapid settling.

5—When sufficient soap has been removed, the oil separates from the emulsion. Addition of salt hastens the separation, but the oil so obtained contains most of the soap. Therefore, the addition of salt is not advisable until sufficient soap has been removed so that separation of the oil has already begun.

Experimental Runs

H. WIGHTIANA OIL (2.5 per cent acidity)—One hundred and fifty liters of hot water (about 80° C.) were run into a 400-liter steel drum provided with a faucet at the bottom; 0.5 kg. of lye (74 per cent NaOH) was added, and then 100 liters of *H. wightiana* oil were thoroughly mixed in.

After the emulsion had stood 24 hours the clear lower layer (about 125 liters) was drawn off. Hot water was run in, with stirring, up to the 350-liter mark.

After 2 days the slightly opalescent lower layer (200 liters) was drawn off. The washing with water was repeated four more times, with settling each time until the lower layer cleared, 24 hours usually being sufficient.

Ninety-five liters of oil were obtained, with an acidity of 0.2 per cent. This oil was steamed as described above and filtered, while hot, through folded filters. The filtrate was dried by heating in an enamel-ware kettle, filtered again, and sterilized in bottles at 150° C.

CHAULMOOGRA OIL (25.5 per cent acidity)—In an open, copper, steam-jacketed kettle 20 liters of chaulmoogra oil and 30 liters of water were heated to boiling. A solution of 1.02 kg. of lye (74 per cent NaOH) in 5 liters of water, calculated to be about 10 per cent in excess, was stirred in. The mixture was kept hot (about 95° C.) for 5 hours.

The nearly clear soap solution (about 35 liters) was drawn off. A hot solution of 200 grams of lye in 35 liters of water was stirred in, and the mixture kept hot overnight.

The clear lower layer (about 37 liters) was drawn off. A hot solution of 100 grams lye in 32 liters of water was stirred in, and the mixture kept hot for 7 hours.

The slightly milky lower layer (34 liters) was drawn off. A little clear oil was noted on top, but most of the oil was in a creamy emulsion. This was broken by the addition of 100 grams of salt, which produced a lower aqueous layer of about 3 liters and an upper layer of oil containing a little water and soap.

The contents of the kettle were transferred to an open pail and heated by an atmosphere of direct steam for several hours. The small amount of soap was removed by filtering twice while warm, the aqueous solution being separated after the first filtration. A final filtration in the cold gave a clear product; yield 10.4 liters, acidity 0.28 per cent.

In using this method steaming may be done first or after the first filtration.

Hydnocarpic Acid

One of the objects of the earlier paper[2] was the evaluation of various oils as potential sources of chaulmoogric, hydnocarpic, or other acids which might be found valuable. Chaulmoogric acid is readily obtained from any of the chaulmoogra-group oils (especially *Hydnocarpus alcalae*), but this acid, in pure form, has found no extensive therapeutic application. Hydnocarpic acid is not so readily obtainable.

Recently sodium hydnocarpate has been required in this colony for clinical investigations. Hydnocarpic acid was originally obtained by Power and Barrowcliff[9] from *Hydnocarpus wightiana* and other oils by fractional crystallization of the barium salts. Dean and Wrenshall[10] fractionally distilled the fatty acids of chaulmoogra oil and recrystallized the lower boiling fractions. By a large number of fractional crystallizations they obtained about 50 grams of hydnocarpic acid from a kilogram of low-grade oil and better yields from oil of higher grade. Sacks and Adams,[11] using a similar method but only five crystallizations, obtained about 20 grams per kilogram of chaulmoogra oil.

Ghosh[12] crystallized the fatty acids from a number of oils and obtained fractions melting at 60° C., or somewhat less, which he called hydnocarpic acid. Fractions melting at above 50° C. gave sodium salts which were found[13] to be suitable for therapeutic use, and a medicinal product made in this way is sold by a Calcutta firm as "sodium hydnocarpate." Since crystallization of the chaulmoogra or hydnocarpus fatty acids does not produce hydnocarpic acid, and since fractions made in the manner described are obviously mixtures and yield chaulmoogric acid on further crystallization, the names "hydnocarpic acid" and "sodium hydnocarpate" should not be applied to these products.

The most practicable way to isolate hydnocarpic acid seems to be by distillation followed by crystallization. The writers preferred to distil the ethyl esters rather than the fatty acids, because the former are more easily made in fairly large quantities than the latter, provided one has a constant steam supply, they are more stable, and much more easily distilled.

Dean and Wrenshall, distilling the fatty acids or the ethyl esters at 1 to 4 mm., had difficulty in controlling the fractionation by temperature, owing to slight fluctuations in pressure, and eventually used a single fractionation of the fatty acids, controlled only by volume. Since there seems to be no advantage in such low pressures, at least for the ethyl esters, the present writers used an adjustable mercury trap to hold the pressure at 20 mm. The column

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[9] *J. Chem. Soc. (London)*, **87**, 884 (1905).

[10] *J. Am. Chem. Soc.*, **42**, 2626 (1920).

[11] *Ibid.*, **48**, 2395 (1926).

[12] *Indian J. Med. Research*, **8**, 211 (1920).

[13] Rogers, *Indian Med. Gaz.*, **54**, 165 (1919).

was not so long as would be desirable, but by three or four fractionations it was possible to concentrate most of the ethyl hydnocarpate in a 4° C. fraction (210–214° C.).

Preparation of Hydnocarpic Acid

Crude *H. wightiana* oil of good quality (2.5 per cent acidity) was converted into ethyl esters by boiling with alcohol and sulfuric acid.[14] The ester was washed with water and dried. A standard 3-liter, long-necked, round-bottom, Pyrex boiling flask was used for distillation. The neck was nearly filled with broken glass supported by an inverted cone of wire netting, which was hung from the cork. The cork was impregnated with glue and had two holes to accommodate the stillhead and an inlet tube for the introduction of portions. The inlet tube did not intrude beyond the cork, and was also used to drain off the residue by inverting the flask. The stillhead, or deplegmator, was a simple "distilling tube" 2 by 24 cm. with side arm but without constriction at the bottom. Constricted distilling tubes did not allow sufficient flow-back.

First Distillation—Two liters of ethyl esters were placed in the flask and two portions of 600 cc. each were collected. The remainder was discarded (or distilled for the preparation of chaulmoogric acid if desired). The flask was washed with alcohol, without removal of the main cork, each time the residue was drained off. The second 600-cc. portion was again placed in the flask with 1400 cc. of crude ethyl esters. Two 600-cc. portions were again distilled, the second of which was distilled with 1400 cc. more of crude ester. A final total of 1800 cc. of first fraction and 600 cc. of second fraction were thus obtained.

Second Distillation—These two fractions were refractionated, the second being added to the flask when the temperature rose to 217° C. Result: (I) 120–212° C., 450 cc., (II) 212–217° C., 1120 cc.; (III) 217–230° C., 590 cc.

Third Distillation—The three fractions were redistilled. Result: (I) 120–200° C., 40 cc.; (II) 200–212° C., 560 cc.; (III) 212–214° C., 890 cc.; (IV) 214–220° C., 410 cc.; (V) 220–230° C., 220 cc.

A small portion of the 212–214° C. cut was saponified. The resulting fatty acid showed a freezing point (thermometer bulb immersed) of 52.5° C., and $[\alpha]^{30}_{D}$, + 61.7°.

Fourth Distillation—Result: (I) 120–200° C., 74 cc.; (II) 200–210° C., 252 cc.; (III) 210–212° C., 453 cc.; (IV) 212–214° C., 723 cc.; (V) 214–216° C., 178 cc.; (VI) 216–220° C., 100 cc.; (VII) 220–230° C., 200 cc.

Fractions II to V were saponified. The freezing points and $[\alpha]^{30}_{D}$ of the fatty acids were as follows: (II) 51.4° C., +57.4°; (III) 53.7° C., +61.1°; (IV) 53.8° C., +62.3°; (V) 51.4° C., +62.5°.

The melting points of the fatty acid fractions, by the usual capillary tube method, were about 2° C. higher than the above values, which were taken with the thermometer bulb immersed in the half-frozen liquid. Power and Barrowcliff record a melting point of 59–60° C., and $[\alpha]_{D}$, +68.1°, for pure hydnocarpic acid. It is evident that nearly pure ethyl hydnocarpate can be obtained from *H. wightiana* ethyl esters by fractional distillation alone. The purity had apparently not reached the maximum obtainable by distillation, but for the present purposes purification by recrystallization was started at this point.

Recrystallization—Fractions III and IV were combined and recrystallized six times from about 2 volumes of 80 per cent alcohol (with slow cooling each time to about 15° C.). The alcohol adhering to the final crystals was removed by mixing them with hot water. The fatty acid solidified in a cake on cooling, and the remaining water was removed by remelting. The product weighed 360 grams; freezing point, 58.2° C.; melting point (in capillary tube) 60° C.; $[\alpha]^{30}_{D}$, +70.7° (20 per cent solution in alcohol; the rotation in chloroform was found to be the same).

Fractions II and V, combined, were crystallized from each of the six mother liquors (from the above) in turn. Product: 343 grams; freezing point 57.8° C.; melting point 59.5° C.; $[\alpha]^{30}_{D}$, +69.7°.

The six mother liquors were then separately treated with hot water. The six portions of fatty acids thus obtained had the following properties:

PORTION	WEIGHT	FREEZING POINT	$[\alpha]^{30}_{D}$
	Grams	*° C.*	*Degrees*
I	150	36	+45
II	113	41	+47
III	132	42	+49
IV	87	48	+54
V	45	46.2	+54
VI	35	50.1	+57

These fractions from the mother liquors evidently contained considerable hydnocarpic acid, and were reserved for further crystallization in combination with other similar fractions. A basket centrifuge is better adapted than a porcelain funnel (used in the above) to the draining of the extremely fine crystals which impure fractions give, even on very slow crystallization.

Yields—The ethyl esters used in the foregoing run were obtained from 4.7 kg. of oil. The two crops melting at 60° and 59.5° C., therefore, represent a yield of 150 grams per kilogram of oil. Apparently 25 to 30 per cent of the oil consists of hydnocarpic acid, and a large part of this can be isolated by sufficiently thorough fractionation.

Preservation of Hydnocarpic Acid—Hydnocarpic acid is rapidly attacked by the air when left in loose crystals. When allowed to solidify after melting, however, it keeps quite well. Heating a thin layer in air for more than a few minutes to drive off solvent results in lowering of the melting point.

Lower Boiling Fractions—Power and Barrowcliff considered it probable that *H. wightiana* oil contains a lower homolog of hydnocarpic acid with fourteen carbon atoms. Dean and Wrenshall found in chaulmoogra oil no evidence of members of the chaulmoogric series below hydnocarpic acid.

In the fourth distillation of *H. wightiana* ethyl esters recorded above it was found that only 74 cc. distilled below 200° C. By combining the low-boiling fractions from the distillation of about 100 liters of esters it was found that on refractionation most of this portion distilled above 200° C. No evidence was obtained of any appreciable quantity of C_{14} acid, but there was a definite concentration at 160–165° C. This fraction showed a specific rotation of about +16°, unchanged by refractionation. The writers have not yet succeeded in isolating the substance responsible for the rotation.

Hydnocarpic Acid from Chaulmoogra Oil—Power and Gornall[15] found in chaulmoogra oil a considerable quantity of palmitic acid. One would therefore expect the ethyl hydnocarpate fraction from this oil to be quite impure. This was found to be the case. On fractionating 5.4 liters of neutral ethyl esters from chaulmoogra oil three times, about the same yield of crude ethyl hydnocarpate fractions was obtained as from *H. wightiana* oil. The best of these fractions, however, gave on saponification fatty acid freezing at 42° C.; $[\alpha]^{30}_{D}$, +43.8°.

The oil used was a medium-grade commercial chaulmoogra oil of 25 per cent acidity. Unfortunately, no authentic crude samples of a better grade were on hand for comparison, to determine whether rancidity was partly responsible for the poor result. The results were no better,

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[14] Perkins, *Philippine J. Sci.*, **24**, 627 (1924).

[15] *J. Chem. Soc.* (*London*), **85**, 846 (1904).

however, when the oil was thoroughly refined before making the ethyl esters. A run was also made with a crude *H. wightiana* oil of 9.5 per cent acidity, hydnocarpic acid of freezing point 53.3° C. being obtained, by three distillations.

It is therefore concluded that chaulmoogra oil is not suitable for the economical production of hydnocarpic acid.

Analysis of Minor Oils

In continuation of the analysis of various chaulmoogra-group oils begun in the earlier paper,[2] examinations were made of the seeds of *Asteriastigma macrocarpa* (from the Conservator of Forests, Travancore, India), *Hydnocarpus cauliflora* (from the Provincial Treasurer, Cotobato, P. I.), *Hydnocarpus ovoidea* (from W. A. V. Wiren, Catarman, Samar, P. I.), and *Hydnocarpus woodii* (from D. D. Wood, Conservator of Forests, British North Borneo). Table I shows the general characteristics of the oils obtained by extraction of these seeds.

The *Asteriastigma* seeds are very similar in appearance to those of *Hydnocarpus alcalae*, and the high freezing point of the fatty acids of the former approaches that of the latter (55° C.). Fractionation of the ethyl esters gave further evidence of the similarity of these two oils, in that the first fraction from each gives chaulmoogric acid instead of hydnocarpic, on hydrolysis and recrystallization. The *Asteriastigma* oil is inferior to *H. alcalae* oil in rotatory power, however.

The seeds and oil of *Hydnocarpus cauliflora* are very similar to those of *H. hutchinsonii*.

The very low optical rotation of *H. oviodea* oil precludes its classification, chemically, as a chaulmoogra-group oil.

The data for *H. woodii* are somewhat different from those reported in the earlier paper for a small and rather old sample. On fractionating the ethyl esters from this oil it was found to be very similar to the oil of *T. kurzii*.

Table I—Characteristics of Some Minor Oils

Oil	*Asteriastigma macrocarpa*	*Hydnocarpus cauliflora*	*Hydnocarpus ovoidea*	*Hydnocarpus woodii*
Sp. gr., 30°/30° C.	0.936	0.946	0.915	0.949
n_D^{30}	1.4709	1.4732	1.4637	1.4755
Freezing point, ° C.	30	25	25	21
Rotation 100 mm., $[\alpha]_D^{30}$	36	42	1	49
Iodine number, Hanus	87.6	84	47	96
Saponification number	201	201	215	206
Acidity, as per cent oleic	8.2	0.8	5.8	2.5
Fatty acids:				
Freezing point, ° C.	50	42	40	44
$[\alpha]_D^{30}$	39	38	0.7	55

A sample of seeds obtained from a Calcutta firm as *Hydnocarpus castanea* was examined, and the ethyl esters from it were fractionated. Data on this oil are not included in the table because the writers were not able positively to identify it botanically and because the oil was found indistinguishable chemically from that of *T. kurzii*.

Repellents for Blowflies[1]

By R. C. Roark,[2] D. C. Parman, F. C. Bishopp, and E. W. Laake[3]

Bureau of Chemistry and Bureau of Entomology, Washington, D. C.

BLOWFLIES are true flies that deposit their eggs or larvae on meat or in wounds on living animals or man. The larvae feed on the tissues of their host and usually cause death within a few days unless remedial measures are taken.

There are many genera of blowflies, such as *Calliphora, Lucilia, Sarcophaga, Cochliomyia,* etc. One species of the last-named genus, *C. macellaria* Fab., is known in the United States as the screw-worm fly, and is estimated to cause an annual loss of at least $4,000,000 to the livestock owners in the southwestern states. In Australia and other wool-producing countries great loss among sheep is caused by *Lucilia* and *Calliphora*. The study of materials which may be used to kill blowfly maggots in wounds on animals, or to repel the flies, or to prevent their ovipositing in the wounds, is therefore one of great economic importance.

Previous Work

Chloroform has been extensively used to kill maggots in wounds, but benzene has been found by Parman[4] to be more suitable and is now generally used in this country.

For use as a repellent, nearly every material with a strong or disagreeable odor has been suggested at one time or another. Such materials as pyridine, fish oil, bone oil, and various essential oils have been proposed for this use by many authors in the agricultural literature. Proprietary preparations sold as screw-worm fly repellents usually contain crude carbolic acid, which is effective in keeping the flies away from wounds on which it is applied but the lower phenols are very toxic to cattle and other animals, and death of the host often results from the use of these preparations. Investigations conducted by the Bureaus of Entomology and Chemistry

Number of Screw-Worm Flies, *C. macellaria* Fab., Observed Visiting Fresh Beef Liver Treated with Various Repellents Compared with the Number Observed Visiting Untreated Fresh Beef Liver

(Figures are totals of several tests made at different times.)

REPELLENT APPLIED[a]	DILUTED		UNDILUTED	
	Number ratio	Percentage ratio	Number ratio	Percentage ratio
Powders:				
Copper carbonate	3:324	1	1:966	0.1
Pyrethrum powder	14:231	6	50:862	6
Powdered fresh cloves	9:87	10	71:1502	5
Iodoform	37:319	12	76:1116	7
Pinene hydrochloride	55:276	20	1:366	0.3
Chloroacetophenone	57:260	22	0:770	0
Hexachloroethane	145:329	44	15:154	10
Black pepper	55:101	54	53:199	27
Naphthalene	133:232	57	212:929	23
Derris powder	216:350	62	30:634	5
Liquids:				
Wood naphtha	26:296	9	0:160	0
Pine oil No. 4	240:1635	15	2:932	0.2
Clove oil	422:1599	26	105:1107	10
Turpentine, crude	75:286	26	21:747	3
Chloropicrin	599:1822	33	Not tested undiluted	
Pine tar oil (sp. gr. 1.065)	553:1568	35	10:951	1
Pine tar	59:160	37	93:2373	4
Cade oil	519:1366	38	59:1207	5
Ceylon citronella oil	259:455	57	6:212	3
Star anise oil	787:1366	58	142:1456	10
Pyridine	192:312	62	68:1447	5
Guaiacol	841:1366	62	2:505	0.4
American pennyroyal oil	101:160	63	206:2209	9
β-Naphthyl ethyl ether[b]	1066:1366	78	60:1506	4
Bergamot oil	565:293	193	22:366	6

[a] Materials are arranged in the order of decreasing effectiveness as repellents when diluted.

[b] Impure material which was liquid at the temperature of the tests.

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[1] Part of paper presented by Mr. Roark before the Division of Agricultural and Food Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Insecticide and Fungicide Laboratory, Miscellaneous Division, Bureau of Chemistry.

[3] Investigations of Insects Affecting the Health of Animals, Bureau of Entomology.

[4] *J. Agr. Research,* **31,** 885 (1925).

of the United States Department of Agriculture[5] have resulted in the discovery of several promising screw-worm fly repellents. One of these, pine-tar oil—obtained by the destructive distillation of the wood of the long-leaf pine, *Pinus palustris* L.—is recommended as the most suitable for application upon wounds on animals on account of its cheapness, availability, non-toxicity, and adhesiveness, and is now being used on an extensive scale by ranchmen in Texas and other southwestern states.

Experimental

During 1926 additional tests were made with the most promising repellents found up to that time. This work was carried on at Uvalde and Dallas, Texas, where screw-worm flies are abundant. In order to test the strong repellents under as severe conditions as possible, they were diluted, the powders with kaolin and the liquids with medicinal mineral oil, in the ratio of 9 parts diluent to 1 part repellent. The procedure of testing was the same as that previously described; that is, 4-ounce (113-gram) cubes of fresh beef liver, over the surface of which the repellent mixtures were smeared, were exposed from 2 to 5 days in pint Mason jars in an open shed where flies were abundant. The quantity of repellent mixture applied to each bait was 5 cc. for the liquids, or 5 grams for the solids. Untreated meat was exposed at the same time, and the efficacy of the repellent is estimated by comparing the number of flies visiting the treated jar with the adjacent untreated or check jar. A percentage ratio of 100 indicates no repellent or attractant action; one of 0 represents perfect repellent action, while a percentage ratio of over 100 indicates that the material increased the attractiveness of meat to blowflies.

A few of the more significant results are shown in the accompanying table.

It is of interest to note that strongly odorous materials, especially the essential oils, which are quite effective in repelling screw-worm flies from meat when applied undiluted, lose nearly all their efficacy or may become actually attractive—e. g., bergamot oil—when diluted 1 to 9 with an inert vehicle; whereas copper carbonate, which is entirely inodorous is nearly as effective in 10 per cent strength as when applied undiluted.

Conclusion

These results, together with other observations, have led to the belief that the most effective blowfly repellents are not necessarily highly odorous materials, such as essential oils, or even highly irritating materials, such as chloropicrin and other "tear gases," but are materials which can absorb, adsorb, or inhibit the formation of the volatile compounds evolved by decomposing meat which attract the flies to the meat. In addition to various copper compounds, such strong antiseptics as mercuric chloride, potassium permanganate, sodium salicylate, etc., when applied to meat render it almost entirely non-attractive to blowflies.

Tests are now being conducted to determine the practicability as blowfly repellents of copper carbonate and certain other powders when applied upon the wounds of animals under outdoor conditions.

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[5] *J. Econ. Entomol.*, **16**, 222 (1923); **18**, 776 (1925); **19**, 536 (1926); *U. S. Dept. Agr., Bull.* **1472** (March, 1927).

Effect of pH on Adsorption by Carbons[1]

By S. M. Hauge[2] and J. J. Willaman

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Because of the great discrepancies in the results of various investigators, it has been apparent for some time that some factors in the evaluation of decolorizing carbons are not under control. The present writers have undertaken to show the effect of pH on adsorption by carbons. Data are presented which indicate that the more acid a solution is the greater is the adsorption of caramel and of benzoazurin, both of which are negatively charged colloids, while alkalinity favors adsorption of electropositive substances, such as methylene blue. The adsorption of amphoteric substances, such as proteins, is at a maximum in the general region of the isoelectric point of the protein, and is at decided minima in extremes of acidity and alkalinity. Adsorption of dextrose, a non-electrolyte, is not affected by pH.

In the application of carbons to specific requirements as encountered in industries, three factors should be considered—the electrical properties of the substances to be adsorbed, the electrical properties of the available carbons, and the permissible pH of the solutions used. Information concerning these properties should act as a guide in the choice of the carbon best adapted to the specific need, as well as the optimum conditions for adsorption efficiency. Thus, carbons may be prepared for specific requirements.

....

THE well-known property possessed by carbons of removing coloring materials and other substances from solutions is commonly called adsorption. This phenomenon is not a characteristic of all carbons to the same degree, nor is it limited to any specific type of substances. Both organic and inorganic substances, colloids and crystalloids, substances which reduce surface tension and others which do not, are known to be adsorbed. Michaelis[38,*] writes: "There are only two exceptions known hitherto which are not at all adsorbed by charcoal: the sulfates of alkali-metal ions, according to investigations of Rona and myself, and glycocol, according to Abderhalden and Fodor."

Much of the research of recent years has been directed toward the production of highly active carbons, increasing the activity of carbons, and the reactivation of carbons. As a result several highly active decolorizing carbons have appeared on the market in response to the demand of industries requiring very efficient carbons. During some preliminary work in 1922 on the production of active carbons, very irregular and inconsistent results were obtained in attempting to evaluate these carbons. Some factor was apparently not under control, and it was soon evident that at least one important factor was the pH of the medium in which the carbon was acting. Therefore, the series of experiments reported herein was begun.

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[1] Received March 21, 1927. Published with approval of the Director as Paper No. 689, Journal Series of the Minnesota Agricultural Experiment Station. Abridged from a doctor's thesis submitted by the senior author to the University of Minnesota.

[2] Now at the Purdue University Agricultural Experiment Station.

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

Researches on the evaluation and industrial applications of carbons have not kept pace with the rapid development in the production of active carbons. Attempts to evaluate carbons by determining their adsorptive capacities have given results which are often erratic and sometimes inconsistent. This may be partly explained by the fact that most methods hitherto employed to determine the activity of carbons have been empirical and lacking in control of all important variables. Even with the same type of solution and with similar carbons, the results obtained by different investigators are not always comparable. Therefore, each concern wishing to use carbons as adsorbents has deemed it necessary to evaluate them under the condition in which they are to be used and against substances to be removed, in order to determine their value for their particular need.

Carbons have their greatest application in the sugar industry, and they have been used both in direct white-sugar manufacturing and in sugar refining. Their use has been extended to other fields, however, as in the purification of organic and inorganic chemicals, such as lactic, citric, and phosphoric acids, alcohols, acetone, maltose and glucose sirups; decolorization of waxes, gelatin, glue, oils, and fats; purification of petroleum oils and water; recovery of gold from solutions; separation of alkaloids; and preparation of pharmaceuticals.

Mode of Action of Carbons

Adsorption is defined by Ostwald[42] as "that change in concentration which colloids or other dispersed systems suffer at the surfaces where they come in contact with other bodies." He also points out that "this change in concentration is the only constantly observed phenomenon that is common to all the myriad manifestations generally grouped under the term adsorption. After such concentration differences have come to pass, a long series of secondary changes may take place."

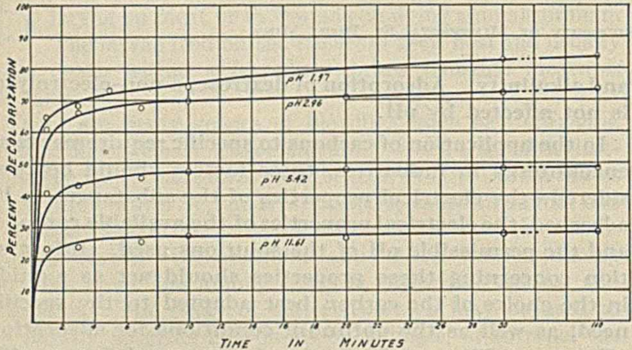

Figure 1—Rate of Adsorption of Caramel by Norit at Various pH Values

To bring about this change in concentration, energy is expended. Ostwald[41,42] states that "a whole series of different kinds of energy plays a role" in adsorption and makes a generalization of Willard Gibbs' theorem that is common to all forces in adsorption which reads as follows: "Adsorption will take place whenever there exists in the surface a difference in energy potential which can be decreased through a change in concentration of the dispersed materials bordering upon this surface."

Ostwald[42] further classifies the types of adsorption resulting from these differences in potential existing at the surface as:

(1) Electrical adsorption, in which the difference of potential is electrical in nature. When the dispersed phase carries an electrical charge opposite that of the solid, substances will be adsorbed by decreasing this difference in potential by neutralization of charges.

(2) Mechanical adsorption, where the difference of potential is due to surface tension. Positive adsorption takes place whenever a decrease in surface tension results from an increase in concentration in the interface.

(3) Chemical adsorption results when the difference of potential is chemical in nature.

(4) Thermic adsorption results from thermic differences of potential in surfaces.

(5) Photic adsorption occurs when the difference of potential is photic in character.

It thus appears that a series of different energies may play a role in adsorption. Since the data secured during the investigation herein reported show that many of the phenomena of adsorption by carbon can be explained on electrical grounds, only that type of adsorption will be discussed here.

A possible explanation for lack of parallelism between surface tension as measured against air and adsorption by charcoal is the formation of electrical charges on the surfaces.[9] In consequence Michaelis divides the total tension at the surface into two classes: "the purely mechanical tension, which causes the usual adhesion and cohesion in the absence of free electrical charges, and an electrical negative tension or expansion effect, due to the covering of the surface with charges of like signs."

In studying the electrical charges on carbons, Perrin[38,p.54] found that charcoal was electronegative in alkaline solutions and electropositive in acid solutions. Cylinder carbon was found to be electronegative under all conditions by Bethe and Toropoff[38,p.54]. Umetsu[38,p.54] confirmed the earlier work of Perrin, using blood charcoal, and also found that carbon prepared from sugar was electronegative, similar to the cylinder carbon determined by Bethe. Later Ogawa[40] showed that the charge on sugar char was not only electronegative but could be also electropositive by activation of the carbon. His endosmotic determinations showed that the amount of water transported by normal sugar char per minute decreased from 0.0348(−)cc. in 0.02 *N* sodium hydroxide to 0.0033(−)cc. in 0.02 *N* hydrochloric acid solutions, while the activated sugar char transported 0.0039 (−)cc. of water in 0.02 *N* sodium hydroxide, 0.00025 (±)cc. in 0.002 *N* sodium hydroxide, and 0.0103(+)cc. in 0.02 *N* hydrochloric acid solutions. This shows conclusively that activation produces effects which influence the electrical charge carried by the carbon in solutions. This evidence is in contradiction to Michaelis'[9,p.244] statement: "Sugar charcoal, on the other hand, does not adsorb the anions at all, not even very easily adsorbed anions of acid organic dyes. In agreement with this we find that sugar charcoal is never charged positively by acids but always negatively."

Adsorption tests with carbon show that the basic dyes are best adsorbed by carbons in acid solutions and acid dyes are best adsorbed in alkaline solutions. On the basis of such observations, Tanner[54] presents a discussion on the application of the adsorption theory of dyeing to carbons. He likens the impurities in a solution to be adsorbed to the dyes and the charcoal to the fiber. He states:

> That charcoal will act like a piece of cloth in removing dye from solution is not new to dye chemists, but the application of this knowledge to the decolorization of sugar sirups and other solutions seems to have been entirely overlooked. Industrially, charcoal is applied in a most empirical manner. Much assistance could be had in setting the correct conditions for the most efficient usage of charcoal if some of the generalities of dyeing be kept in mind.

The relation of the charge on the adsorbent to the charge on the adsorbate is possibly the most important factor in dyeing as well as in adsorption by chars. Bancroft[2] states:

> A fiber tends to adsorb everything in solution in amounts varying with the nature, concentration, and temperature of the solution, and the nature of the fiber. A basic dye is one which con-

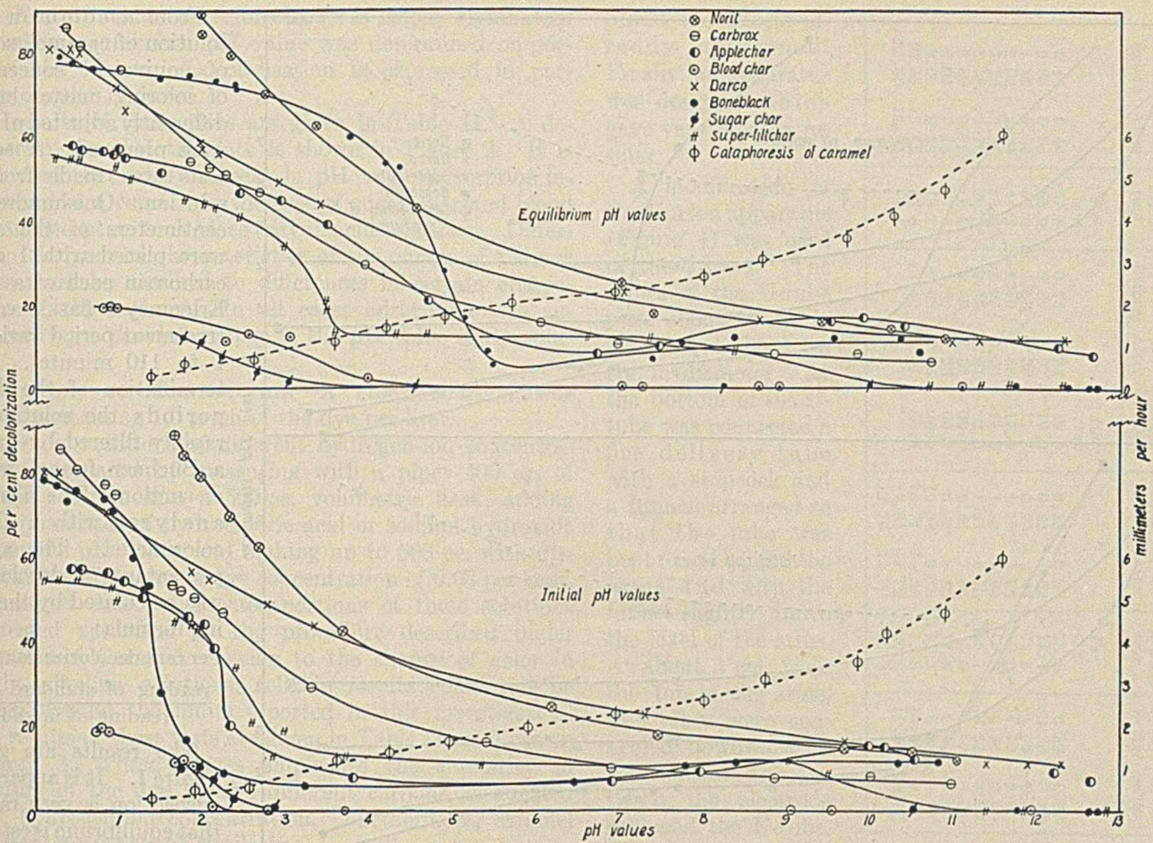

Figure 2—Adsorption of Caramel by Various Chars at Various Hydrogen-Ion Concentrations

> tains the color in the acid radical*** In order to get the maximum adsorption of an acid dye, we should have present an ion of opposite charge, which is readily adsorbed. In case of basic dyes, the dye should be more readily taken up in a neutral or alkaline solution. Acids (hydrogen ions) decrease the dyeing of basic dyes and increase that of acid dyes. This action is proportional to the concentration of hydrogen ions. Bases (hydroxyl ions) have just the opposite effect.

The effect of acid and alkali on the decolorization of sugar and molasses solutions has been known in a qualitative way by many investigators.[10,23,25,54,57,62] In fact, for a long time it has been a common factory practice to decolorize sugar solutions in a slightly acid medium rather than in one that is neutral or alkaline. However, the literature shows that very little quantitative work has been done on the relation between hydrogen-ion concentration and decolorization.

Brewster and Raines[12] studied the effect of pH on the decolorization of cane juice. They found that decolorization increased with hydrogen-ion concentration. In order to reduce inversion of sugar to a minimum, they advocated acidifying with phosphoric acid to pH 4, allowing action for a time, and then neutralizing with lime to pH 6.4. Later they[13] advocated the application of hydrogen-ion control in sugarhouse liquors, and finally took out a patent[14] on the control of hydrogen-ion concentration in the use of decolorizing carbons. Recently Blowski and Bon[7] reported similar effects on raw sugar liquor using a range of pH 4.5 to 8.5. Williams and Gebelin[59] advocate pH between 6.8 and 8.5 for good clarification. Further data on the accurate determination of hydrogen-ion concentration in sugarhouse control have been recently published.[1,3]

The Present Problem

In order to test the importance of pH in the relation between carbon and the substances to be adsorbed, it was believed necessary to investigate adsorbates of various electrical properties; therefore electronegative, electropositive, amphoteric, and non-electrolytic substances have been used, with special reference to their adsorption by a number of charcoals throughout an extensive range of hydrogen-ion concentration.

Materials and Methods

The Carbons—The carbons chosen for this investigation were of two types—animal charcoals high in mineral and relatively low in carbon, and vegetable carbons low in mineral and high in carbon. By such a choice it is possible to compare representative carbons which have been and are used extensively in commercial practices. The following carbons were used:

1—Apple char, prepared from apple pomace (made available through courtesy of Best-Clymer Company of St. Louis).
2—Blood charcoal, Merck.
3—Bone black, Merck.
4—Carbrox, prepared from rice hulls,[50,51] manufactured by Carbrox Co., Inc., New Orleans.
5—Darco, a vegetable carbon purchased from the Darco Sales Corporation, New York.
6—Norit, a vegetable carbon prepared from a secret material, which Tanner[55] believes to be birch wood.
7—Sugar char, prepared from purified sucrose by caramelizing until a char is produced and then heating the char in a nickel crucible with limited air at 1000° C. for 2 hours in a muffle furnace.
8—Superfiltchar, a chemically prepared decolorizing carbon, probably of vegetable origin, sold by the Industrial Chemical Co., Tyrone, Pa.

Physical and Chemical Analyses of Carbons—Since considerable emphasis has been placed on the general characteristics of carbons, determinations were made of ash, nitrogen, and density (Table I).

Ash. The vegetable carbons contain ash with percentages ranging from 0.22 in the case of sugar char to 23.09 in apple

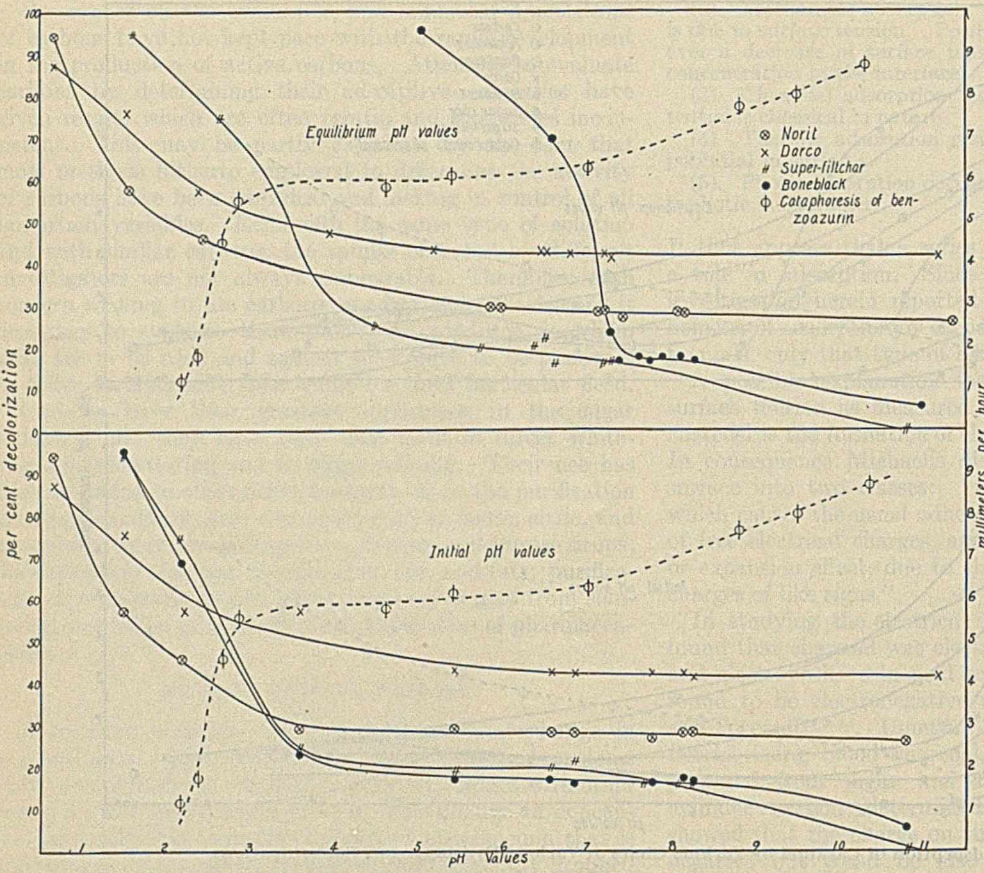

Figure 3—Adsorption of Benzoazurin by Various Chars at Various Hydrogen-Ion Concentrations

char, while in the animal charcoals the percentage of ash ranges from 19.36 to 83.47.

Nitrogen. The Kjeldahl method was used in the determination of nitrogen. The results show that the animal charcoals contain many times as much nitrogen as the vegetable carbons. Sugar char was free of nitrogen.

Apparent Density. The importance of the density of carbons has been pointed out by several investigators.[20,46] The apparent densities of carbons were determined for the various carbons in both air and toluene.

Table I—Physical and Chemical Analyses of the Carbons

CARBON	ASH	NITROGEN	APPARENT DENSITY In air	APPARENT DENSITY In toluene
	Per cent	*Per cent*		
Apple char	23.09	0.56	0.372	1.896
Blood charcoal	19.36	8.20	0.864	1.833
Bone black	83.47	1.13	1.017	2.632
Carbrox	10.34	0.70	0.333	1.796
Darco	22.08	0.46	0.510	1.732
Norit	2.25	0.18	0.306	1.865
Sugar char	0.22	0.00	0.670	1.534
Superfiltchar	3.47	0.09	0.284	1.522

The apparent density in air of these samples of charcoal was determined by filling a 100-cc. graduated cylinder with carbon and tamping the cylinder until constant volume was observed. The volume of carbon was then weighed and the density calculated.

The apparent density in toluene was determined by measuring the volume of toluene displaced by a weighed portion of carbon in a pycnometer and from this the density was calculated.

RATE OF ADSORPTION—In making adsorption tests it is important to know the time required for equilibrium to be established between the adsorbent and the solution. A number of tests were made to determine the rate of adsorption of caramel by Norit at various pH's.

From a common stock solution of caramel, solutions of equivalent concentration of coloring matter but with differently adjusted pH values were prepared. A series of tests was made from each solution. One hundred cubic centimeters of the solution were placed with 1 gram of carbon in each of a series of Erlenmeyer flasks and the treatment period varied from 1 to 110 minutes. At the termination of the different periods the solutions were rapidly filtered by means of a Büchner funnel with aid of suction. The filtrate was analyzed with a Duboscq colorimeter. The apparent percentage of decolorization was calculated by the following formula:

$$\text{Per cent decolorization} = 100 - \frac{\text{reading of standard} \times 100}{\text{reading of unknown}}$$

The results are given in Figure 1. It is apparent that adsorption is very rapid and that equilibrium is established within a few minutes. These results agree with those of other investigators. Firth[26] found that iodine was adsorbed by charcoal very rapidly the first few minutes and then rather slowly. He classified the first as true adsorption and the latter as absorption. Yoe[61] found that the rate of adsorption of arsenious acid on aluminum oxide was quite rapid, about 50 per cent of the total adsorption taking place within the first 5 minutes. Blowski and Bon[7] found that approximate equilibrium was attained after 15 minutes' contact between carbon and sugar liquor, and that no further color adsorption took place after one hour.

Thirty minutes appeared to be ample time for equilibrium to be established between the carbon and the solution, and this period was generally adopted.

Adsorption of Electro-Negative Substances

ADSORPTION OF CARAMEL—Twenty-four grams of sucrose were placed in a 400-cc. beaker and heated for a half hour at 220° C. in a sulfuric acid bath. The caramelized sugar was dissolved in warm water and made up to a volume of 3.5 liters. To insure a uniform stock solution, a sufficient amount was prepared at once to supply the necessary solutions for all tests.

A series of solutions of different hydrogen-ion concentrations was prepared by taking 140 cc. of the stock solution, adding hydrochloric acid or sodium hydroxide to adjust the hydrogen-ion concentration, and bringing the final volume up to 160 cc. Exactly 100 cc. were transferred from each solution to an Erlenmeyer flask containing 1 gram of carbon, shaken occasionally for a half hour, and filtered. A portion of the remaining 60 cc. was used for the electrometric determination of the initial hydrogen-ion concentration, and the remainder was used as a standard in the Duboscq colorimeter in analyzing the filtrate for the degree of color removed. By using the corresponding standard with each filtrate the error due to the effect of acidity on color change is largely eliminated. The final or equilibrium pH value was determined on portions of the filtrate. Decolorization is expressed in percentage of color removed.

The results of these tests are given in Table II. A detailed comparison of the data is shown in Figure 2. It is to be noted that with decrease in pH value adsorption increased and vice versa. In the case of sugar char and blood charcoal adsorption took place only in acid solutions. Differences in the general characteristics of the curves of various carbons must be ascribed to differences in certain characteristics of the carbons. In all cases adsorption was accompanied by a decided change in the pH value of the solution.

ADSORPTION OF BENZOAZURIN—A stock solution was prepared containing 1.0 gram of the dye per liter.

A series of solutions of different hydrogen-ion concentrations was prepared by measuring with a pipet 400 cc. of the stock solution into a 500-cc. volumetric flask, adding definite quantities of hydrochloric acid or sodium hydroxide to adjust the pH value, and making up to 500 cc. with distilled water. This gave a dye concentration of 0.08 per cent. One hundred cubic centimeter portions of these solutions were tested according to the procedure described under Adsorption of Caramel. Owing to the change of color in strongly alkaline solutions, reliable results could not be obtained beyond the limits reported in this investigation.

The results of these tests are given in Table III and shown in Figure 3. These curves emphasize the similarity in adsorption of the dye by the different carbons as affected by the hydrogen-ion concentration. Furthermore, caramel and benzoazurin behave similarly.

In the tests with both materials, data were obtained which show that the efficiency of the different carbons was increased enormously by increasing the acidity.

Experiments in Electrophoresis

The data thus far presented have shown that the hydrogen-ion concentration of the solution has a decided effect on the adsorption of electronegative substances. Since either the adsorbent or the adsorbate, or both, could be affected by the reaction of the medium, experiments were instituted to determine the nature of the electrical charges on the two compounds.

Careful surveys of the literature on the electrical properties of dispersed substances, the theories of cataphoresis, the velocity of migration of particles in an electric field, the charge on particles, etc., have been presented by Burton,[18,19] Svedberg,[53] Bancroft,[3] Taylor,[56] and many others.

Many methods and many types of apparatus have been used for the measurement of cataphoresis. Svedberg[53] classifies the methods into three types: "(1) rate of migration of boundary between sol and dispersion medium measured; (2) change in concentration of dispersed phase in a volume near the boundary measured; (3) migration of the individual particles measured directly in the ultra-microscope." The first appeared to be the most promising for suspensions of caramel and of benzoazurin.

APPARATUS—Various types of U-tube apparatus were tried in these experiments to determine the velocity of migration of caramel and benzoazurin in solutions of different pH values. Since the migration is slow and, therefore, the period of time must be long, many difficulties were encountered. With the ordinary U-tube having the electrodes in contact with the liquid in the arms of the tube, the chief interference was due to (1) convection currents around the electrodes which displaced the boundary line of the colloid, and (2) the accumulation of electrolysis products which produced the effects already mentioned. Finally, an apparatus was designed which gave very reliable results.

A modification of the Burton apparatus (Figure 4) was used in these tests. The arms of the U-tube were about 12 cm. in length and about 1.5 cm. in diameter. At the bottom of the U-tube was connected a fine delivery tube with a stopcock and a funnel, arranged so that the tube was bent round behind the arms and with the funnel slightly above the level of the arms. At about 3 cm. from the top of the arms, side tubes were connected downward to form a bridge between the electrode cells and the U-tube. This arrangement prevented the accumulation of gas bubbles, which often break the circuit in liquid bridge connections. The electrode cells were 9 cm. long and 3 cm. in diameter, with a capacity of about 50 cc., assuring ample volume for the accumulation of electrolysis products. These cells were so arranged as to be of the same height as the arms of the U-tube. They were fitted with stoppers containing two holes, the larger hole for the escape of gases and the smaller for the electrode.

METHOD—A series of solutions having the same specific conductivity, but different pH values, was prepared of the different materials to be tested. Since an appreciable error may be introduced by using solutions of different specific conductivity from those of the

Table II—Effect of pH on Decolorization of Caramel Solutions by Various Chars

APPLE CHAR			BLOOD CHAR			BONE BLACK			CARBROX			DARCO			NORIT			SUGAR CHAR			SUPERFILTCHAR		
pH		Decolorization	pH		Decolorization	pH		Decolorization	pH		Decolorization	pH		Decolorization	pH		Decolorization	pH		Decolorization	pH		Decolorization
Before	After		Before	After		Before	After		Before	after		Before	After		Before	After		Before	After		Before	After	
		Per cent			*Per cent*			*Per cent*			*Per cent*			*Per cent*			*Per cent*			*Per cent*			*Per cent*
0.44	0.46	57.6	0.75	0.84	19.0	0.13	0.30	78.9	0.29	0.37	86.0	0.13	0.18	80.9	1.67	1.99	89.1	1.79	1.85	11.8	0.13	0.26	54.9
0.83	0.95	52.9	0.89	0.97	19.0	0.42	1.52	73.7	0.86	0.91	77.6	0.86	0.97	71.2	1.77	2.00	84.3	1.93	2.00	10.8	0.86	0.97	53.0
1.32	1.52	51.0	1.68	2.30	11.3	0.95	2.43	71.3	1.66	1.86	53.7	1.84	1.97	58.3	1.98	2.34	79.2	2.15	2.24	7.4	1.67	1.80	44.9
2.03	2.94	44.3	1.79	2.56	12.8	1.18	3.76	60.0	1.73	2.07	52.1	2.79	2.92	49.0	2.34	2.75	70.0	2.40	2.67	3.3	2.40	2.97	33.4
2.15	3.51	38.8	1.93	3.06	11.8	1.53	4.89	27.9	2.26	2.70	46.8	3.34	3.41	44.0	2.68	3.36	62.6	2.80	3.03	1.4	2.60	3.47	20.2
2.36	4.70	20.3	2.15	3.97	2.0	1.81	5.13	16.7	3.32	3.93	29.3	7.29	6.98	23.1	3.34	4.57	42.8	3.72	4.56	0.0	3.98	4.31	12.8
3.82	6.72	8.0	2.40	7.01	00.0	6.46	7.36	6.9	5.42	6.04	15.4	9.69	8.66	16.2	6.19	6.98	25.0	9.02	8.25	0.0	5.35	6.63	11.8
6.92	7.16	7.5	2.80	7.25	00.0	8.40	8.35	11.8	6.90	6.95	10.2	10.53	9.81	11.8	7.47	7.39	18.0	9.56	10.00	0.0	9.02	7.36	11.8
9.99	9.52	15.8	9.02	8.65	00.0	10.38	9.55	11.8	8.83	8.84	8.0	11.11	10.57	8.6	9.73	9.46	16.7	11.40	11.30	0.0	9.56	8.36	8.6
10.53	10.42	13.8	11.40	11.12	00.0	10.77	10.35	11.8	10.01	9.83	8.3	11.61	11.30	11.8	10.52	10.25	14.3				11.40	10.70	0.0
12.66	12.65	7.5				11.81	11.72	00.0	11.00	10.72	6.3	12.33	12.33	11.8	11.09	10.90	11.8				11.81	11.72	0.0
						12.73	12.70	00.0													12.73	12.71	0.0

sols,[9,18] a clear solution was prepared having the same pH and specific conductivity as the corresponding colloidal solution.

In filling the apparatus, the colloidal solution to be measured was poured into the funnel and allowed to flow into the small tube until it reached the top of the bore of the stopcock, which was then closed. The water having the same pH and conductivity as that of the colloid solution was then poured into the electrode cells until the U-tube was filled to a height of about 4 cm. The stopcock was then opened slightly and the colloidal solution allowed to run into the U-tube, forcing the water upward into the arms of the tube to the desired height. By careful manipulation a distinct separation between the sol and the water was secured. The initial reading of the boundary line between the sol and the water was recorded. Direct current was supplied by a motor generator. The voltage was fairly constant at 110 volts. At the termination of a definite period of time readings were again taken, and from this the migration was calculated.

Table III—Effect of pH on Decolorizing of Benzoazurin Solutions by Various Chars

Bone Black			Darco			Norit			Superfiltchar		
pH		Decolorization	pH		Decolorization	pH		Decolorization	pH		Decolorization
Before	After		Before	After		Before	After		Before	After	
		Per cent			*Per cent*			*Per cent*			*Per cent*
1.49	5.02	95.7	0.65	0.67	87.4	0.65	0.66	94.3	1.49	1.60	94.8
2.18	6.59	69.0	1.49	1.53	75.9	1.49	1.55	57.5	2.18	2.63	74.3
3.57	7.29	23.1	2.18	2.39	57.5	2.18	2.44	46.0	3.57	4.47	24.9
5.43	7.60	17.4	3.57	3.93	47.4	3.57	5.85	29.6	5.43	5.71	19.3
6.56	7.90	17.4	5.43	5.16	43.1	5.43	5.97	29.1	6.56	6.35	20.0
6.85	7.76	16.7	6.56	6.45	42.9	6.56	7.18	28.6	6.85	6.49	21.9
7.77	7.37	16.7	7.77	6.80	42.2	7.77	7.42	27.0	7.77	6.60	16.0
8.13	8.10	17.4	8.13	7.21	42.2	8.13	8.07	28.1	8.13	7.18	16.0
8.25	8.27	16.7	8.25	7.27	41.2	8.25	8.15	28.6	8.25	7.27	16.7
10.80	10.96	5.8	10.80	11.16	41.2	10.80	11.35	25.9	10.80	10.80	0.0

Cataphoresis of Caramel and Benzoazurin—The results of the cataphoresis measurements of the various caramel solutions are recorded in the dotted lines in Figure 2 and of the benzoazurin solutions in Figure 3.

In the case of the caramel solutions the velocity of migration decreases continuously with the decrease of pH. Since the migration is a result of the charge on the particles, the curve indicates the relative magnitude of the charges on the particles at different pH values, if we may assume that the size of the particle stays constant. The general trend of the curve would indicate that the isoelectric point for caramel is somewhere in the lower range of pH value. This point could not be attained in the present case, because in solutions which had pH values below 2.5 precipitation took place on standing a long time, increasing in amount with increasing acidity. However, in none of the solutions above pH 2.5 was there any sign of precipitation, even after a year and a half.

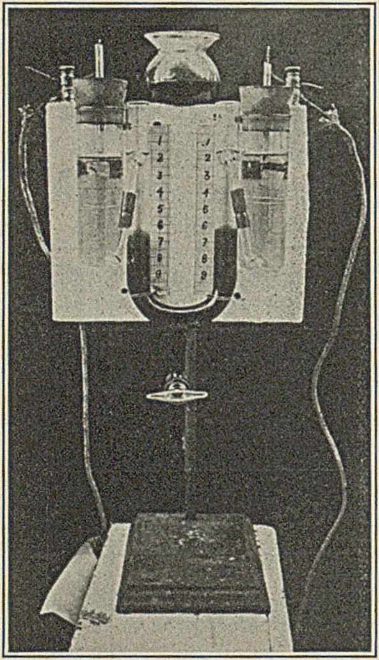

Figure 4—Apparatus Used in Cataphoresis Measurements

With the benzoazurin solutions as the pH was decreased the rate of migration fell gradually until a pH of 2.5 was reached at which point there was an abrupt fall in the migration. With the particular solutions involved, it was not feasible to go lower on the pH scale, where possibly an actual isoelectric point of the dye might have been found.

Electro-Endosmosis of Carbons—The attempt was made to measure the kind and quantity of the charge on carbon particles suspended in solutions of various hydrogen-ion concentrations. Briggs' apparatus[15] was employed. It was found that carbons in solutions of low pH were charged positively, while those in solutions of high pH were charged negatively. The values obtained for flow of water were so small that they were not considered reliable in a quantitative sense. They were far lower than the values secured by Briggs with carborundum. After these attempts were abandoned, Ogawa[40] published values for carbon that compared very favorably with the results of the present writers. The experiments showed that the charge on carbon does change in sign from an alkaline to an acid solution, and vice versa.

Adsorption of an Electropositive Substance

Experiments were next conducted to determine the effect of hydrogen-ion concentration on the adsorption of electropositive substances. Since basic dyes are all electropositive, methylene blue was chosen as a typical example. Briggs and Bull[16] found that methylene blue forms a true solution in acid or neutral solutions, while in alkaline solutions a suspension is formed which precipitates with increased alkalinity. Evidently, the degree of dispersion decreases as the reaction of the solution approaches strong alkalinity. Since precipitation is a result of neutralization of charges, it is very probable that the magnitude of the positive charge gradually decreases towards the precipitation point and the process is opposite to that of caramel, or of benzoazurin. Consequently, adsorption should be more pronounced when the charge is small—that is, on the alkaline side of neutrality.

Stock solutions of methylene blue were prepared in two concentrations: (1) a 0.0025 M solution, used in the tests with sugar char, blood charcoal, and bone black; and (2) a 0.0125 M solution, used in the tests with Darco.

In the determination of the hydrogen-ion concentration of methylene blue solutions difficulties were experienced with the hydrogen electrode. Determinations on the dye solution always resulted in low pH values. This same electrode, which gave low results with the dye solution, gave correct readings with the standard buffer solutions, a peculiarity which was also observed by Briggs and Bull.[16] They attribute this to the adsorption of dye by the platinum electrode, which tended to lower the adsorption of hydrogen and rendered the electrode inaccurate. The dye may also be reduced by the hydrogen in contact with platinum black, and this decolorizing action causes errors. Consequently, in these tests the acidity and alkalinity of the methylene blue solution are expressed in cubic centimeters of 0.1 *N* acid or alkali added to the solution of methylene blue.

A series of solutions was prepared by taking 100 cc. of the stock solution, adding a definite number of cubic centimeters of 0.1 *N* acid or alkali, and making the final volume to 125 cc. with water. To 1-gram samples of the carbons were added 100 cc. of these dye solutions and the adsorption was measured as described before.

The results with sugar char, Darco, blood char, and bone black are given in Table IV and Figure 5. Addition of alkali caused an immediate and pronounced increase in adsorption, especially notable in the case of Darco.

Table IV—Adsorption of Methylene Blue by Various Carbons

Treatment	Per Cent Decolorization			
	Sugar char	Blood charcoal	Bone black	Darco
Cc.				
Hydrochloric acid:				
25	0.0	24.5	41.2	65.1
5	0.0	23.2	41.2	59.1
1	0.0	23.2	45.0	52.9
0.75	0.0	20.8	38.3	...
0.50	0.0	23.2	39.8	52.9
No treatment	0.0	23.2	39.8	59.1
Sodium hydroxide:				
0.50	3.9	24.5	46.3	72.9
1	13.8	29.9	53.7	76.7
5	24.3	39.1	73.6	97.3
15	30.6	45.1	78.8	97.2
25	32.5	46.3	81.3	97.8

The effect of pH on the adsorption of methylene blue by cotton was studied by Clibben and Geake,[22] who found that the amount of dye adsorbed increased with pH. Marker and Gordon[37] found that the adsorption of basic dyes by inorganic gels increased with pH.

INFLUENCE OF ASH ON ADSORPTION—With sugar char adsorption takes place only in the alkaline media. Inasmuch as this carbon is nearly ash-free, it seemed advisable to reduce the ash of some other carbon for comparison. To obtain as great a contrast as possible between the original carbon and the final product, bone black was chosen because of its high ash content.

A quantity of bone black was digested in 10 per cent hydrochloric acid solution, refluxed at boiling temperature for extended periods, filtered, and washed. This process was repeated until the filtrate gave a negative test for calcium and phosphorus, which took several weeks. To remove the last traces of acid, the carbon was refluxed with distilled water, filtered, and washed. This process was repeated for several days until the filtrate was neutral to litmus and a negative test for chlorine was obtained. The carbon was then dried.

The original and the treated bone black were then compared against 0.002 *M* methylene blue, with various additions of alkali and acid. The results are shown in Figure 6. The striking fact is that the curve for the treated bone black crosses that for the original on the alkaline side and becomes much more efficient as an adsorbent. On the acid side it is less efficient. It should be kept in mind that the carbon content is much greater in the treated than in the original bone black, and that hence much of the adsorption by the latter is due to the calcium phosphate in it. The point brought out by these comparisons is that the capacities of the two bone blacks are changed in relation to the reaction of the medium.

Adsorption of Amphoteric Substances

Though numerous substances possess amphoteric properties, proteins were chosen for the present work because they are readily available, and solutions suitable for these tests are easily prepared. Furthermore, much study has already been given to the properties of proteins which is of valuable aid in presenting this phase of the work.

Loeb[35] demonstrated by a series of curves the influence of pH on the total swelling, viscosity, osmotic pressure, and conductivity of gelatin solutions. These physical properties are at a minimum at the isoelectric point. Hardy[35, p.6] demonstrated by experiments on the migration of suspended particles of coagulated white of egg in an electrical field that they were positively charged on the acid side of the isoelectric point, negatively charged on the alkaline side, and possessed no charge at the isoelectric point.

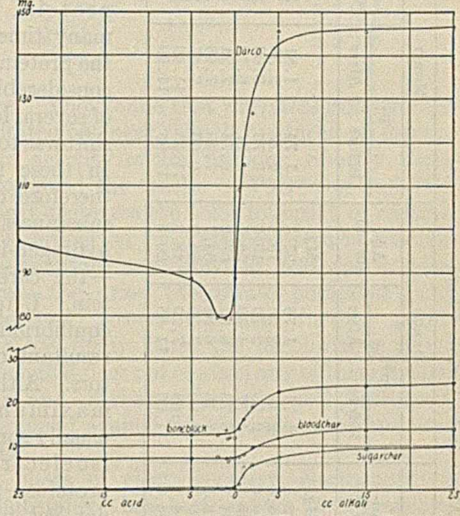

Figure 5—Adsorption of Methylene Blue by Various Chars in Presence of Various Additions of Acid and Alkali

ADSORPTION OF EGG ALBUMIN AND GELATIN—The egg albumin was secured from the Coleman and Bell Company. Stock solutions of two concentrations were prepared by dissolving 10 grams of egg albumin per liter in one case and 5 grams in the other. In order to have as homogeneous a system as possible, avoiding large undissolved particles, the solutions were filtered. The solutions of the higher concentrations were used for the tests with bone black, blood char, Carbrox, and sugar char; while the other was used for Darco, Norit, and Superfiltchar. In the gelatin experiments 0.5 per cent solutions were used.

A series of solutions was prepared with varying pH values by pipetting 400 cc. of the stock solution of protein into 500-cc. volumetric flasks, adding quantities of hydrochloric acid or sodium hydroxide, and diluting the solution to a final volume of 500 cc. The adsorption tests were made as follows: To 1-gram portions of the respective carbons were added 100 cc. of these solutions, and the mixture was shaken at intervals for an hour. After settling, the supernatant liquid was centrifuged to eliminate the carbon. The pH values of the solutions, before and after the treatment with carbon, were determined electrometrically. The protein contents were determined by the Kjeldahl method.

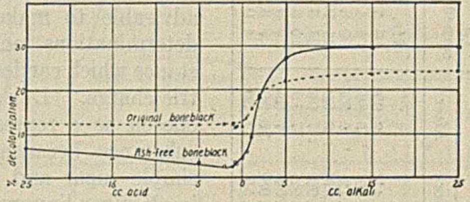

Figure 6—Effect of Removal of Ash from Bone Black on Its Decolorizing Action

The results with egg albumin are presented in Table V

Table V—Effect of pH on Adsorption of Egg Albumin by Various Chars

BLOOD CHAR			BONE BLACK			CARBROX			SUGAR CHAR			DARCO			NORIT			SUPERFILTCHAR		
pH		Adsorbed	pH		Adsorbed	pH		Adsorbed	pH		Adsorbed	pH		Adsorbed	pH		Adsorbed	pH		Adsorbed
Before	After		Before	After		Before	After		Before	After		Before	After		Before	After		Before	After	
		Mg.			*Mg.*			*Mg.*			*Mg.*			*Mg.*			*Mg.*			*Mg.*
1.41	2.18	2.0	1.41	2.92	19.5	1.41	2.35	2.1	1.41	1.53	2.1	1.74	1.76	25.3	1.74	1.81	30.6	1.74	1.81	6.1
2.51	3.15	31.4	1.89	5.86	76.4	2.51	2.83	32.6	1.89	2.14	6.4	2.17	2.20	18.1	2.17	2.30	18.1	2.17	2.31	8.6
3.12	3.67	45.5	3.12	6.38	50.8	3.85	4.52	63.8	2.51	2.67	46.6	2.75	2.79	19.9	2.75	3.08	26.3	2.75	2.90	7.0
3.85	4.49	39.2	3.85	6.82	41.9	6.67	6.28	50.0	3.12	4.82	38.5	4.77	4.30	50.7	4.77	6.19	77.3	4.77	3.94	15.7
4.75	7.05	23.5	5.92	7.06	24.5	7.83	7.06	40.4	3.85	6.41	34.9	6.78	6.62	57.2	6.78	7.21	58.4	6.78	5.23	29.6
7.45	7.74	4.4	7.92	7.16	15.6	8.88	7.61	8.2	5.92	6.79	12.2	7.18	6.84	64.7	7.48	7.43	57.8	7.48	5.72	25.9
10.01	7.74	0.0	8.04	7.65	13.3	10.01	8.76	3.4	6.67	7.24	9.7	7.60	7.25	54.9	9.68	7.47	23.5	7.60	5.95	28.6
11.08	10.51	0.0	11.08	10.90	8.6	11.08	10.67	1.6	8.04	7.57	4.6	9.68	7.29	48.2	11.45	11.40	20.2	11.45	10.96	8.8
11.55	11.53	0.0	11.55	11.50	4.0	11.55	11.50	2.5	11.55	10.42	4.6	11.96	11.85	26.3	11.96	11.90	6.6	11.96	11.54	6.1

and in Figures 7, 8, and 9, and with gelatin in Table VI and Figure 10. There is a marked similarity in the type of adsorption curves for all the carbons and for both proteins. There is a zone of maximum adsorption usually between pH 3 and 6. This zone apparently differs more with the carbons than it does with the protein. It was noted many times that the pH of the protein solutions shifted considerably over a period of several hours; usually the shift was towards neutrality. In these mixtures we are therefore dealing with two substances which affect the hydrogen-ion concentration—the carbon and the protein. Undoubtedly, the equilibrium attained is a resultant of both these factors. Although the zone of maximum adsorption is usually somewhere near the isoelectric point of the proteins—pH 4.7—we are not yet justified in saying definitely that carbons adsorb proteins most efficiently at their isoelectric point. The data presented here do indicate, however, that pH is an important factor in the removal of proteins from solutions by carbon.

Adsorption of a Non-Electrolytic Substance, Dextrose

Since variations in hydrogen-ion concentrations have considerable influence on the adsorption of electrolytic substances, it was deemed advisable to make similar determinations on a substance which carries no electric charge. Dextrose was chosen as a representative substance because it is a simple sugar and is found in all sugar liquors.

The adsorbability of sugars by charcoals has been pointed out by Kolthoff,[33] Rona and Michaelis,[49] Rona and Von Toth,[48] and others,[52,60] while Rakusin[45] and Peck[44] state that sucrose and glucose are not held by carbons.

The stock solution contained 5 grams of dextrose (Pfanstiehl) per liter. The general procedure was the same as described previously. The Koch and Ruhsam method[17, p. 420] was used for the determination of sugar in the solutions before and after treatment with carbon.

Table VI—Effect of pH on Adsorption of Gelatin by Various Chars

DARCO			NORIT			SUPERFILTCHAR		
pH		Adsorbed	pH		Adsorbed	pH		Adsorbed
Before	After		Before	After		Before	After	
		Mg.			*Mg.*			*Mg.*
1.38	1.44	62.9	1.75	1.81	51.0	1.38	1.39	21.0
2.25	2.36	55.3	2.06	2.16	44.6	2.25	2.25	20.5
4.45	4.10	75.4	3.02	3.29	48.3	4.45	4.09	31.7
5.90	5.18	80.7	3.45	3.82	73.1	6.89	5.03	46.6
6.89	5.98	86.6	4.80	4.97	92.7	7.11	6.22	34.2
7.11	6.38	73.2	6.94	6.11	89.5	8.39	7.12	32.5
8.39	7.20	63.9	7.58	7.17	66.1	9.72	9.52	34.4
9.72	8.68	66.7	7.85	7.59	57.2	11.01	11.00	28.6
11.01	10.71	61.8	10.83	10.70	44.1	11.62	11.52	14.0
11.99	11.75	63.7	11.64	11.50	36.3	11.99	11.94	6.3

The initial and final pH of each solution and the amount adsorbed are given in Table VII. Small amounts of dextrose were adsorbed by all three carbons, the least by bone black. The amounts were very irregular, however, and apparently had nothing to do with the pH of the solutions.

Table VII—Effect of pH on Adsorption of Dextrose by Various Chars

BONE BLACK			DARCO			NORIT		
pH		Adsorbed	pH		Adsorbed	pH		Adsorbed
Before	After		Before	After		Before	After	
		Mg.			*Mg.*			*Mg.*
1.65	5.21	17	1.65	1.74	25	1.65	2.04	13
2.46	6.28	9	2.46	2.51	24	2.46	2.63	9
2.96	7.02	8	2.96	3.02	33	2.96	5.02	19
3.03	7.05	8	3.03	3.08	28	3.03	5.92	8
3.55	7.04	3	3.55	3.16	26	3.55	6.10	27
3.69	7.05	0	3.69	3.39	23	3.69	6.16	26
6.14	7.50	12	6.14	3.98	23	6.14	6.15	21
7.11	7.26	6	7.11	4.15	33	7.11	6.24	32
9.10	7.75	10	9.10	5.09	30	9.10	6.35	28
10.15	8.85	9	10.15	9.00	27	10.15	8.04	27
10.92	10.60	1	10.92	10.67	27	10.92	10.10	30
11.12	10.93	8	11.12	10.92	30	11.12	10.51	30
11.58	11.42	10	11.58	11.26	27	11.58	11.07	47

Apparent Isoelectric Points of the Carbons

According to Kroetz,[34] the isoelectric point of a charcoal is the pH of the buffer solution that is not changed in reaction by the addition of the charcoal. He found this point to be pH 7.58 for the charcoal he studied. It will be noted that in all the data in these experiments the addition of the carbons caused a change in the pH value of the solution. It will be further noted that in any one series these values always changed toward a certain point. These points, or zones, as nearly as could be determined, were assembled from the various tables and tabulated in Table VIII. They represent the apparent isoelectric points or zones of the carbons used in these experiments and against the various substances adsorbed. Darco has the lowest apparent isoelectric zone. All carbons have a lower zone with the proteins than with any of the other adsorbates. It should be pointed out again that this zone is the resultant of two factors, the carbon and the colloid to be adsorbed. At present, therefore, we cannot ascribe any definite significance to these values. That carbons actually have an isoelectric zone was determined electro-endosmotically by the writers and by Ogawa,[40] as mentioned above.

Bartell and Miller,[5,6,39] however, interpret the change in reaction accompanying adsorption as being hydrolytic in nature. Miller[39] states that "when a basic dye is adsorbed by these charcoals, acid is set free, and when an acid dye and certain salts are adsorbed alkali is set free." Accordingly, the pH should be shifted only in one direction for each type of compound. Miller, however, did not cover a range of pH values, and hence his data could not disclose an apparent isoelectric zone.

Discussion

From the foregoing experiments it would appear that one of the most important factors in determining the adsorbability of substances by carbons is the hydrogen-ion concentration of the solutions. The importance of determining the reaction of the solution has been overlooked by most investigators, and for this reason most of the earlier tests on the adsorptive power of carbons are of little value for a comparative study of the decolorizing efficiency of various carbons.

Table VIII—Apparent Isoelectric Zones of Various Carbons in Presence of Different Adsorbates

(Figures refer to pH)

ADSORBATES	APPLE CHAR	BLOOD CHARCOAL	BONE BLACK	CARBROX	DARCO	NORIT	SUGAR CHAR	SUPERFILTCHAR
Caramel	7.2–7.4	7.3–8.6	7.4–7.7	7.0–8.8	3.4–7.0	7.0–7.4	8.2–10.0	6.6–7.3
Benzoazurin			7.6–7.7		3.9–5.1	7.2–7.4		5.7–6.3
Egg albumin		7.7	7.1–7.2	4.9–5.1	2.7–4.3	7.2–7.4	7.2–7.5	2.9–3.9
Gelatin					2.3–3.6	5.0–6.1		2.2–3.5
Dextrose			7.2–7.7		3.2–3.4	6.1–6.3		

In the work here reported, only the relation of hydrogen-ion concentration to the adsorption of various types of compounds, together with a change in reaction accompanying adsorption, was determined.

As regards rate of adsorption, Figure 1 shows that equilibrium is established in a very short time and that the rate of adsorption is independent of the pH value of the solution.

The differences in the general properties of the carbons (Table I), such as carbon content, percentage of ash, percentage of nitrogen, and density are not reflected in the tests described in this paper, and hence do not appear to be very important factors in determining the degree of adsorption.

The activity of carbons has, from time to time, been ascribed to various impurities generally found in different preparations of carbon. Possibly the foremost of these theories is that the presence of nitrogen in the form of some complex is responsible for adsorption.[27,30] In 1868 Wallace[58] pointed out that the presence of nitrogen was always associated with good decolorizing carbons. Patterson[43] believed that the decolorizing action of charcoals is due principally to an organic nitrogenous substance which he isolated with sulfuric acid, and which was from sixteen to forty times as active as bone black. Knecht[31,32] observed that the decolorizing action was directly proportional to the nitrogen content of the char. Following the suggestion of Bancroft,[4] the work of Patterson was repeated by Hall.[28] He extracted a substance with the empirical formula $C_{25}H_{20}N_4O_6$, to which he claims charcoal owes its activity.

In 1921 the authors attempted to repeat the work of Hall, but without success. They found that when this isolated substance was precipitated on sugar char, it produced no demonstrable increase in activity of the carbon. Shortly thereafter, Tanner[54] explained the results of Patterson and Hall by the fact that acid decreases the color intensity of caramel solutions. This is supported by Patterson's own observations "that the precipitate suspended in acid was a good decolorizer, whereas the dried precipitate possessed practically no decolorizing power." Tanner further points out that kelpchar has many times the decolorizing action of bone black, although it does not contain any of this nitrogen complex. Clark[21] and Zerban, Freland, and Sullivant[63] also present an argument against the nitrogen constituents as decolorizing agents.

Adsorption by chars of electronegative, electropositive, and amphoteric substances has been shown in the accompanying tables to be greatly affected by the reaction of the medium. This seemed to be a more important factor in most cases than the nature of the carbon. Thus the order of relative values of the various carbons in caramel solutions at a pH of 7 would be: Norit, Darco, Superfiltchar, Carbrox, apple char, bone black, blood charcoal, and sugar char; while if they were tested at pH 4 quite different results would be obtained, with the order of efficiency changed to: bone black, Norit, apple char, Carbrox, Superfiltchar, blood charcoal, and sugar char. It is apparent that methods

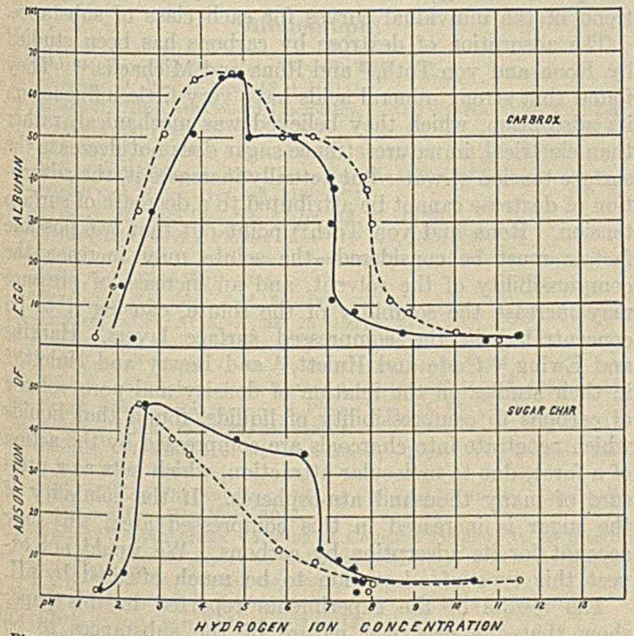

Figure 7—Adsorption of Egg Albumin by Various Chars at Various Hydrogen-Ion Concentrations

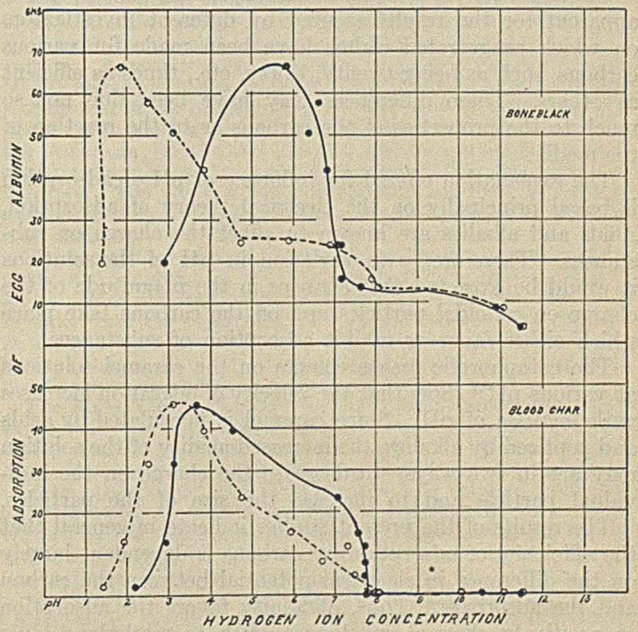

Figure 8—Adsorption of Egg Albumin by Various Chars at Various Hydrogen-Ion Concentrations

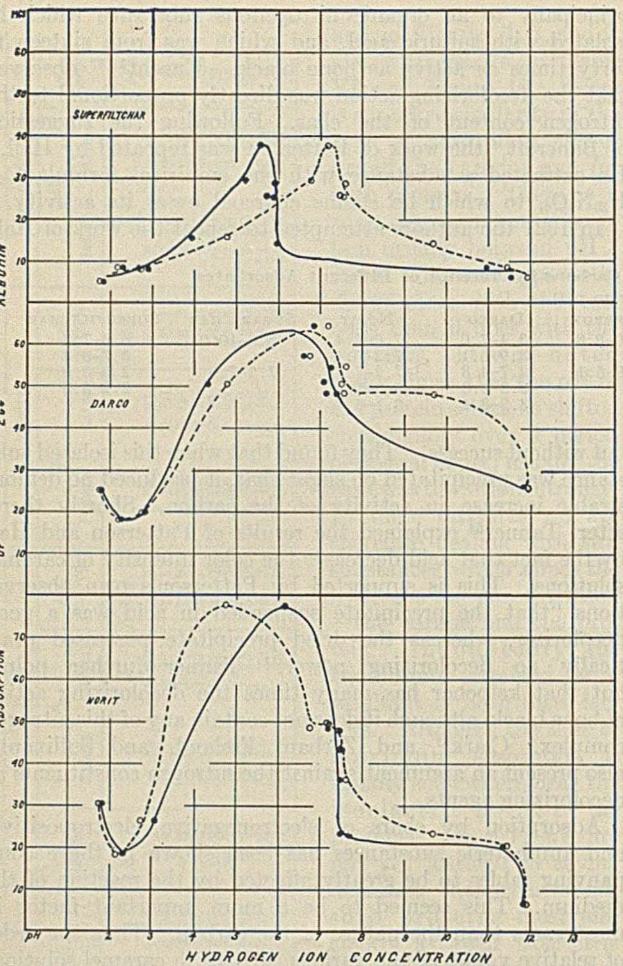

Figure 9—Adsorption of Egg Albumin by Various Chars at Various Hydrogen-Ion Concentrations

in which the solutions are adjusted to one pH value do not disclose the possibilities of the carbons for adsorption at other values. Similar relations could be pointed out for the other substances used.

On the basis of these relationships, an explanation is apparent for the results secured by different investigators on which exaggerated claims have been made for various carbons, such as being twenty, thirty, etc., times as efficient as others. These differences may have been due not so much to the properties of the carbons as to the reaction of the media.

The explanation offered for influence of pH on adsorption is based principally on the electrical theory of adsorption. Acids and alkalies are known to affect the charge on substances. Therefore, with variation in pH of the solutions it would be expected that changes in the magnitude of the charge on colloidal particles and on the carbons take place which either favor or inhibit adsorption of substances.

The cataphoretic measurements on the caramel solutions at various pH's show that the velocity of migration increases with increase of pH. Since caramel is flocculated by acids and peptized by alkalies, the increased acidity of the solution may act in two ways—to decrease the charge on the individual particle and to increase the size of the particles.

The results of the present studies indicate in general that the efficiency of adsorption by carbons is dependent largely on the difference in electrical potential between the carbon and the adsorbate. Thus, alkalinity favors the adsorption of positively charged substances, such as methylene blue; acidity favors the negatively charged, such as caramel and benzoazurin; and amphoteric substances, such as proteins, are best adsorbed in the region of pH 3 to 6, with decided minima at extremes of acidity and alkalinity. The adsorption of a non-electrolytic substance such as dextrose is not affected by pH. These generalized relations are brought out in Figure 11. Each curve represents the general trend of the individual curves for each class of substance.

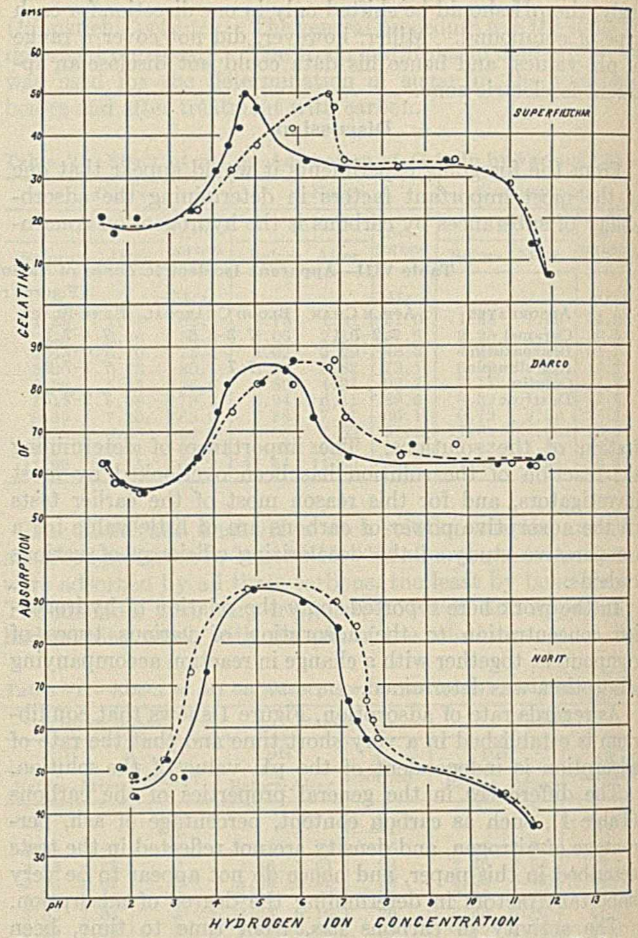

Figure 10—Adsorption of Gelatin by Various Chars at Various Hydrogen-Ion Concentrations

The adsorption of dextrose by carbons has been studied by Rona and von Toth,[48] and Rona and Michaelis.[49] They found that strong mineral acids have very little influence on its adsorption, which they believed was mechanical, rather than electrical, in nature. Since sugar does not decrease the surface tension of water but actually increases it, the adsorption of dextrose cannot be attributed to a decrease of surface tension. Rona and von Toth[48] point out that two possible factors must be considered—the solute may increase the compressibility of the solvent, and an increase of pressure may increase the solubility of the solute, causing it to be concentrated in the compressed surface layers. Harkins and Ewing,[29] Cude and Hulett,[24] and Lowry and Hulett,[36] in their studies on the relation of density and pore volume of carbons to compressibility of liquids, found that liquids which penetrate into charcoals are compressed by the action of a force, due to molecular attraction, which acts as a pressure of many thousand atmospheres. If the solubility of the sugar is increased in this compressed area, this may account for its adsorption by carbons. We would not expect this type of adsorption to be much affected by pH.

The results of the experiments reported in this paper show that the electrical nature of the substances to be adsorbed is a deciding factor in determining the degree of adsorption under definite conditions of pH. A careful choice of conditions would make it possible to adsorb one type of compound and leave an oppositely charged substance largely in solution, and thus increase the preferential adsorption of the carbon.

It is recognized that in all industries the extreme range of pH necessary to adsorb efficiently all types of compounds would not be applicable. Therefore, the use of fuller's earth, kaolin, and other substances which possess characteristics in electrical charges different from carbon, may under certain conditions be used more effectively than carbon for the adsorption of certain types of substances.[54]

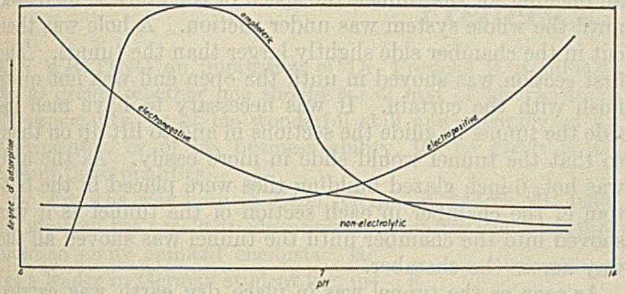

Figure 11—Generalized Curves Showing Relation between Hydrogen-Ion Concentration and Adsorption by Chars of Substances Having Various Electrical Properties

The value of carbons for industrial purposes might be greatly increased if a carbon were produced which would be active at the permissible pH for the substance involved. Although carbon is not electrically charged by itself—that is, it does not possess active groups, such as COOH, to give it a charge, but acquires electrical properties due to the medium in which it is in contact—the electrical properties can be greatly modified by processes of activation. This is proved conclusively by the work of Ogawa,[40] who showed that the isoelectric point of carbon was shifted during the process of activation by heat alone. It may be possible to produce a carbon which would be positive at all pH's. This would be a great addition to the carbons now available and greatly simplify the problems of decolorization, since most colored impurities met with in the industries dealing with biological materials are negatively charged.

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Airplane to Be Used against Sugar-Cane Insect

The expenditure of $50,000 to conduct a large-scale experiment on the effectiveness of airplane dusting to control the sugar-cane moth borer has been authorized by the Secretary of Agriculture. Approximately 5000 acres of sugar cane in the heart of the sugar-producing area of Louisiana will be dusted with sodium fluosilicate to determine its efficiency in controlling the borer. The experiment is being conducted at the request of the American Sugar-Cane League, planters, manufacturers of cane products, bankers, and others interested in the sugar-cane industry. The borer is found throughout the territory, and its damage to the cane crop runs from 15 to 30 per cent of the total crop annually.

The most effective way to control this borer, says the Department of Agriculture, is to submerge seed cane in water for 72 hours before planting, which is certain death to the borer. It is hoped that the experiment in airplane dusting may prove to be equally effective and more economical. The first dusting begins August 1. Two further applications will be made a month apart, around September 1 and October 1.

The Bureau of Entomology will have direct supervision of the work, with W. H. Larrimer in administrative charge in Washington and T. E. Holloway, assisted by E. W. Brandes and R. D. Rands, of the Bureau of Plant Industry, will be in charge of field operations. The 5000 acres will be selected from cane areas in which have been planted disease-resistant varieties developed by the Office of Sugar-Cane Investigations of the Bureau of Plant Industry. The preservation of these valuable varieties for seed purposes is of vital importance to the industry. An advisory committee of representatives of the American Sugar-Cane League, the University of Louisiana, and other individuals and organizations interested in the sugar-cane industry, will coöperate with the Department.

Repairing Sulfuric Acid Chamber Bottom during Operation[1]

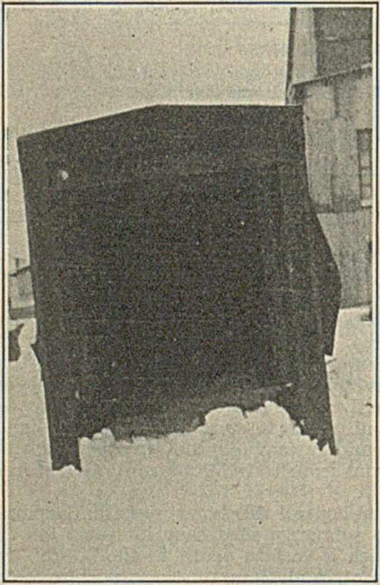
By W. C. Kendrick and M. E. Souder

Armour Fertilizer Works, Chicago, Ill.

At our sulfuric acid plant a leak developed in the bottom of No. 1 chamber, which extended the full width of the chamber, a distance of 35 feet. The leak was a slow one, but soon cut away the wooden bottom supporting the lead to such an extent that the wood gave way, allowing the lead to sag. There was immediate danger of the lead breaking from the weight of the acid, which would have caused a loss of the acid in the chamber and a shutdown of plant, or the expense of by-passing the gas to No. 2 chamber, which would also have curtailed production. At this time it was imperative that the plant be kept in operation. It was not possible to stop the leak with fire clay, phosphate rock, acid phosphate, pyrites fines, or lead dross. It was finally decided to attempt to patch the bottom by building a wooden tunnel, in several sections.

First it was necessary to design a sectional tunnel that would be easy to handle, and one that would protect the lead burner and helpers from danger of gas and would dam off the acid that would have to be left in the chamber to form a lute around the curtain.

The tunnel was made in six sections 3 feet wide, 4 feet high, and 6 feet long, and one short section 3 feet wide, 4 feet high, and 3 feet long, the roof of all sections being A-shaped. The framework of each section was made of 2 by 4 inch timbers, and the sides and top of No. 1 of tongued and grooved flooring, with no floor in any of the sections. The first section that entered the chamber had the head end closed. To protect the wood construction, also as an extra precaution against gases and acid that would be dropping on the tunnel, each section was covered with three-ply composition roofing which was given a heavy application of pitch. A male joint was made on one end of each section and a female on the other. To insure against gases getting through the joints, an air-tight connection was made by filling the female side with acid-proof cement.



Tunnel for Repairing Sulfuric Acid Chamber

The next problem was to take care of the acid that would be in the tunnel and build a dam around this wooden tunnel to protect the bottom boards from sulfuric acid left in the chamber to lute the curtain and keep it out of the tunnel while repairs were being made. The third board from the bottom was made with square edges and held in place from the inside by cleats or wooden buttons, and on the outside a flap of composition roofing was put on to extend below the third board and cover the opening when the board was removed.

Prior to cutting a hole in the side of the chamber to make an opening for the tunnel, the speed of the fan was increased until the whole system was under suction. A hole was then cut in the chamber side slightly larger than the tunnel. The first section was shoved in until the open end was not quite flush with the curtain. It was necessary to have men inside the tunnel to guide the sections in and to lift up on them so that the tunnel would slide in more easily. As the acid was hot, 6-inch glazed building tiles were placed in the bottom of the chamber in each section of the tunnel as it was shoved into the chamber until the tunnel was shoved all the way across the chamber.

As soon as the tunnel was in place dry earth was carried in bags, spread the entire length of the tunnel, and mixed with the acid until practically all acid was taken up, leaving the earth in a heavy mucky or pasty form. To dispose of this muck the loose boards were taken out one at a time and the muck was shoveled through the openings mentioned above into the chambers to form a dam around the tunnel. The bottom or lead inside of the tunnel was then cleaned and dried up with soda ash.

It was very warm inside the tunnel and the men were not allowed to stay inside very long at a time while the tunnel was being put in place; once in place, the tunnel was free from gas while the men were cleaning out.

The opening in the chamber side was made at 10:00 A. M., and by 3:00 P. M. the plant was back to normal operation. After drying up the acid in the tunnel, a strip of lead 18 inches wide was cut out all the way across the chamber and the wood flooring was then renewed. By the time the wood flooring was removed a draft was created through the tunnel, drawing from the outside end and passing through the openings in the sides through which the muck was shoveled. Fresh air also came up through these openings, making working conditions comfortable in the tunnel. The work of putting in a new wood floor was completed by 6:00 P. M. The lead work started soon after this and continued throughout the night, and the patch was finished at about 11 o'clock the next morning.

The tunnel was removed by several men pulling on a rope fastened in the back of tunnel. It had to be kept in mind that should the connections on any of the sections be broken gas troubles would develop, and for this reason the rope was taken to the extreme back end of the tunnel and securely fastened. To help break the tunnel loose from the dam that had been built around it, two or three men went into the tunnel and lifted up slightly on the sections as the men outside pulled on the rope. After once getting it started it was very easy to pull out. A patch was put over the hole in the side of the chamber curtain and burned in spots to hold it in place, and the section of the upstand that had been taken out was burned back in place, the woodwork replaced, and the chamber was ready for operation.

To avoid cutting the bottom of the chamber where there was a buckle or the lead was thin, when pushing in the sections, it would be an improvement to put under each section runners of 1.5 or 2 inches dressed plank, beveled at the ends.

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[1] Received April 7, 1927.

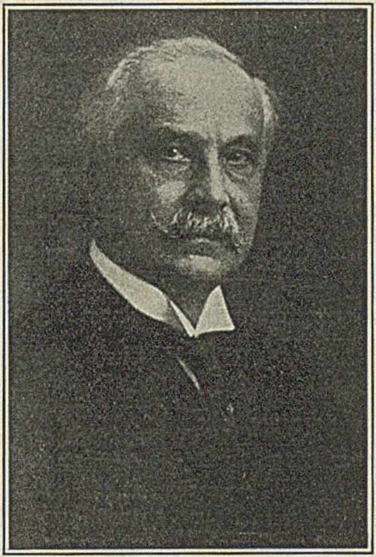
This repair job cost less than $300 and the cost of shutting down the plant many times that amount. It was surprising how quickly the plant was back to normal operation. There was no increase in niter consumption and no reduction in yield.

It is well to point out the danger of such operations unless every precaution is taken to prevent leakage of gas or acid through or around the tunnel walls. These sulfur and nitrous gases are extremely irritating, even in considerable dilution, and very dangerous if at all concentrated.

AMERICAN CONTEMPORARIES

Frederick W. Frerichs

IN WRITING an impression of Dr. Frerichs it is difficult to decide whether one should speak first of his charming personality, or of his wonderful skill and accuracy as an experimenter, or of his business ability, for he excels in all three of these qualities.



Frederick W. Frerichs

Dr. Frerichs was born in Etzel, Germany, March 23, 1849, and received the excellent education in chemistry which has produced so many eminent chemists. He was a leader in German student life, including the famous duels, although he bore no marks of the eleven in which he participated. The same skill and accuracy which characterized him as a chemist seemed to have been used in these duels, so that his opponents carried away the evidence. He received the degree of Ph.D. at Göttingen in 1874. From 1874 to 1879 he was an assistant to Professor Woehler, in charge of the analytical laboratory. During the same time he served in the army, obtaining the rank of lieutenant of reserves. While in Göttingen he designed various pieces of laboratory apparatus, one of which was the well-known Sartorius analytical balance,[1] for which he received a gold medal at the Louisiana Purchase Exposition at St. Louis, in 1904. From 1877 to 1879 he was associate editor of *Post Zeitschrift für das Chemische Grossgewerbe*, and in these years he traveled extensively in Germany, Austria, and England, being admitted to more than two hundred factories.

In 1879 Dr. Frerichs became manager of the paint and varnish factory of Herman Frenkel in Leipzig. In 1880 he accepted a position with the Mallinckrodt Chemical Works in St. Louis. He was soon advanced to the position of superintendent and held this position until 1886. Here he began to show skill as a chemical engineer, not only in making improvements in chemical processes, but in directing the workmen in the plant.

In 1887 he entered into business for himself, becoming a stockholder and director of the Herf and Frerichs Chemical Company in St. Louis. This company manufactured fine chemicals and introduced the manufacture of salicylic acid, acetanilide, ammonia, and the treatment of bismuth ores on a large scale. When in 1903 the manufacture of a number of these articles became unprofitable, the company sold out part of its plant to Merck & Company in New York, retaining only the ammonia works.

Dr. Frerichs then specialized in anhydrous ammonia, and developed a new method for its production. He not only developed the manufacturing methods to a high degree of efficiency, but devised methods of analysis to test the purity of the product. His painstaking and thorough scientific work resulted in producing on a commercial scale anhydrous ammonia of extraordinary purity. He also demonstrated on a commercial scale that ammonia of high purity was much more economical for the production of artificial ice, thus proving what has often been shown, that work of the highest scientific refinement is commercially profitable. His mechanical skill is shown in the designing of test apparatus for ammonia. Here, as elsewhere, he could manufacture at minimum cost.

His skill, thoroughness, and high accuracy are admirably shown in the design of a soda ash plant, which he described in one of the many admirable chemical engineering papers which he published in the *Transactions of the American Institute of Chemical Engineers*. For this process he made wooden models of the apparatus so that his design might be accurately produced on a large scale.

His business permitted him to have several months' leisure during the winter. A part of this time he spent in New York attending grand opera, which he greatly enjoyed, and part he spent in entertaining his friends, at which he was a past master, making a most charming host. In this he shows himself to be the true gentleman who lives to enjoy life after a period of technical service of a very high order.

The chemical engineering profession recognized his work as a chemical engineer by electing him president of the American Institute of Chemical Engineers. He afterwards became treasurer of this society and only recently resigned from this work on account of failing health. Recognition was also given him for his many valuable contributions to the literature of the profession by awarding him the medal of the Institute.

J. C. OLSEN

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[1] *Ann.*, **178**, 365 (1875).

New Books

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Dutch Patent Law and Chemical Inventions[1]

By W. Wessel[2]

Izaak Evertslaan 25, Arnhem, Holland

Editor's Note—The approximate cost for maintaining a Dutch patent during the fifteen years of its existence is $700, exclusive of the sum expended in procuring the patent. The Dutch patent law has a compulsory working clause which requires that a patent be worked from a date within five years from its granting and continuously thereafter.

A Dutch patent covers not only the kingdom in Europe but also the colonies with their large and varying possibilities. English, German, French, and other inventors take out a large number of Dutch patents, but American inventors as a rule either do not seem to recognize the value of a Dutch patent or are not willing to go through the necessary expense and trouble.

The preliminary examination by the Dutch officials is very severe, and it is understood that inventors are disappointed that such a small country as Holland makes so many difficulties. On the other hand, a patent in Holland is especially valuable as it also covers the Dutch colonies. Furthermore, the grant of a patent proves to a certain extent that the invention is a valuable one and the patent is not easily invalidated. In the Chemical Department of the Patent Office in particular, a number of very skilled and able officers are investigating patent applications and even though they may be rather "difficult," their work nearly always results in valid patents.

After reading Thomas' excellent article on the law of chemical patents[3] it occurred to the writer that, in view of the great differences between American and Dutch patent law and practice, a brief account of the Dutch law as far as it relates to chemical inventions might be of interest. The Dutch Patent Law of 1910 did not become operative until June 1, 1912; there was a patent law back as far as 1817, but this was abolished in 1869.

The Dutch patent law resembles the German law in many respects. The German patent law states in paragraph 1:

> 1—Patents will be granted for new inventions which set forth a worthwhile improvement.
>
> The following exceptions are noted:
>
> (1) ****
>
> (2) Inventions relating to articles of food and medicinals, as well as substances which are chemically prepared, in so far as the invention does not involve a distinct process for the preparation of the product.

In the second part of paragraph 4:

> 4—If a patent is granted for a process, its scope also extends to the products directly prepared by the process.

Article 4 of the Dutch patent law agrees mainly with this German wording:

> If a patent is granted for a process of preparing a substance (German "Stoff")***the patent covers also this substance if prepared according to that process. For a substance as such no patent is granted.

The Dutch word "stof" has been translated as "substance." Perhaps "material" would be better, as may follow from the following explanation of this article.

As stated above, according to the German patent law no patents are granted for medicinals or chemicals. Therefore, claims such as the following are not acceptable in Germany:

> As new products, cellulose ethers containing combined with the cellulosic molecule ether-forming groups derived from polyhydric alcohols (claim 10 of U. S. Patent 1,502,379 to Henry Dreyfus).

Process claims would be allowable, for instance:

> Process for the manufacture of cellulosic derivatives characterized by the introduction into the cellulosic molecule of at least one group derived from halogen substitution products of polyhydric alcohols containing at least one free hydroxyl group whereby such hydroxyl is retained in the resulting cellulosic derivative. (Combination of claims 1 and 2 of U. S. Patent 1,502,379.)

Such claim covers also the product obtained by that process, but does not cover the same product if obtained by other processes which are not obvious equivalents of the process claimed.

So far Dutch and German patent laws are alike. A claim of the following wording would be acceptable in Germany but not in Holland:

> A waterproofing composition composed of a heavy hydrocarbon oil, asphalt, rubber, and a filler (U. S. Patent 1,500,537 to Thompson).

This composition is not prepared by chemical reactions, thus being patentable in Germany. The composition, being a "material" ("stof"), according to Dutch law is not patentable in Holland. However, the invention may be patented by drafting a claim of about the following wording:

> A process for making waterproofing composition consisting in mixing a heavy hydrocarbon oil with rubber, asphalt and a filler.

Such process claim also covers the composition per se, so that if a waterproofing composition containing a heavy hydrocarbon, rubber, asphalt, and a filler is used or sold by any person not a licensee or assignee or prior user, this use or selling constitutes infringement.

It will be clear from this example that German and Dutch patent laws differ with respect to chemical inventions, but that process claims give a broader protection both in Holland and in Germany than in the United States.

It should be borne in mind, however, that there are numerous process claims of preparing known compositions. In such cases it is by no means easy to prove infringement, as the patentee must show that the alleged infringer has actually used the process according to the patent. If mixtures are patented it will be very easy to prove infringement, but if known chemical compounds are patented by means of process claims the proof will be very difficult. Again, if a patent is granted for a process of preparing a new product, infringement will be considered to have taken place, but not if the alleged infringer is able to prove that he has used a process which materially differs from that claimed by the patentee. In case of new products the burden of the proof is up to the alleged infringer.

However it is generally recognized in Holland that article 4 does not sufficiently protect chemical inventions and a bill is pending in Holland which probably will improve the Dutch patent law in several respects, including chemical inventions.

Nevertheless, the spirit of article 4 is very good, as chemical industry would be severely handicapped if patents covered a new product independent of the process. If, for in-

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[1] Received April 9, 1927.

[2] Dutch Registered Patent Agent.

[3] This Journal, 19, 176, 315, 426 (1927).

stance, a product claim for a valuable new chemical compound had been granted and the patentee had given only one method of preparing the new compound, nobody would be interested in improving the methods as any novel process would not be workable without licenses from the original discoverer of the new compound. France has proved that such law is bad.

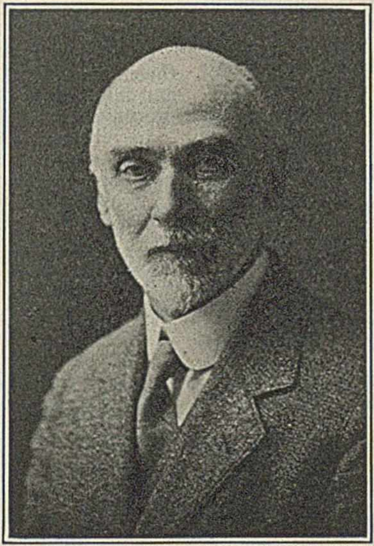
If, for example, the product as prepared by the patentee's process costs $5.00 per kilogram and another manufacturer is able to sell the same compound for $2.00 as a result of a very cheap and quite different process, it is better to have an independent process patent for the second inventor, who materially increases the industrial possibilities.

It is not possible here to go further into the pros and cons of Dutch patent law with respect to chemical inventions. The writer has given considerable attention to this subject in a book[4] which was issued in 1924, and if this book has even a slight influence on the revision of Dutch patent law as far as chemical inventions are concerned he will be satisfied.

[4] "De begrippen werkwijze, stof en voortbrengsel in het Nederlandsche Octrooirecht." (The expressions "process," "compound," and "product" in Dutch patent law.)

Henry Paul Talbot

Doctor Talbot died suddenly on June 18 during what was thought to be a satisfactory convalescence from a major operation. It may be truly said of him that he was a martyr to his sense of duty. During many months of increasing ill health he continued to serve as dean of students of Massachusetts Institute of Technology, to which office he was appointed in 1921, and in the words of President Stratton, "he filled the difficult position of mediator, counselor and friend to the undergraduate body in a manner that commanded the admiration and won the hearts of all students who came in contact with him."



Henry Paul Talbot

Doctor Talbot was born in Boston, May 15, 1864. He was graduated from Massachusetts Institute of Technology in 1885 with the degree of B.S., having specialized in analytical chemistry. He served the Institute for several years as an instructor in that subject before leaving for Leipzig, where he received his Ph.D. degree in 1890. While in Germany he turned his attention more specifically to organic chemistry, and his viewpoint was further broadened to include the concepts of the new physical chemistry, which was then coming into being. Returning to the Institute, he was appointed assistant professor and at once introduced physical chemistry into its curriculum. This was one of the first physical chemistry courses established in this country.

Thereafter, until his death Doctor Talbot served the Institute with fine devotion and to such effect that his loss there is regarded as irreparable. He was appointed to a full professorship in 1898, and for twenty years following 1901 he was head of the Department of Chemistry. He was chairman of the faculty from 1919 to 1921, and during the critical ad interim period following the death of President Maclaurin served as chairman of the Administrative Committee of the Institute.

Doctor Talbot's interest in chemistry and his service to the profession extended far beyond the school which absorbed his major energies. From 1898 until his death he was a member of the Council of the AMERICAN CHEMICAL SOCIETY, and also served as one of its Directors. He was a member of many important committees, had been an associate editor of the *Journal of the American Chemical Society*, and chairman of the Division of Inorganic and Physical Chemistry. He was elected president of the New England Chemistry Teachers' Association and was for several years chief examiner in chemistry of the College Entrance Examination Board.

During the World War Doctor Talbot did especially effective work as a member of the small advisory board of the United States Bureau of Mines and later of the War Department and actively supervised much of the work on war gases.

In 1921 he received from Dartmouth College the honorary degree of D. Sc.

He was an interested and helpful member of many scientific bodies; an author of a widely used textbook on "Quantitative Analysis," and a joint author with Prof. Arthur A. Blanchard of "The Electrolytic Dissociation Theory."

No bald summary of effort and achievement can, however, adequately evaluate the distinguished position of Doctor Talbot in American chemistry, or indicate the far-reaching effects of his influence in shaping the policies of Massachusetts Institute of Technology and molding the character of the thousands of students, who, looking to him as guide and instructor, found also in him a sympathetic and understanding friend.

As a classmate of "Harry" Talbot, it is a privilege to testify to his unswerving loyalty to the Class of '85 and to the high sense of duty which conspicuously characterized all his relations. A notable provision of his will makes the school which he had served so long his residuary legatee and expresses the hope that the funds so derived may be used to enable junior members of its faculty to attend meetings of the societies of their professions.

Doctor Talbot is survived by his wife, who was Miss Frances E. Dukehart of Baltimore. There were no children.

ARTHUR D. LITTLE

Calendar of Meetings

American Chemical Society—74th Meeting, Detroit, Mich., September 5 to 10, 1927.
  Division of Organic Chemistry—Second National Symposium on Organic Chemistry, Columbus, Ohio, December 29 to 31, 1927.

American Electrochemical Society—Fall Meeting in the form of an excursion through the Northwest, September 4 to 20, 1927.

American Refractories Institute—Clifton Hotel, Niagara Falls, Canada, September 15, 1927.

Eleventh Annual Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., September 26 to October 1, 1927.

BOOK REVIEWS

Statistical Mechanics with Applications to Physics and Chemistry. By R. C. Tolman. A. C. S. Monograph. Chemical Catalog Company, Inc., New York, 1927. Price, $7.00.

The average physical chemist will probably find himself gasping for breath as soon as he strikes the second chapter, in which the fundamental equations of classical mechanics are developed from the principle of least action. However, after surmounting this initial difficulty, the reader will be rewarded by the clear and concise presentation of such topics as the theorem of Liouville, the ergodic hypothesis, Maxwell-Boltzmann distribution law, and principle of equipartition of energy, which are of fundamental importance in statistical mechanics.

In view of the rapid state of flux of the newer quantum theory, the author has preferred to present an outline of the theory in its older definite form, basing it on the Wilson-Sommerfeld rule of quantization and Bohr's correspondence principle, and then points out the effect of incorporating the ideas of the quantum theory in statistical mechanics.

These considerations take up the first eight chapters, and in the other sixteen a number of problems are discussed, among them: specific heats of diatomic gases and solids; determination of the most probable state of a system; vapor pressure of crystals and glasses at very low temperatures; gaseous equilibria; collisions of first and second kinds; rates of physical and chemical processes; temperature coefficient of reaction; and photochemical reactions.

The volume contains a large amount of material ordinarily found only in abstruse treatises on mathematical physics, such as the discussions of the H-theorem of Boltzmann and Clausius' virial. Yet the mathematics used is fairly elementary and the presentation is admirable.

It is hoped that this volume will create additional incentive among physical chemists to become familiar with a field of theoretical science in which they should be just as much interested as the pure physicist.

Saul Dushman

The Dyeing of Cotton Fabrics. By Franklin Beech. 3rd edition, revised and enlarged by A. J. Hall. 296 pages. D. Van Nostrand Company, New York, 1927. Price, $5.00.

Apparently the object of this book is to give information of value to the dyer in the dyehouse. If this assumption is correct, the purpose is not realized in such a way as to make the book of real use to the American dyer at least. To be valuable, a manual of dyeing must enable the dyer to achieve practical results, which depend on the production of (1) the required shade (hue), (2) a dyeing that is free from streaks, (3) a dyeing that meets the requirements with respect to fastness and is economical enough to be commercially successful. Within the limits of the book the treatment of the characteristics of the cotton fiber, its preparation for dyeing, the mechanics of the dyeing process, and the after-treatment are all as adequate as one could ask; but the most essential feature, to give the dyer an idea of how to produce shades, is extremely unsatisfactory. The directions are presented as a mass of brief recipes, apparently taken from a dyer's notebook and divided into groups according to the hue—for instance, blues, reds, browns, etc. Inasmuch as no reference color is given, it would be impossible to discover what shade one would obtain without actually making a dyeing. Even within the limits of the recipes given, there would be considerable confusion, because words are much less precise than dyeings in describing color and therefore the dyer would not know which recipe to choose unless he had the practical experience which would make the recipe unnecessary. For example, recipe No. 7 under direct dyeing blues, is described as a sky blue and the dyer is told to "prepare the dyebath with 1 lb. Diamine sky blue FF, 1 lb. Turkey-red oil, 20 lbs. Glauber's salt. Dye at the boil for one hour." Recipe No. 30, which is described as a pale blue, calls for the use of "1 lb. of Chicago Blue 6B, 3 lbs. soda, 20 lbs. salt at the boil for 1 hour." Actually the two dyestuffs are identical except for the trade name. This confusion is characteristic of other recipes.

Apart from the lesson that a description of dyeings is useless without showing the dyeings themselves, the book emphasizes the necessity of bringing any manual up to date. Some of the chapters are hopelessly antiquated. To read them one would expect to find vegetable dyes used frequently for dyeing cotton, one would believe the use of sodium hydrosulfite in the indigo vat to be exceptional rather than standard, just as one would assume that the naphthol AS colors are very secondary when compared with para red.

Had the manuscript been submitted to those who are familiar with dyeing practice as carried out today it would have been sufficient to avoid publication of a book which, as far as American practice goes, is entirely useless.

R. E. Rose

Principles of Soil Microbiology. By Selman A. Waksman. 897 pages. Williams & Wilkins Co., Baltimore, 1927. Price, $10.00.

In the author's own words this work "is a collection of known facts concerning microörganisms found in the soil and their activities; it is a study of the literature dealing with the science in question; it is an interpretation of the facts already presented; it indicates the various lines of investigation and notes where further information is especially wanted.*** The book may, therefore, be looked upon more as an introduction to further research rather than as an ordinary textbook; as of help to those working in the allied sciences, who are desirous of obtaining some information concerning the soil population and its activities."

Soil microörganisms are considered under the main heads of their "occurrence and differentiation;" "isolation, identification, and cultivation;" "chemical activities;" and "soil microbiological processes and soil fertility."

In relation to the complex dynamic equilibrium represented by the soil, in itself, and in its relation to the growing plant, its microbiological population is of fundamental importance. The study of soil microbiology in its various ramifications extends into a number of other related scientific fields and much of the literature pertaining thereto is identified with these other fields. To survey and interpret this comprehensive volume is to render a distinct service to the advancement of the science. "Principles of Soil Microbiology" is a laudable effort in this direction.

Paul R. Dawson

Practical Chemistry. Fundamental Facts and Applications to Modern Life. By Newton Henry Black and James Bryant Conant. Revised edition. 522 pages. The Macmillan Company, New York, 1927. Price, $1.80.

This book is essentially a student's textbook and not a treatment of "practical" chemistry as the title indicates. The subject matter is clear and concise; it is profusely and well illustrated with cuts of up-to-date plants and laboratories, diagrammatic sketches of set-ups, and schematic drawings of processes that are explicit and to the point, always bringing in an industrial application wherever possible.

The general principles of chemistry are followed by a discussion of gases, although the authors unfortunately relegate to an appendix the explanation of the common gas laws. Nothing is gained by placing the chapters on carbon monoxide and dioxide and nitrogen so early in the book, unless for gas grouping. Nitrogen in Chapter VII appears to be too far removed from ammonia in Chapter XX, and nitric acid and fixation of nitrogen in Chapter XXI. Also the "two oxides of carbon" in Chapter VI do not appear to be related to carbon, coal, and fuel gases in Chapter XXVIII, and alcohol and gasoline in Chapter XXIX. The discussion of fats and soaps would fit in better with the class homology concepts of organic chemistry if it followed organic acids in Chapter XXIX and were not included in Chapter XXX, on food and clothing. Chapter XXIX is mistitled—more than alcohol and gasoline are discussed. The subject matter in this chapter would bear revision.

The use of curves and sketches helps much to make the solubility reading interesting and worth while. The summaries and questions at the end of the chapters are well selected, although the later chapters do not equal the earlier ones in completeness and value. The references to collateral reading matter should stimulate the student's interest in chemistry. Profuse use of bold-face type to indicate important statements and words makes easier reading than the italics so commonly used, although unfortunately the authors did not adhere religiously to this practice, for some important statements are italicized, tending to confuse the student as to the relative value of the two types of notation.

The historical side of general chemistry is well handled for an elementary book and a large number of cuts of famous chemists are scattered throughout the book.

The diagram on page 16, Figure 13, showing the composition of the earth's crust, including the atmosphere, is unfortunately in error, since nitrogen has no place in the eight important elements in the earth's crust and the atmosphere.

F. C. Vilbrandt

Gas Storage of Fruit. By Franklin Kidd, Cyril West, and M. N. Kidd. Food Investigation Special Report 30, of the Department of Scientific and Industrial Research. 87 pages, including tables and charts. His Majesty's Stationery Office, London. Price, 1s. 9d. In the United States, The British Library of Information, 44 Whitehall St., New York, N. Y. Price, 45 cents.

A publication similar to the bulletins of our government scientific bureaus, giving complete records of experiments dealing with the effects produced by varying amounts of oxygen and carbon dioxide in the atmosphere on the keeping quality of English apples in storage. There are interesting chapters on functional diseases and their control during storage, comparisons of gas storage and cold storage, the influence of temperature, and gas storage during overseas transportation, etc. The rather meager chemical data, together with an abundance of charts and wastage tables, are placed in the appendices, an arrangement which does not facilitate a study of the data. The pamphlet is of value to those interested in the storage and transportation of fruit.

E. M. Chace

Chimie Industrielle. By Paul Baud. 2nd edition completely revised. 1022 pages. Masson et Cie., Paris, 1927. Price, 100 francs unbound.

This volume will no doubt prove extremely helpful to the student whose lectures in general chemistry have not yet given him a clear mental picture of the industrial application of the reactions to which he has been introduced. The field of usefulness of the work might have been greatly extended, however, had more emphasis been placed on recent developments in the industry. For example, the advanced student or engineer is much more likely to require detailed information on the subject of ammonia oxidation, which is granted but three pages, than on the older arc process, which occupies eleven pages.

There are instances where the arrangement of the material might be criticized, but this objection is partly nullified by the inclusion of frequent cross references.

In attempting to do justice to so broad a field, even the expanse of eleven hundred pages must prove insufficient in some measure. Thus, the more purely scientific data which have been included in this edition are by necessity of such a fragmentary nature that their usefulness for reference purposes is slight.

The book when regarded strictly as a text, however, is a useful work, and is well printed on good paper.

H. C. Hetherington

Der Chemische Krieg. By Rudolph Hanslian. 2nd revised and enlarged edition. 411 pages. E. S. Mittler & Sohn, Berlin, 1927. Price, paper, 17 marks; bound, 20 marks.

The second edition of this book is much more voluminous than the previous one which appeared in 1925, but the data and ideas presented in regard to chemical warfare are essentially the same. The new features of interest are the bibliography, which is complete and up to date, and the discussion of recent attempts to make international agreements for the purpose of abolishing the use of chemical agents in warfare.

The discussion of the attempts to abolish chemical warfare by international agreement is excellent. After presenting the opinions on both sides of this question the author concludes that the objections against the use of chemical agents cannot stand. He points out that the propaganda carried on by the Allies against the use of chemical warfare by the Germans was merely for the purpose of influencing public opinion. He believes that the public is beginning to realize this and that chemical warfare is not the diabolical weapon pictured during the war. He speaks of the Washington agreement as a supreme swindle and feels that the Great Powers will try to avoid another failure of this character because of its effect on faith in international agreements.

The chapters dealing with the origin and development of gas attacks, combat gases, the development of toxic and screening smoke, and means of defense against gas are complete and well-written, but are essentially the same as similar chapters in the first edition.

G. A. Rankin

Technologie der Textilfäsern. By R. O. Herzog. **Band III—Künstliche Organische Farbstoffe.** By H. E. Fierz-David. Julius Springer, Berlin, 1926. xvi + 719 pages. Price, 63 marks.

This is the most recent work on artificial dyestuffs, and in it Dr. Fierz-David follows the general arrangement of Schultz in his "Farbstofftabellen."

The volume starts with a brief discussion of the history of manufactured dyes and the general characteristics of the colors so produced. Following this are chapters on the different classes of dyes, accompanied by tables of references to German patents and Friedländer's "Fortschritte der Teerfarbenfabrikation." As is fitting in a modern book of this type, the author pays special attention to the indigoids and anthraquinone colors, and has extensive chapters on each. All descriptions are well documented and a bibliography of the more important books on dyes is the closing feature. Of especial interest is the final chapter on the optical properties of dyestuffs, in which is discussed the spectrophotometric characteristics of certain dyes and the identification of azo dyes by means of the absorption bands of their components.

As the author says in his introduction, there are many textbooks on dyes, but he has been unusually successful in bringing a complicated subject up to date in a comprehensive way. Other books by the same author have been translated into English for the benefit of those who find trouble with the original German, and it is recommended that this volume receive similar treatment.

Horace T. Herrick

Petroleum Development and Technology in 1926. 970 pages. Published by the Petroleum Division, American Institute of Mining and Metallurgical Engineers, 29 West 39th St., New York, N. Y. Price, $6.00.

The American Institute of Mining and Metallurgical Engineers has rendered a valuable service by bringing together in this volume the papers presented before its Petroleum Division at Tulsa, Okla., October, 1926, and New York in February, 1927.

The text is divided into eight parts, each of which contains a considerable number of papers by authorities, followed by more or less extensive discussions by men whose names are familiar to those engaged in these special fields. Part 1 is devoted to production engineering; Part 2, to refining technology; Part 3, to transportation engineering; Part 4, to corrosion; Part 5, to production; Part 6, to petroleum economics. Parts 7 and 8 are round-table discussions on educational and engineering research problems in petroleum engineering.

Among the educational problems discussed are basic training and prerequisites; laboratories and equipment; graduate courses; availability of lecturers; geological, petroleum production, and refinery engineering; transportation; economics; and management. The research problems include geological and production engineering and refining technology.

Many will find Part 4 of particular interest, for here are such topics as corrosion in the presence of oily substances, the non-corrosive ferrous alloys, corrosion in petroleum industry pumping equipment, corrosion of underground pipe lines, soil corrosion investigation, scale and corrosion problems in gasoline plants, refinery corrosion problems, corrosion in oil and gas wells, and sulfur in petroleum.

We recommend this splendid volume to those working in the field of petroleum technology.

The Chemical Industry. International Economic Conference, Geneva, May, 1927. 134 pages. Published by League of Nations, Economic and Financial Section. World Peace Foundation, 40 Mt. Vernon St., Boston, Mass. Price, $1.00.

This document was prepared by the Economic and Financial Section of the League of Nations from information furnished to it by governments, by members of the Preparatory Committee for the Conference, and by industrial organizations, which prepared memoranda at the request of members of the committee.

The salient phases of the subject and its international aspects are examined from this mass of information, and the statistical tables and summaries, as a consequence, are the most comprehensive, authentic, and up to date available, though incomplete.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Foreign and Domestic Commerce

Paper and Paper Products in Columbia, Venezuela, Ecuador, and the Guianas. B. M. Frost. *Trade Information Bulletin* 477. 27 pp. Paper, 10 cents.

Bureau of Mines

Acid Processes for the Extraction of Alumina. G. S. Tilley, R. W. Millar, and O. C. Ralston. *Bulletin* 267. 85 pp. Paper, 15 cents.

Area of Unsupported Roof in Coal Mines. Conditions and Factors for Consideration. J. W. Paul. *Circular* 6040. 3 pp. Issued June, 1927.

Coal-Dust Explosion Tests in the Experimental Mine 1919 to 1924, Inclusive. G. S. Rice, J. W. Paul, and H. P. Greenwald. *Bulletin* 268. 176 pp. Paper, 35 cents.

Coal-Mine Fatalities in May, 1927. W. W. Adams. *Reports of Investigations* 2815. 8 pp. Issued June, 1927.

Consumption of Explosives in May, 1927. W. W. Adams. *Reports of Investigations* 2816. 10 pp. Issued June, 1927.

Effective Rock-Dusting of Coal Mines. G. S. Rice. *Circular* 6039. 7 pp. Issued June, 1927.

Fatalities in the California Petroleum Industry during the Calendar Year 1926. H. C. Miller. *Reports of Investigations* 2814. 19 pp. Issued June, 1927.

Fluorspar, Its Mining, Milling, and Utilization, with a Chapter on Cryolite. R. B. Ladoo. *Bulletin* 244. 185 pp. Paper, 35 cents.

Fuel Briquets in 1926. F. G. Tryon. *Mineral Resources of the United States, 1926.* Part II, pp. 1–8. Paper, 5 cents.

Gold, Silver, Copper, Lead, and Zinc in Arizona in 1925. Mine Report. V. C. Heikes. *Mineral Resources of the United States, 1925.* Part I, pp. 563–600. Paper, 10 cents.

Gold, Silver, Copper, Lead, and Zinc in Idaho and Washington in 1925. Mine Report. C. N. Gerry. *Mineral Resources of the United States, 1925.* Part I, pp. 517–62. Paper, 10 cents.

Iron Blast-Furnace Reactions. S. P. Kinney, P. H. Royster, and T. L. Joseph. *Technical Paper* 391. 65 pp. Paper, 15 cents.

Metallurgical Limestone. Oliver Bowles. *Circular* 6041. 16 pp. Issued June, 1927.

Mica. W. M. Myers. *Circular* 6044. 26 pp. Issued June, 1927.

Placer-Mining Methods and Costs in Alaska. N. L. Wimmler. *Bulletin* 259. 236 pages. Paper, 55 cents.

Precipitation of Gold and Silver from Cyanide Solution on Charcoal. John Gross and J. Walter Scott. *Technical Paper* 378. 78 pp. Paper, 15 cents.

Precipitation of Lead and Copper from Solution of Sponge Iron. G. L. Oldright, H. E. Keyes, Virgil Miller, and W. A. Sloan. *Reports of Investigations* 2812. 4 pp. Issued June, 1927.

Rare Metals: Cobalt, Molybdenum, Nickel, Titanium, Tungsten, Radium, Uranium, and Vanadium in 1925. F. L. Hess. *Mineral Resources of the United States, 1925.* Part I, pp. 601–22.

Resistance of Metal-Mine Airways. G. E. McElroy and A. S. Richardson. *Bulletin* 261. 149 pp. Paper, 35 cents.

Sulfur and Pyrites in 1925. H. M. Meyer. *Mineral Resources of the United States, 1925.* Part II, pp. 385–91. Paper, 5 cents.

Summary of Mineral Production in Foreign Countries 1920–1924. L. M. Jones. *Mineral Resources of the United States, 1925.* Part I, pp. 441–516. Paper, 15 cents.

Technology and Uses of Silica and Sand. W. M. Weigel. *Bulletin* 266. 204 pp. Paper, 40 cents.

Sulfur and Pyrites in 1925. H. M. Meyer. *Mineral Resources of the United States, 1925.* Part II, pp. 385–91. Paper, 5 cents.

The Chromium Situation from a Domestic Standpoint. J. W. Furness. *Circular* 6038. 12 pp. Issued June, 1927.

The Flotation of Oxidized Ores. Thomas Varley. *Reports of Investigations* 2811. 22 pp. Issued June, 1927.

Bureau of Standards

Electrodeposition of Chromium from Chromic Acid Baths. H. E. Haring and W. P. Barrows. *Technologic Paper* 346. 37 pp. Issued June 10, 1927. Paper, 15 cents.

Organizations Coöperating with the National Bureau of Standards. *Miscellaneous Publication* 96. 11 pp.

Progress in Elimination of Waste. An Extract from the Fourteenth Annual Report of Secretary of Commerce. Herbert Hoover. 29 pp.

United States Government Master Specifications for Paint, Black, Semipaste, and Ready Mixed. *Circular* 94, 3rd ed. 9 pp. Paper, 5 cents.

Same. Paints, Iron Oxide and Iron Hydroxide. *Circular* 93, 3rd ed. 10 pp. Paper, 5 cents.

Wave-Length Measurements in the Arc and Spark Spectra of Zirconium. C. C. Kiess. *Scientific Paper* 548. 4 pp. Paper, 5 cents.

Department of Agriculture

A Comparison of the Direct Measurement of the Heat Production of Cattle with the Computation of the Heat Production by the Respiratory-Quotient Method. E. B. Forbes, Max Kriss, W. W. Braman, and R. B. French. *Journal of Agricultural Research,* 34 (May 1, 1927), 865–78.

Anthelminic Properties of Santonin. J. E. Shillinger. *Journal of Agricultural Research,* 34 (May 1, 1927), 839–45.

Drug Plants under Cultivation. W. W. Stockberger. *Farmers' Bulletin* 663. 38 pp. Paper, 10 cents.

Net-Energy Values of Corn Silage, Soy-Bean Hay, Alfalfa Hay, and Oats. E. B. Forbes, W. W. Braman, Max Kriss, J. A. Fries, C. D. Jeffries, R. W. Swift, R. B. French, and J. V. Maucher, Jr. *Journal of Agricultural Research,* 34 (April 15, 1927), 785–96.

Relation of Size of Oil Drops to Toxicity of Petroleum-Oil Emulsions to Aphids. E. L. Griffin, C. H. Richardson, and R. C. Burdette. *Journal of Agricultural Research,* 34 (April 15, 1927), 727–38.

Suitability of American Woods for Paper Pulp. S. D. Wells and J. D. Rue. *Department Bulletin* 1485. 102 pp. Paper, 20 cents.

The Discoloration of Canned Cranberries. F. W. Morse. *Journal of Agricultural Research,* 34 (May 1, 1927), 889–92.

The Gossypol Content and Chemical Composition of Cottonseed during Certain Periods of Development. W. D. Gallup. *Journal of Agricultural Research,* 34 (May 15, 1927), 987–91.

Geological Survey

Geology and Ore Deposits of the Leadville Mining District, Colorado. S. F. Emmons, J. D. Irving, and G. F. Loughlin. *Professional Paper* 148. 368 pp. Paper, $2.50.

Geology of the Knik-Matanuska District, Alaska. K. K. Landes. *Bulletin* 792-B. 22 pp.

Large Springs in the United States. O. E. Meinzer. *Water-Supply Paper* 557. 94 pp. Paper, 30 cents.

Manganese-Bearing Deposits near Lake Crescent and Humptulips, Washington. J. T. Pardee, *Bulletin* 795-A. *Contributions to Economic Geology, 1927.* Part I, pp. 1–24. Paper, 10 cents.

Mineral Industry of Alaska in 1925 and Administrative Report. F. H. Moffit. *Bulletin* 792-A. 40 pp.

Organic Precipitation of Metallic Copper. T. S. Lovering. *Bulletin* 795-C. *Contributions to Economic Geology, 1927.* Part I, pp. 45–52. Paper, 5 cents.

Potash Brines in the Great Salt Lake Desert, Utah. T. B. Nolan. *Bulletin* 795-B. *Contributions to Economic Geology, 1927.* Part I, pp. 25–44. Paper, 10 cents.

Quality of Water of Colorado River in 1925–1926. W. D. Collins and C. S. Howard. *Water-Supply Paper* 596-B. *Contributions to the Hydrology of the United States, 1927.* Pp. 33–43.

Surface Water Supply of the United States, 1923. Part IX—Colorado River Basin. N. C. Grover, Robert Follansbee, A. B. Burton, and R. C. Rice. *Water-Supply Paper* 569. 189 pp. Paper, 25 cents.

Same. Part VIII—Western Gulf of Mexico Basins. N. C. Grover and C. E. Ellsworth. *Water-Supply Paper* 568. 169 pp. Paper, 30 cents.

Same. 1924. Part III—Ohio River Basin. N. C. Grover, A. W. Harrington, A. H. Horton, Lasley Lee, H. E. Grosbach, W. R. King, W. E. Hall, and E. D. Burchard. *Water-Supply Paper* 583. 298 pp. Paper, 35 cents.

Public Health Service

Court Decisions on Pasteurization. J. A. Tobey. *Public Health Reports,* 42 (July 1, 1927), 1756–60.

Experimental Bacterial and Chemical Pollution of Wells via Ground Water. *Public Health Reports,* 42 (June 10, 1927), 1581–2.

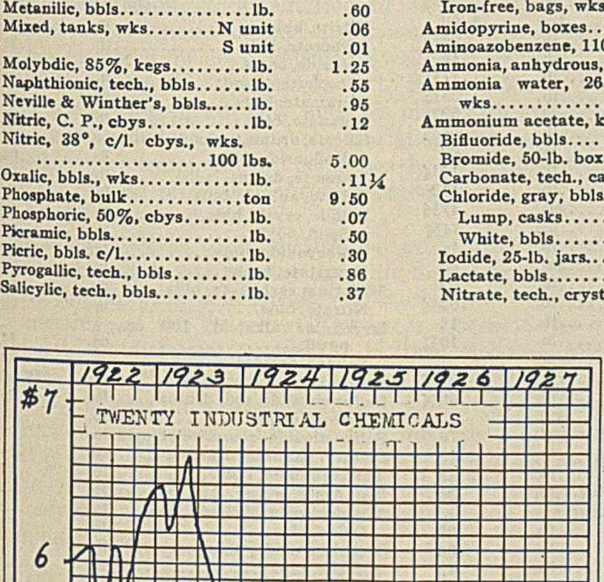
Recent Developments in Sewage Chlorination. L. H. Enslow. *Public Health Reports,* 42 (June 17, 1927), 1623–42.

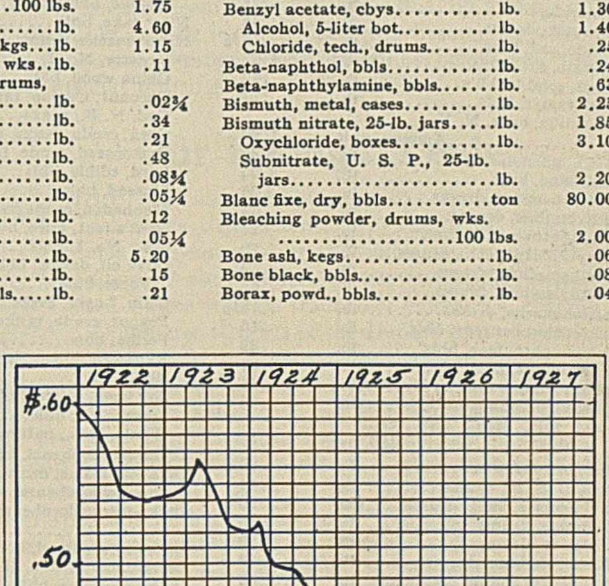
Review of Literature on Physiological Effects of Abnormal Temperatures and Humidities. R. R. Sayers and S. J Davenport. Reprint 1150 from *Public Health Reports.* 63 pp. Paper, 10 cents.

MARKET REPORT—JULY, 1927

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON JULY 15

Acetanilide, tech., bbls.	lb.	.21
U. S. P., bbls.	lb.	.35
Acetic anhydride, 92–95%, cbys.	lb.	.29
Acetone, C. P., drums, wks.	lb.	.12
Acetophenetidine, bbls.	lb.	1.60
Acid, Acetic, 28%, c/1. bbls.	100 lbs.	3.38
56%, c/1. bbls.	100 lbs.	6.34
Glacial, c/1. bbls.	100 lbs.	11.92
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums.	lb.	.98
Benzoic, tech., bbls.	lb.	.58
Boric, bbls.	lb.	.08½
Butyric, 60%, pure, 5-lb. bot.	lb.	.55
Chloroacetic, mono-, bbls., wks.	lb.	.25
Di-, cbys	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.15
Chromic, pure, 98%, drums.	lb.	.37
Chromotropic, bbls.	lb.	1.00
Cinnamic, 5-lb. cans.	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.45½
Cresylic, pale, drums	gal.	.62
Formic, 85%, cbys., N. Y.	lb.	.10½
Gallic, U. S. P., bbls.	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.55
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.65
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.05
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilicic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis.	lb.	.36
Lactic, 22%, dark, bbls.	lb.	.05½
66%, light, bbls., wks.	lb.	.26
Metanilic, bbls.	lb.	.60
Mixed, tanks, wks.	N unit	.06
	S unit	.01
Molybdic, 85%, kegs.	lb.	1.25
Naphthionic, tech., bbls.	lb.	.55
Neville & Winther's, bbls.	lb.	.95
Nitric, C. P., cbys.	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11¼
Phosphate, bulk	ton	9.50
Phosphoric, 50%, cbys.	lb.	.07
Picramic, bbls.	lb.	.50
Picric, bbls. c/l.	lb.	.30
Pyrogallic, tech., bbls.	lb.	.86
Salicylic, tech., bbls.	lb.	.37
Stearic, d. p., bbls. c/l.	lb.	.11
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.35
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.00
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.30
Tartaric, U. S. P., cryst., bbls.	lb.	.37
Tobias, bbls.	lb.	.85
Tungstic, kegs.	lb.	1.00
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	3.70
Amyl, 10%, Imp. drums.	gal.	1.40
Butyl, drums, c/l. wks.	lb.	.19¼
Cologne Spirit, bbls.	gal.	3.90
Denatured, No. 5, Comp. denat. c/l, drs.	gal.	.43
No. 1, Comp. denat., drs.	gal.	.45½
Isobutyl, ref., drums.	lb.	...
Isopropyl, ref., drums.	gal.	1.00
Propyl, ref., drums.	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.35
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.15
Chrome, casks, wks.	100 lbs.	5.25
Potash, lump, bbls., wks.	100 lbs.	3.50
Soda, bbls., wks.	100 lbs.	3.25
Aluminum, metal, N. Y.	lb.	.26
Aluminum chloride, anhyd., drums.	lb.	.35
Aluminum stearate, 100-lb. bbl.	lb.	.23
Aluminum sulfate, comm'l bags, wks.	100 lbs.	1.40
Iron-free, bags, wks.	100 lbs.	1.75
Amidopyrine, boxes.	lb.	4.60
Aminoazobenzene, 110-lb. kgs.	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.11
Ammonia water, 26°, drums, wks.	lb.	.02¾
Ammonium acetate, kegs.	lb.	.34
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes.	lb.	.48
Carbonate, tech., casks.	lb.	.08¾
Chloride, gray, bbls.	lb.	.05¼
Lump, casks.	lb.	.12
White, bbls.	lb.	.05¼
Iodide, 25-lb. jars.	lb.	5.20
Lactate, bbls.	lb.	.15
Nitrate, tech., cryst., bbls.	lb.	.21
Oxalate, kegs.	lb.	.35
Persulfate, cases.	lb.	.27½
Phosphate, dibasic, tech., bbls.	lb.	.18
Sulfate, bulk, wks.	100 lbs.	2.40
Thiocyanate, tech., kegs.	lb.	.40
Amyl acetate, tech., drums.	lb.	2.00
Aniline oil, drums.	lb.	.15
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.90
Antimony, metal.	lb.	.11⅞
Antimony chloride, anhyd., drums.	lb.	.17
Oxide, bbls.	lb.	.16¼
Salt, Dom., bbls.	lb.	.18
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.15
Vermilion, bbls.	lb.	.37½
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.08
Arsenic, metal, kegs.	lb.	.45
Red, kegs, cases.	lb.	.10½
White, c/l. kegs.	lb.	.03¾
Asbestine, bulk, c/l.	ton	16.00
Barium carbonate, bbls., bags, wks.	ton	47.50
Chloride, bags, wks.	ton	60.00
Dioxide, bbls., wks.	lb.	.13
Hydroxide, bbls.	lb.	.04½
Nitrate, casks.	lb.	.08
Barium sulfocyanide, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums.	lb.	.65
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzene, pure, tanks, mills.	gal.	.22
Benzidine base, bbls.	lb.	.70
Benzoyl chloride, carboys.	lb.	1.00
Benzyl acetate, cbys.	lb.	1.30
Alcohol, 5-liter bot.	lb.	1.40
Chloride, tech., drums.	lb.	.25
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.63
Bismuth, metal, cases.	lb.	2.25
Bismuth nitrate, 25-lb. jars.	lb.	1.85
Oxychloride, boxes.	lb.	3.10
Subnitrate, U. S. P., 25-lb. jars.	lb.	2.20
Blanc fixe, dry, bbls.	ton	80.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs.	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, powd., bbls.	lb.	.04½





Bordeaux mixture, bbls.	lb.	.11
British gum, com., c/l.	100 lbs.	4.37
Bromine, bot.	lb.	.47
Bromobenzene, drums	lb.	.50
Bromoform, 5-lb. bot.	lb.	1.65
Butyl acetate, 100-gal. drums	gal.	1.45
Cadmium bromide, 50-lb. jars	lb.	1.20
Cadmium, metal, boxes	lb.	.70
Cadmium sulfide, cs.	lb.	1.20
Caffeine, U. S. P., 5-lb. cans	lb.	3.05
Calcium acetate, bags	100 lbs.	3.50
Arsenate, bbls.	lb.	.07½
Carbide, drums	lb.	.05½
Chloride, drums, wks.	ton	21.00
Lactate, tech., bbls.	lb.	.35
Nitrate, bbls.	ton	52.00
Phosphate, monobas., bbls.	lb.	.07
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Amer., bbls.	lb.	.72
Jap., cases	lb.	.66
Crude, cases	lb.	.64
Camphor, monobrom, cs.	lb.	1.85
Caramel, bbls.	gal.	.63
Carbazole, bbls.	lb.	.15
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.12
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.07
Casein, stand. gr., bbls.	lb.	.18
Cellulose acetate, kegs	lb.	1.40
Cerium oxalate, kegs	lb.	.32
Chalk, pptd., casks	lb.	.04¼
Charcoal, willow, powd., bbls.	lb.	.06
China clay, imp., bgs.	100 lbs.	15.00
Chloral hydrate, drums	lb.	.60
Chloramine U. S. P., 5-lb. bot.	lb.	1.75
Chlorcosane, 5-lb. bot.	lb.	.55
Chlorine, liq., c/l., cyl.	lb.	.05½
Chlorobenzene, mono-, drums	lb.	.07
Chloroform, tech., drums	lb.	.20
Chlorohydrin, anhyd., drums	lb.	.75
Chromium acetate, 20° sol., bbls.	lb.	.05½
Cinchonidine sulfate, 100 oz.	oz.	.35
Coal tar, tanks, bbls., wks.	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	2.00
Cod-liver oil, bbls.	bbl.	45.00
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec.	100 lb.	12.90
Copper carbonate, bbls.	lb.	.16¾
Chloride, bbls.	lb.	.28
Cyanide, drums	lb.	.48
Oxide, red, bbls.	lb.	.16½
Sulfate, c/l., bbls.	100 lb.	4.95
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.27
Cyanamide, bulk, N. Y.	Ammon. unit	1.80
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	3.25
Dichlorobenzene, drums	lb.	.06
Diethylaniline, drums	lb.	.55
Diethylphthalate, drums	lb.	.25
Diethylsulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.30
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls.	lb.	.15
Dinitronaphthalene, bbls.	lb.	.32
Dinitrophenol, bbls.	lb.	.31
Diphenylamine, bbls.	lb.	.45
Diphenylguanidine, bbls.	lb.	.68
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.10
Ether, nitrous, bot.	lb.	.90
Ether, U. S. P., drums	lb.	.14
Ethyl acetate, 99%, drums	gal.	1.10
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethyl benzyl aniline, 300-lb. drs.	lb.	1.05
Ethylene bromide, drums	lb.	.70
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks.	lb.	.30
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls.	lb.	.07½
Ferrous chloride, cryst., bbls.	lb.	.05
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 95%, bags	ton	25.00
Formaldehyde, bbls.	lb.	.10
Formaniline, drums	lb.	.38
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, 500-lb. drs., c/l.	lb.	.17½
Glauber's salt, bbls.	100 lbs.	1.05
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerol, C. P., drums	lb.	.24
G salt, bbls.	lb.	.50
Hexamethylenetetramine, U. S. P., drums	lb.	.65
Hydrogen peroxide, 25 vol., bbls.	lb.	.06½
Hydroquinone, kegs	lb.	1.25
Indigo, 20%, paste, bbls.	lb.	.14
Iodine, crude, 200-lb. kgs.	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot.	lb.	6.00
Iridium, metal	oz.	110.00
Kieselguhr, bags	ton	60.00
Lead, metal	100 lb.	6.20
Lead acetate, bbls., white	lb.	.15
Arsenate, bbls.	lb.	.14
Oxide, litharge, bbls.	lb.	.08¾
Red, bbls.	lb.	.10
Peroxide, drums	lb.	.25
White, basic carb., bbls.	lb.	.10¾
Sulfate, bbls.	lb.	.10
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks.	ton	4.50
Lithium carbonate, 100-lb. kgs.	lb.	1.45
Lithopone, bbls.	lb.	.06⅛
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks.	ton	48.00
Magnesium, metal sticks, wks.	lb.	.85
Magnesium carbonate, bags	lb.	.06¾
Chloride, drums	ton	37.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.08
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 25 lbs.	lb.	1.58
Mercury, flasks, 75 lbs.	flask	121.00
Meta-nitroaniline, bbls.	lb.	.72
Meta-phenylenediamine, bbls.	lb.	.90
Meta-toluylenediamine, bbls.	lb.	.72
Methanol, 97%, tanks	gal.	.74
Methyl acetone, drums	gal.	.88
Salicylate, cases	lb.	.47
Methyl chloride, cylinders	lb.	.55
Michler's ketone, bbls.	lb.	3.00
Monoethylaniline, drums	lb.	1.05
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls.	lb.	.04½
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.08
Double, bbls.	lb.	.08½
Niter cake, bulk	ton	4.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.13
China wood, bbls.	lb.	.17¾
Coconut, Ceylon, tanks	lb.	.08¼
Cod, N. F., tanks	gal.	.59
Corn, crude, tanks, mills	lb.	.08½
Cottonseed, crude, tanks	lb.	.09
Lard, edible, bbls.	lb.	.15¼
Linseed, bbls.	lb.	.112
Menhaden, crude, tanks	gal.	.47½
Neat's-foot, pure, bbls.	lb.	.14¾
Oleo, No. 1, bbls.	lb.	.14
Olive oil, denat., bbls.	gal.	1.80
Foots, bbls.	lb.	.09
Palm, Lagos, casks	lb.	.07½
Peanut, crude, tanks	lb.	.12
Perilla, bbls.	lb.	.16¼
Rapeseed, bbls., English	gal.	.78
Red, bbls.	lb.	.09¼
Soy bean, crude, bbls.	lb.	.09¼
Sperm, 38°, bbls.	gal.	.85
Whale, bbls., natural winter	gal.	.76
Ortho-aminophenol, kegs	lb.	2.20
Ortho-anisidine, drums	lb.	2.35
Ortho-dichlorobenzene, drums	lb.	.06
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.13
Ortho-toluidine, bbls.	lb.	.29
Palladium, metal	oz.	80.00
Para-aminophenol, kegs	lb.	1.15
Paraldehyde, tech., drums	lb.	.27
Para-formaldehyde, cases	lb.	.45
Para-nitroaniline, drums	lb.	.52
Para-nitrochlorobenzene, drums	lb.	.32
Para-nitrophenol, bbls.	lb.	.50
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.30
Para-phenylenediamine, bbls.	lb.	1.20
Para-toluidine, bbls.	lb.	.38
Paris Green, 500-lb. kgs.	lb.	.19
Phenol, drums	lb.	.16
Phenolphthalein, drums	lb.	1.30
Phenylethyl alcohol, 1-lb. bot.	lb.	7.00
Phosphorus, red, cases	lb.	.60
Phosphorus trichloride, cyl.	lb.	.45
Phthalic anhydride, bbls.	lb.	.18
Platinum, metal	oz.	95.00
Potash, caustic, drums	lb.	.07⅛
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.09
Bichromate, casks	lb.	.08¼
Binoxalate, bbls.	lb.	.16
Bromate, cs.	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05⅝
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.11
Permanganate, drums	lb.	.14½
Prussiate, red, casks	lb.	.39
Yellow, casks	lb.	.18½
Titanium oxalate, bbls.	lb.	.25
Pyridine, drums	gal.	1.50
Quinine bisulfate, 100 oz.	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	1.30
Rochelle salt, bbls., U. S. P.	lb.	.23
R salt, bbls.	lb.	.45
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	19.00
Saltpeter, gran., bbls.	lb.	.06
Silica, ref., bags	ton	18.00
Silver nitrate, 16-oz. bot.	oz.	.40⅛
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.38
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	3.10
Sodium acetate, bbls.	lb.	.04½
Benzoate, bbls.	lb.	.50
Bicarbonate, bbls.	100 lbs.	2.00
Bichromate, casks	lb.	.06¼
Bisulfite, bbls.	lb.	.08½
Bromide, bbls.	lb.	.42
Carbonate, sal soda, bbls.	100 lbs.	1.30
Chlorate, kegs	lb.	.06¼
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.20
Fluoride, bbls.	lb.	.08¾
Hyposulfite, reg., crys., bbls.	lb.	.02½
Metallic, drums, 12¼-lb. bricks	lb.	.27
Naphthionate, bbls.	lb.	.55
Nitrate, crude, bags, N. Y.	100 lbs.	2.50
Nitrite, bbls.	lb.	.08½
Perborate, bbls.	lb.	.21
Peroxide, cases	lb.	.27
Phosphate, trisod	lb.	.04
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.12
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls.	lb.	.04¾
Stannate, drums	lb.	.48½
Sulfate, anhyd., bbls.	lb.	.02¼
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls.	lb.	.40
Tungstate, kegs	lb.	.85
Strontium carbonate, bbls.	lb.	.08
Nitrate, bbls.	lb.	.08
Strychnine alkaloid, 100 oz., powd.	oz.	.56
Sulfate, powder	oz.	.38
Sulfur, bulk, mines, wks.	ton	19.00
Sulfur chloride, red, drums	lb.	.05½
Yellow, drums	lb.	.03¾
Sulfur dioxide, commercial, cyl.	lb.	.08½
Sulfuryl chloride, drums	lb.	.65
Thiocarbanilid, bbls.	lb.	.22
Tin, Amer., stand	lb.	.65
Tin bichloride, 50% sol., bbls.	lb.	.18½
Oxide, bbls.	lb.	.72
Titanium oxide, bbls., wks.	lb.	.40
Toluene, tanks	gal.	.35
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.69
Triphenyl phosphate, bbls.	lb.	.75
Tungsten	WO_3 unit	10.50
Urea, pure, cases	lb.	.18
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.50
Xylidine, drums	lb.	.37
Zinc, metal, N. Y.	100 lb.	6.75
Zinc ammonium chloride, bbls.	lb.	.06¼
Chloride, granulated, drums	lb.	.06¼
Oxide, Amer., bbls.	lb.	.07⅛
Stearate, bbls.	lb.	.19
Zinc dust, bbls., kegs, c/l.	lb.	.09